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Metal-Assisted Cycloaddition Reactions in Organotransition Metal Chemistry

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Hans-Werner Fröhuf was born in Mannheim, Germany, in 1941. He received his diploma (Dipl.-Ing. 1968) and doctoral degrees (Dr.-Ing. 1971) from the Technische Hochschule Darmstadt. Postdoctoral work followed with H. E. Zimmerman in Madison, WI (DFG fellowship 1972–1973), and with E. Koerner von Gustorf at the Max-Planck-Institut für Strahlenchemie in Mülheim a.d. Ruhr (1973–1976). He then became Assistant at the newly founded University of Duisburg and was heavily involved in the planning and building of the chemical department. He completed his Habilitation in organic chemistry in 1980 with a thesis on carbonyl complexes of zero-valent iron with 1,4-diaza-1,3-diene and 1,3-diene ligands. From 1983 to 1986 he held a C2-professorship in Duisburg and then joined the faculty at the Inorganic Department of the University of Amsterdam, Holland. His research interests in transitionmetal organic and coordination chemistry include the synthesis, structure, and solution dynamics of heterodiene complexes, elucidation of their thermal and photochemical reactions with unsaturated organic compounds, and the application of these stoichiometric or catalytic reactions toward organic synthesis. A main focal point during the last decade has been the cycloaddition chemistry of the 1,3-dipolar C=XM fragment in (1,4-dihetero-1,3-diene)ML₃ complexes (M = Fe, Ru, Mn; X = N, O, S).

one way or the other, which naturally will be referred to in the appropriate chapters, but to the best of my knowledge there has been no attempt what so ever to approach the subject systematically according to the type of cycloaddition reaction. [An important review by Schore,¹ *Transition-Metal-Mediated Cycloaddition Reactions of Alkynes in Organic Synthesis*, is organized according to the ring size formed in the cycloaddition reaction. His overview naturally contains reactions also discussed in this review and will further only occasionally be referred to.] In order to do so, it will be necessary to establish a nomenclature, i.e., to agree on a specific notation by which the type of reaction is identified, and, most importantly, to define several categories with respect to the role of the metal.

B. Definitions and Notations

In the nomenclature of organic cycloaddition reactions² there are two different ways to characterize

I. Introduction

A. Organic and Organometallic Cycloaddition Reactions

Cycloaddition reactions in organic chemistry are not only among the synthetically most useful reactions, they are also among the theoretically and mechanistically best understood reactions. It is not surprising therefore that they are extensively covered in the review literature and in monographs. This situation changes drastically when a metal is involved. There are several reviews on particular types of cycloaddition reactions where metals take part in

Table 1. Characterization of Cycloaddition Reactions by Electronic and Topological Indicators

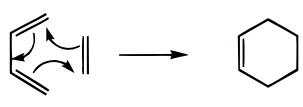
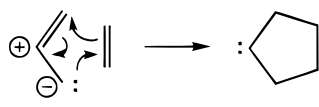
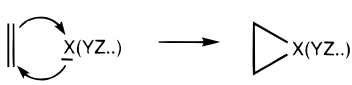
| | type of characterization: electronic (Woodward-Hoffmann) | topological (Huisgen) | |
|------------------------|--|-----------------------------------|--|
| Diels-Alder reaction | $[\pi 4_s + \pi 2_s]$ | $[4 + 2]$ |  |
| 1,3-dipolar cycloaddn. | $[\pi 4 + \pi 2]$ | $[3 + 2]$ |  |
| cheletropic reaction | — | $[m + 1]$ $m = 2, 4, 6, \dots$ |  |

Table 2. Definition of Categories of Cycloaddition Reactions in Which Metals Take Part

| metal assisted | organometal | metal catalyzed |
|---|---|---|
| The ML_n -fragment... | | |
| ...is present in one of the reactants ^a and may be present in the product, e.g., as a substituent, i.e., not within the formed ring. | ...forms integral part of one or more of the reactants and of the formed ring. | ...does not form stable complexes with reactants or product, i.e., is only present in reactive intermediates. |
| ...influences the activation barriers, and the chemo-, regio-, and stereoselectivity. | | ...influences the activation barriers, and the chemo-, regio-, and stereoselectivity. |
| The products formed constitute... | | |
| carbo- or heterocycles | metalla(hetero)cycles | carbo- or heterocycles |
| ^a This reactant need not be a stable compound, but may be formed in situ. | | |

the type of reaction—one electronic and one topological in nature (cf. Table 1). The first is typically used in the traditional concerted reactions such as the Diels–Alder reaction and the 1,3-dipolar cycloaddition, which are electronically equivalent. In both, a four-electron component reacts with a two-electron component, i.e. $[\pi 4 + \pi 2]$. But in the first case the four electrons are distributed among four atoms, of the diene, which gives rise to a six-membered cycloadduct, whereas in the second case the four electrons are part of a three-atom fragment, the 1,3-dipole, and a five-membered ring is formed. This ambiguity with respect to the outcome does not exist when the topological characterization, $[4+2]$ and $[3+2]$ respectively, is used in the first place. Unfortunately, both notations use numbers between square brackets and the subscript indicators of the electronic notation, π , supra, and antara, are frequently omitted. It is therefore important to note that throughout this article the type of reaction will always be identified by topology, i.e., the numbers between square brackets refer to the number of atoms that will constitute the cycloadduct. Only occasionally, and only in the text, the electronic notation will be used, e.g., for stereochemical reasoning, but then the appropriate subscripts will be given. The notation by topology is preferred for two reasons. Firstly, there are no mechanistic implications, i.e., whether it is a concerted or stepwise reaction, and secondly, it is also readily applicable to the so called cheletropic³ and multicomponent cycloadditions.

Three categories shall be defined with respect to the role of the metal (cf. Table 2):

(i) Metal-Assisted Cycloaddition Reactions. A metal, or rather a metal-ligand fragment ML_n , is bound to (at least) one of the starting materials and

influences the reaction through its electronic and sterical properties, i.e., it may enhance the reactivity, it may induce regio- and stereoselectivity, or it may act as a protecting group for reactive sites and thus create chemoselectivity. The metal may also be present in the product, but not within the newly formed ring. The products are therefore carbo- or heterocycles, eventually bearing a coordinated metal fragment.

A subclass to this category are reactions which might be distinguished as “metal induced”, and examples of which will be included without such a distinction. They differ from the aforementioned in only one respect: the actual starting complex for the cycloaddition reaction is not a stable compound but is formed in situ. Thus an organic substrate initially reacts with a metal complex in a stoichiometric fashion to produce the actual starting compound for a metal-assisted cycloaddition reaction.

(ii) Organometal Cycloaddition Reactions. A metal atom is integral part of one or both of the reactants and is hence also present within the cycloadduct which therefore represents a metalla(hetero)cycle. Naturally, these initial metallaheterocycles can react further and undergo insertion and/or reductive elimination reactions. This way new organic ligands are formed. Organometal cycloaddition reactions are therefore equally interesting for organometallic and organic synthesis.

(iii) Metal-Catalyzed Cycloaddition Reactions. The metal fragment does not form stable complexes with either of the reactants nor with the product. It is only present in reactive intermediates. Within the catalytic cycle it normally plays a role comparable to the metal-assisted case, i.e., it influences the activation barrier, and/or the regio- and

stereoselectivities. However, it is just as well possible that the metal is directly involved in a cycloaddition step as in category ii. So, as a matter of fact, one could also choose to subdivide the first two categories into stoichiometric and catalytic reactions. It is, however, more practical to treat the stoichiometric and catalytic reactions separately, because, in the latter, very often mechanistic details with respect to the role of the metal are not known with certainty.

C. Scope of This Review

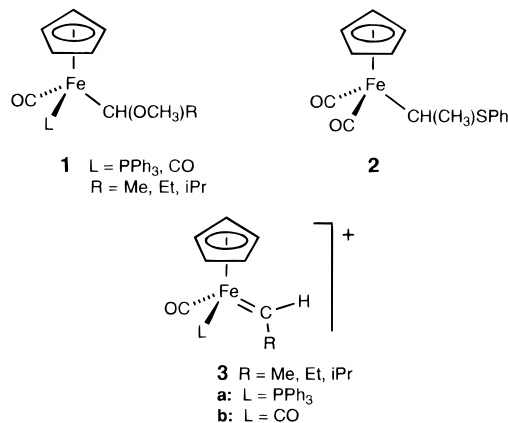
Originally, the intention was to write a review article containing three main chapters corresponding to the above-defined categories i–iii. However, in the course of writing the volume of the accumulating material suggested that it would be wise, with respect to tractability, to rather publish separate reviews. The present paper on (stoichiometric) metal-assisted cycloaddition reactions therefore deals with reactions defined under category i, and shall in due time be followed by (stoichiometric) organometal cycloadditions. Metal-catalyzed cycloaddition reactions have in the meantime been covered sufficiently by the reviews of Lautens⁴ on *Transition Metal-Mediated Cycloaddition Reactions* and of Ojima⁵ on *Transition Metal-Catalyzed Carbocyclizations in Organic Synthesis*. The title of the review of Lautens suggests considerable overlap with the present article. However, since Lautens et al. explicitly state that “processes which are catalytic in the metal were favored over stoichiometric reactions unless there were compelling reasons to include them”, while here catalytic reactions are only exceptionally being mentioned, the two articles are for the overwhelming part complementary. The transition metals involved in the present review are concentrated in groups 6 to 10 of the periodic table with a few exceptions to the left and right. The literature has been scanned from 1960 into October 1996 by CAS-On-line search. Patent literature has not been taken into account in this review.

II. Metal-Assisted Cycloaddition Reactions

A. [2+1] Metal-Assisted Cycloaddition Reactions

One important use of the metal in [2+1] addition reactions is to stabilize and transfer six-electron species of main group elements. [For many of the reactions discussed in this section, it has been unequivocally shown (cf. eqs 2, 5–9), that they proceed within the coordination sphere of the metal, i.e., with the 1- and 2-atom fragments bonded to the metal at the same time. Mechanistically, an obvious alternative to a direct formation of the 3-ring would be an organometal [2+2] cycloaddition to an intermediate metalla-4-ring and consecutive reductive elimination. It is therefore debatable whether these reactions should be discussed here or in the context of organometal cycloaddition reactions.] A review by Dötz⁶ *Carbene Complexes in Organic Synthesis* contains a chapter on cycloaddition reactions, including [2+1] cycloaddition reactions. In 1988 Wulff et al.⁷ gave an account of cyclopropanations and cycloadditions of transition metal carbene complexes. Meth-

ylene and alkylidene transfer reactions from intermediate cationic iron complexes **3** to olefins⁸ have been developed concurrently by the groups of Brookhart⁹ and Helquist.^{10,11} A review *Cyclopropanes from Reactions of Transition-Metal-Carbene Complexes with Olefins* has appeared.¹² Complexes **3** are generated in situ from isolable precursors **1**⁹ or **2**¹¹ through O- and S-methylation and elimination of the respective (thio-)ether. The triphenylphosphine substituted





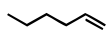
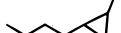
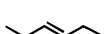

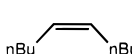




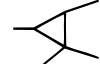



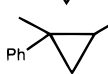

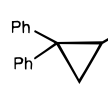


complexes **3a** were sufficiently stable to be characterized by ¹H and ¹³C NMR.⁹ In situ-prepared [(η⁵-C₅Me₅)(CO)₂Fe=CH₂]⁺[OTf][−] has been used to cyclopropanate styrene.¹³ Its stoichiometric reaction with isolated [(η⁵-C₅Me₅)(CO)₂Fe(η²-diene)][BF₄] (diene = 1,7-octadiene, 1,5-cyclooctadiene, isoprene, 4-vinylcyclohexene) gives regiospecifically the respective η²-alkenylcyclopropane complexes.¹⁴ The η²-alkenylcyclopropane ligands in these complexes are very labile and in solution slowly decoordinate already at room temperature.

Preparatively useful yields of methylcyclopropanes have been obtained by ethylidene transfer, and a marked cis stereoselectivity is normally observed (cf. Table 3). Around 1990 Brookhart et al.^{15,16} have reported on enantiomerically pure or enriched cationic iron–ethylidene complexes **3a,b**, being prepared by three different routes via separation by column chromatography or fractional crystallization of diastereomeric precursor complexes **1** and **2** or of the diastereomeric hydroxy carbene salt generated from Cp(CO)(PR₃)Fe-Ac (R = Me, Et) by using (S)-(+)- or (R)-(−)-10-camphorsulfonic acid. High optical yields have been reported for the enantioselective ethylidene transfer from these complexes to styrene, vinyl acetate, and isopropenyl acetate. The mechanism of the ethylidene transfer reaction has been analyzed by using the stereochemical results obtained in connection with deuterium-labeling experiments and relative reactivity studies. Further, a rationale was developed for the differing diastereoselectivities of the ethylidene transfer from **3a** vs **3b** to the various olefins.

Transfer reactions of more complex alkylidenes (propylidene, isobutylidene) are severely hampered by the much reduced lifetimes of the corresponding complexes **3** due to β-hydride migration or elimination. Naturally, such interference does not apply to benzylidene transfer reactions which can efficiently and stereoselectively be effected with (CO)₅W=CH-

Table 3. Metal-Assisted [2+1] Cycloaddition: Ethylidene Transfer to Olefins from 3b Using Complexes $\text{Cp}(\text{CO})_2\text{FeCH}(\text{OCH}_3)\text{CH}_3$ (1)⁹ and $\text{Cp}(\text{CO})_2\text{FeCH}(\text{SPh})\text{CH}_3$ (2)¹⁰ as Precursors

| olefin | complex, methylating agent | ratio complex:olefin | cyclopropane | isomer ratio | % yield GPLC |
|--|--|-------------------------|--|------------------|-----------------|
|  | 1, Me_3SiOTf | 1:2 |  | a | 86 |
|  | 1, Me_3SiOTf 2, FSO_3Me | 2:1 1:1 |  | >25:1 a | 87 70 |
|  | 1, Me_3SiOTf | 1:4 |  | 1:1 | 48 |
|  | 1, Me_3SiOTf | 1:2 |  | a | 3.4 |
|  | 2, FSO_3Me | 1:1 |  | b | 44 |
|  | 1, Me_3SiOTf | 1:2 |  | >50:1, a | 58 |
|  | 1, Me_3SiOTf | 1:2 |  | >50:1, a | 52 |
|  | 1, Me_3SiOTf 2, FSO_3Me | 2:1 1:1 |  | 4.7:1 (Z:E) a | 91 67 |
|  | 2, FSO_3Me | 1:1 |  | 41:17 (Z:E) | 58 |
|  | 2, FSO_3Me | 1:1 |  | - | 81 |

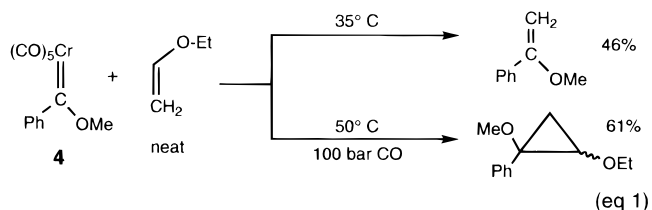
^a Only one product could be detected. ^b Stereochemistry not determined

$\text{C}_6\text{H}_4\text{R}^{17-19}$ or $\text{Cp}(\text{CO})(\text{L})\text{M}=\text{CH}(\text{C}_6\text{H}_4\text{R})^+$ ($\text{M} = \text{Fe}$, Ru ; $\text{L} = \text{CO}$, PPh_3 ; $\text{R} = p\text{-H}$, $p\text{-F}$, $p\text{-Me}$, $p\text{-OMe}$).²⁰⁻²²

Benzylidene transfer from $(\text{CO})_5\text{W}=\text{CHPh}$ to the thiocarbonyl group in thiobenzophenones results in thiirane complexes.²³ The same complexes can also be prepared by reaction of the corresponding $(\text{CO})_5\text{W}$ -(thiobenzophenone) complex with diphenylazomethane. The thiirane ligands can be readily displaced from the metal either by reaction with $\text{NEt}_4\text{-Br}$ in dichloromethane or with pyridine in THF.

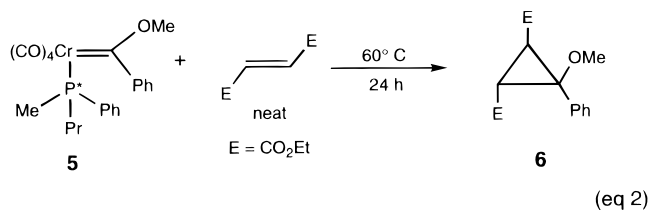
Brookhart et al.²⁴ have reported on cyclopropylcarbene transfer using $[\text{Cp}(\text{CO})_2\text{M}=\text{CH}(\text{c-C}_3\text{H}_5)]^+\text{CF}_3\text{SO}_3^-$ ($\text{M} = \text{Fe}$, Ru). Brookhart²⁴ also gives a list of references to iron carbene complexes of type $[\text{Cp}(\text{CO})(\text{L})\text{Fe}=\text{CRR}']^+$ ($\text{L} = \text{CO}$, PR_3 ; $\text{R}, \text{R}' = \text{H}$, alkyl; H , vinyl; CH_3 , CH_3) which are useful reagents for the transfer of the carbene moiety to olefins to form cyclopropanes. Considering the relative rates with various substituted olefins and the observed stereoselectivities, it appears that the carbene transfer reactions proceed through electrophilic attack by the carbene carbon on the alkene. The precise structure of the transition state is unclear and may be a sensitive function of substituents on the alkene.⁹ In-depth discussions of stereochemical and mechanistic aspects have been given by Brookhart²⁵ and Casey;²⁶ see also Hossain.²⁷ Platinacyclobutanes are involved in the reaction of $(\text{py})\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2$ with diazofluorene.²⁸

The cyclopropanation of olefins by Fischer carbene complexes has been addressed in several reviews and monographs.^{6,12,29-33} In the early 1970s Fischer and co-workers³⁴⁻³⁸ reported on the first carbene transfer reactions of (phenylmethoxycarbene)pentacarbonylchromium (4). It became apparent that the cyclopropanation of olefins did not involve a free carbene. This was indicated by a dependence on the metal (Cr , Mo , W) of the ratio of the formed cyclopropane stereoisomers^{35,36} and corroborated by the observation that the course of the reaction very strongly depended on the electronic properties of the olefin which would not have been the case if a free and very reactive, hence nondiscriminating carbene had been involved.³⁴ With electron-rich olefins, the most important competing reaction of the chromium carbene was metathesis with the olefin^{35,39} which could be shut down by employing high CO pressures (eq 1).^{35,38} With



electron-poor olefins, e.g., methyl crotonate, metathesis was not observed, the only pathway being cyclopropanation.^{34,36} Interestingly, with electron-

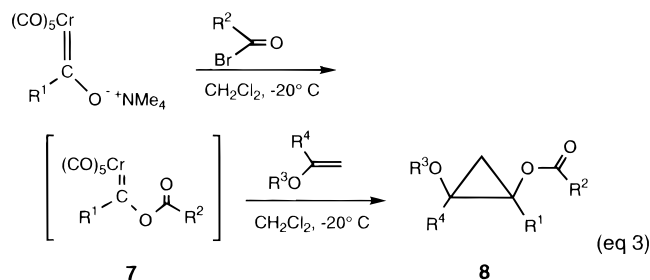
poor olefins another reaction, namely insertion of the carbene ligand into the olefinic C–H bond has been observed as a side^{37,40} or, in the case of (*Z*)- and (*E*)-crotononitriles, even the main reaction route.⁴¹ Direct proof for the absence of a free carbene, i.e., a reaction within the coordination sphere of the metal, was obtained from the reaction in eq 2.³⁷ By using



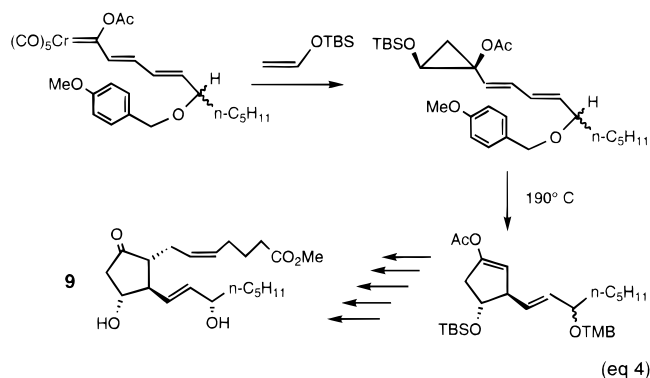
the optically active complex **5**, containing (*R*)-(-)-methylphenylpropyl phosphine as ligand, the optically active cyclopropane **6** was obtained from diethyl fumarate. In the mid-1980s the investigations have experienced a revival. Complementing the work of Brookhart²⁴ on cationic cyclopropyl-iron and -ruthenium complexes (vide supra), Herndon et al.^{40,42} successfully used cyclopropylmethoxycarbene-chromium complexes to prepare cyclopropylcyclopropanes. The range of electron-deficient olefins that are cyclopropanated by $(\text{CO})_5\text{M}=\text{C}(\text{OMe})\text{R}$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) has been greatly expanded.^{43–46} In this connection it has been stated⁴⁴ that the method is limited to mono- and disubstituted olefins, and that Mo- and W-carbene complexes do not offer advantages over the Cr compounds. However, this statement does not take into account the possible utilization of the dependence of the diastereomer ratio^{35,36} in the formed cyclopropanes on the choice of the central metal atom. Reissig et al.⁴⁶ have reported that the reactions of methyl acrylate with styryl-substituted carbene complexes $(\text{CO})_5\text{Cr}=\text{C}(\text{OMe})\text{CH}=\text{CH}\text{R}$ with $\text{R} = p\text{-anisyl}$ and 2-furyl give 30:70 mixtures of the expected vinylcyclopropanes and of cyclopentene derivatives. With $\text{R} = 1\text{-methyl-2-pyrrolyl}$ the cyclopentenenes are formed exclusively. The authors suggest that these formal [3+2] cycloadducts result from a secondary vinylcyclopropane to cyclopentene rearrangement via a zwitterionic intermediate. The [2+1] cycloaddition of the carbene ligand from **4** ($\text{M} = \text{W}$) to the $\text{N}=\text{N}$ bond in 4-methyl-1,2,4-triazoline-3,5-dione or diethyl azodicarboxylate to give diaziridines has also been described.⁴⁷ Since 1988 several reports have appeared on the cyclopropanation by Fischer carbene complexes of electron-rich,^{7,39} electron-deficient,^{48,49} and unactivated^{40,50,51} 1,3-dienes to give substituted vinylcyclopropanes.

Pyrrolocarbene complexes of Cr, Mo, and W have been prepared by Hegedus et al.⁵² and have been demonstrated to give high yields of pyrrole-substituted cyclopropanes with electron-deficient olefins.

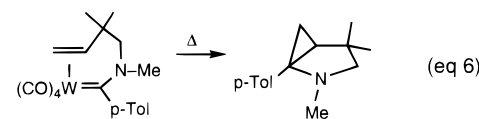
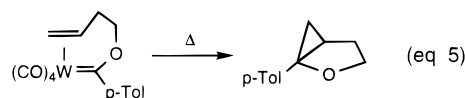
The reaction sequences of Fischer carbene complexes with unsaturated organic moieties contain several branching points^{53,54} (see also the literature on the Dötz reaction, chapter II.F) and the reactivity or the whole reactivity pattern is strongly influenced by the donor properties of the heteroatom at the carbene carbon atom.^{55–57} This is also true for the intermolecular olefin cyclopropanation. Acyloxy-carbene complexes **7** (eq 3), which are generated in



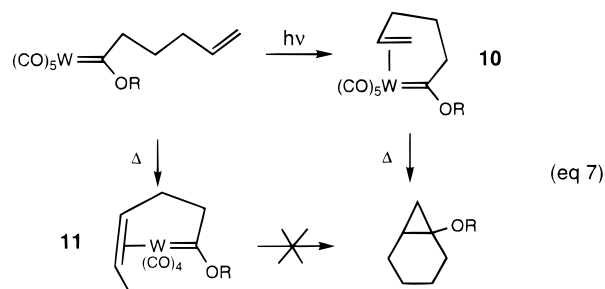
situ, have been found more reactive than the alkoxy complexes (**4**) and readily react with enol ethers in the absence of CO pressure to give a variety of 1,2-dioxygenated cyclopropanes **8** in reasonable yields.⁵⁸ This has been used as the key step in the synthesis (eq 4) of (±)-prostaglandin E_2 methyl ester **9**.⁵⁸ Methyl(methoxymethylene)Cr(CO)₅ has successfully been used to cyclopropanate fullerene C_{60} .⁵⁹ A single isomer of the methanofullerene from cyclopropanation of a 6,6 ring junction was obtained in 20% to >50% yields.



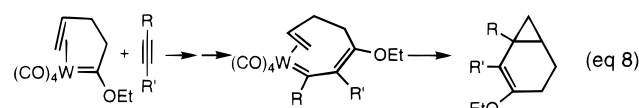
Evidence for coordination of the olefin prior to C–C bond formation has been obtained from the intramolecular cyclopropanation (eqs 5 and 6) of alkenyl-oxy and alkenylamino carbene complexes.^{56,57,60–64}



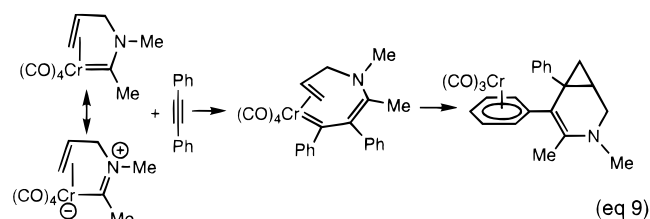
The isolation and X-ray structural characterization⁶⁰ of **10** and **11** has shown that the metal–carbon and the coordinated carbon–carbon double bonds have to adopt nearly parallel orientations for cyclopropanation to occur (eq 7). This has been considered



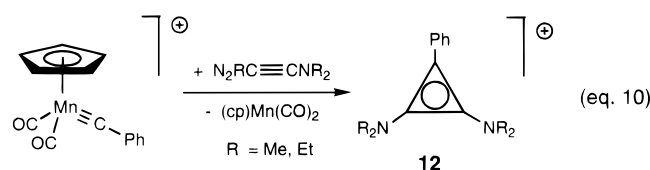
essential for the formation of a metallacyclobutane,⁶⁵ and it is now generally accepted⁶² that this cyclopropanation in fact proceeds via an (intramolecular) organometal [2+2] cycloaddition reaction to an intermediate metallacyclobutane which then reductively eliminates the cyclopropane, and from which on the other hand the formation of the observed metathesis products is readily explained.⁵⁶ The formation of 5-ethoxytricyclo[3.3.1.0^{2,8}]nona-3,6-diene (4,5-homotropilidene) in high yield via intramolecular cyclopropanation of readily prepared ethoxy(cycloheptatrienylmethyl)carbeneM(CO)₅ (M = Cr, W) has been reported by Aumann et al.⁶⁶ Rudler et al.^{67,68} have extended the intramolecular cyclopropanation reaction by an alkyne insertion step, giving access to bicycloheptane systems (eqs 8 and 9).



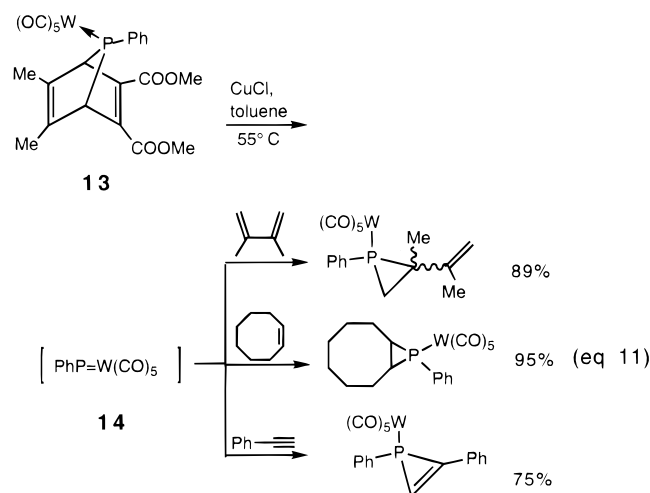
R, R' = Me, Me; Et, Et; Ph, Ph; Ph, H; C₅H₁₁, H; tBu, H; CH₂OMe, H; SiMe₃, H; CMe₂(OH), H; (CH₂)₄C≡CH, H; CO₂Et, H; (CH₂)₄CH=CH₂, H; CH₂CH₂OH, H



The first transfer of an electrophilic carbyne ligand to the carbon-carbon triple bond of bis(dimethylamino)acetylene, producing the cyclopropenyl cations **12** (eq 10) in ca. 60% isolated yield, has been reported by Fischer.⁶⁹



Phosphinidene transfer reactions have been reported by Mathey et al. (eq 11).⁷⁰⁻⁷⁷ Terminal phos-



phinidene complexes **14**, RP=M(CO)₅ (M = Cr, Mo,

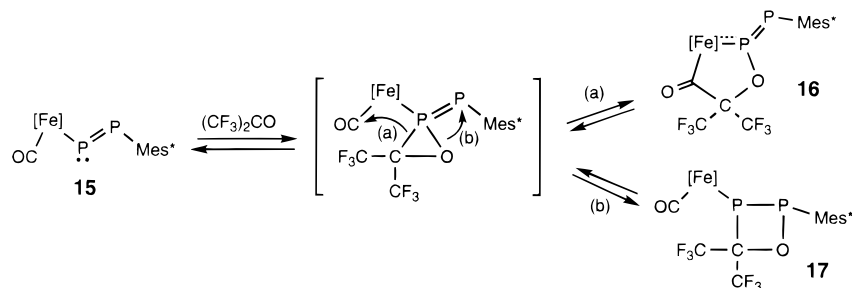
W) were generated in situ from 7-phosphanorbornadiene complexes **13** (cf. sections II.D.1 and II.D.2) at 55 °C with CuCl as catalyst.⁷⁰ In the presence of excess olefins (cyclic or open chain, terminal or internal) and acetylenes, the expected phosphiranes and phosphirenes were formed via **14** in good yields. Electron-rich olefins react faster than electron-deficient ones, and their stereochemistry is always retained in the phosphirane ring. With 1,3-dienes under these conditions, 1,2-addition is exclusively observed. The authors point to the similarities in behavior with that of electrophilic singlet carbenes and assume a concerted process. In one case,⁷⁸ even a chelating diphosphinidene complex, (PCH₂CH₂P)W(CO)₄, has been generated and intercepted. Lammertsma et al. have investigated the [2+1] addition of two terminal phosphinidenes to styrenes^{79,80} and have determined Hammett reaction constants ρ⁺ of -0.76 and -0.60 which support the slightly electrophilic, carbene-like nature of phosphorus in phosphinidene complexes. They also investigated the regio- and stereochemistry of the phosphinidene addition to (substituted) 1,3- and 1,4-cyclohexadienes⁸¹ and norbornadiene.⁸²

Weber has published an extended series of papers on transition metal-substituted diphosphenes [M]P=PR.⁸³⁻⁹⁴ In cycloaddition reactions with organic and organometallic electrophiles (see also sections II.B and II.E), the authors assume that the ring formation in every case is initiated by attack of the complex HOMO, i.e., essentially the lone pair of the metalated phosphorus, at the LUMO of the electrophile. In the reaction of **15**, (η⁵-C₅Me₅)(CO)₂-FeP=PMes (Mes = 2,4,6-*t*-Bu₃C₆H₂), with hexafluoroacetone (Scheme 1),⁸⁶ complex **16** precipitates as the only observable product. On extended standing of **16** in pentane solution, it was partially converted to **17**. While **16** resembles the product of an organometal [3+2] addition, and **17** that of a metal assisted [2+2] addition, the authors suggest, that both originate from the unobserved initial [2+1] cycloadduct shown in brackets.

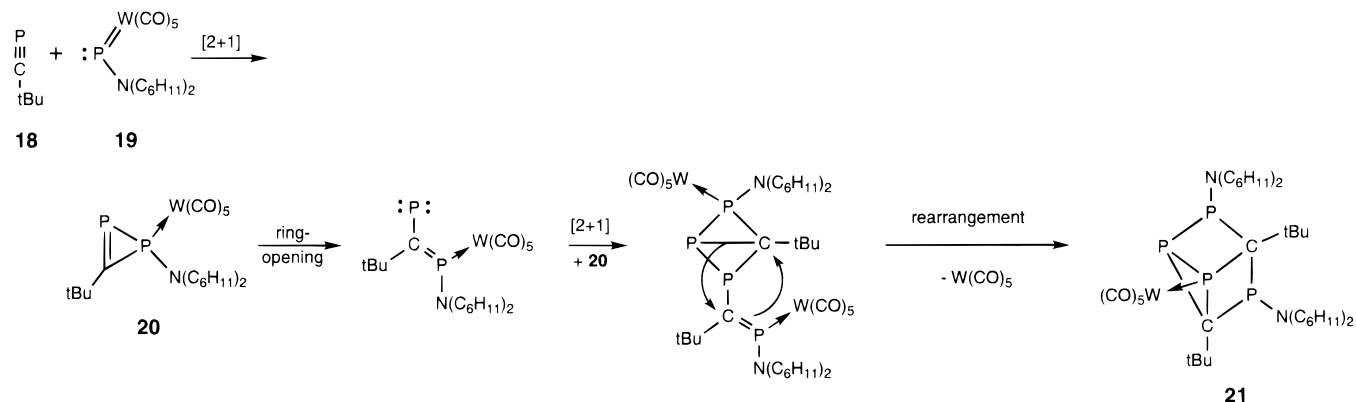
An interesting reaction sequence of aminophosphinidene **19** with phosphalkyne **18** (see Scheme 2), consisting of [2+1] addition, ring opening, second [2+1] addition, and rearrangement to the tricyclopentaphosphahexane **21**, has been described by Mathey and Regitz.⁹⁵

Huttner et al.^{96,97} described [2+1] additions of the reactive P=P double bond in the diphosphene complex [(CO)₅Cr]₂PhP=PPh **22** to sulfur or diazomethane to give thiadiphosphirane and diphosphirane complexes **23** and **24** (eq 12). [This and a few other cycloadditions to the P=P bond in diphosphene complexes are addressed by Weber⁸⁷ in his review on *The Chemistry of Diphosphenes and Their Heavy Congeners: Synthesis, Structure and Reactivity*.] Here, a third, side-on coordinated Cr(CO)₅ fragment is used to initially stabilize the inherently reactive P=P bond. Free diphosphenes RP=PR can only be made if they are stabilized by sterically demanding R groups. Weber has published examples of cyclopropanations of the P=P double bond in diphosphenyl complexes, [M]P=PAr, with sulfur ylides or diazomethane,^{83,93} giving diphosphiranes, and the (step-

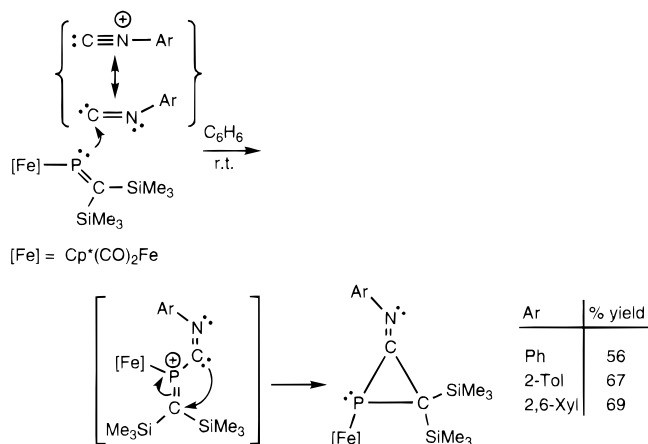
Scheme 1



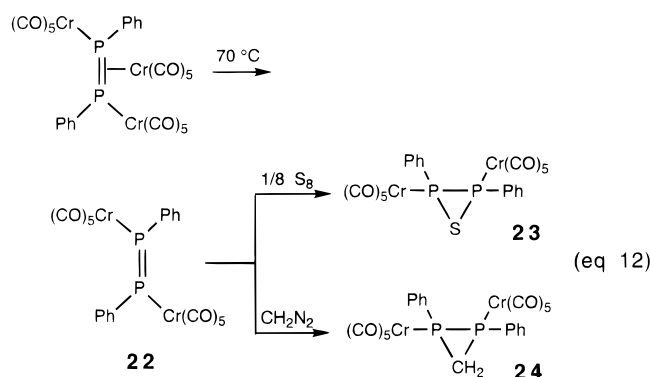
Scheme 2



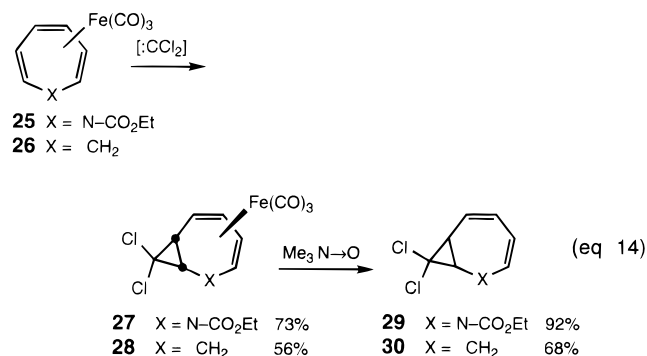
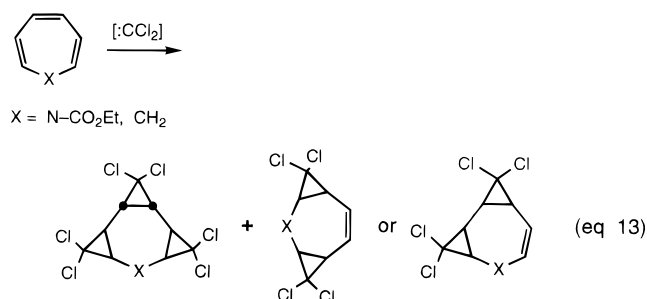
Scheme 3



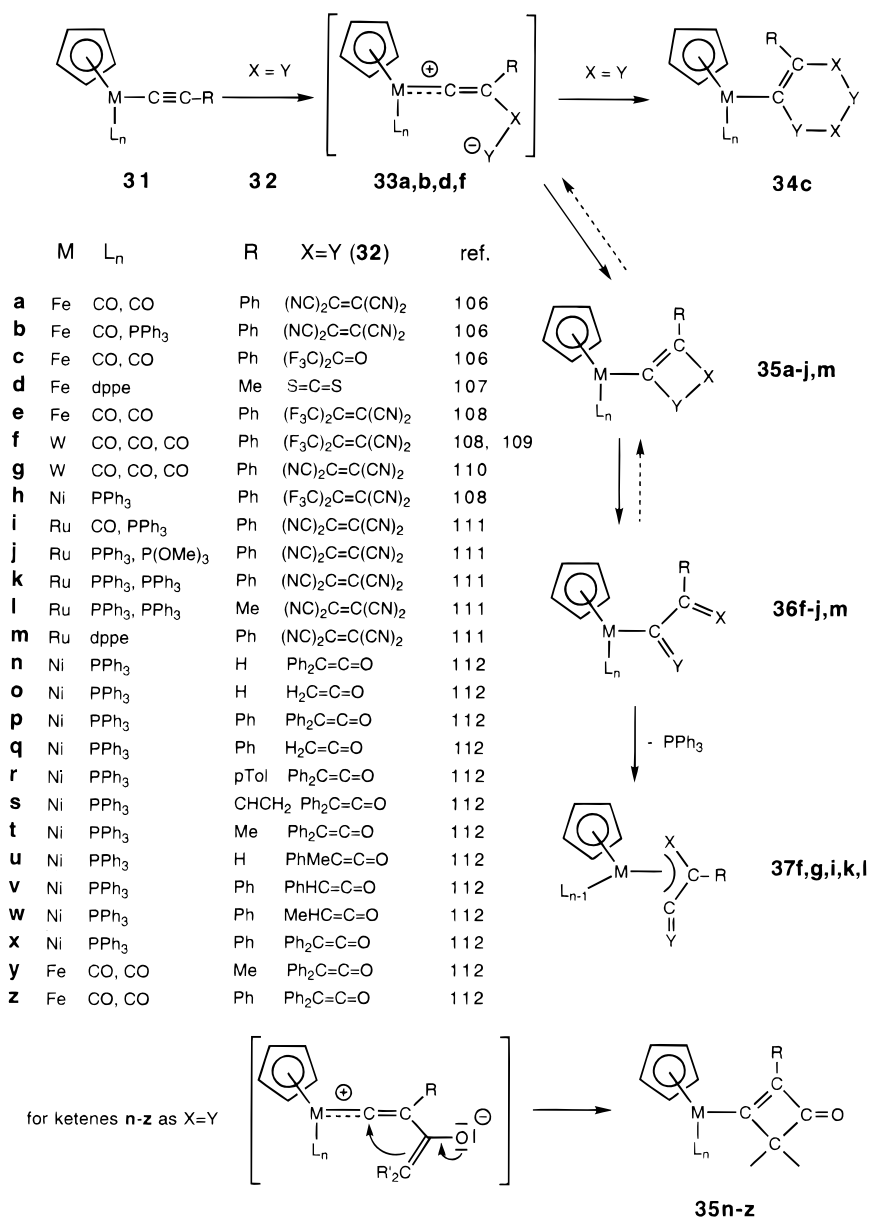
wise) [2+1] cycloaddition of aryl isocyanides to the P=C double bond in (Cp*)(CO)₂FeP=C(SiMe₃)₂ according to Scheme 3, giving iminophosphiranes. The preparation of metala iminodiphosphiranes from metallodiphosphenes and isocyanides has been described by Lentz.⁹⁹



A η^4 -coordinated Fe(CO)₃ fragment can be used as protecting group in the [2+1] addition of dichlorocarbene (DCC) to cyclic^{100,101} or open-chain¹⁰¹ polyenes. Kanematsu et al.¹⁰² reported the highly stereoselective all-trans addition of DCC to medium-membered cyclopolyenes (cf. eq 13). When two of the three π -bonds in *N*-(ethoxycarbonyl)azepine and cycloheptatriene are coordinated to Fe(CO)₃ as in **25** and **26** (eq 14), the monoadducts, which otherwise are not observed at all, are formed exclusively. The organic cycloadducts **29** and **30** can be liberated from **27** and **28** through oxidative decomplexation with trimethylamine *N*-oxide¹⁰⁰ or copper(II) chloride.¹⁰¹



Scheme 4



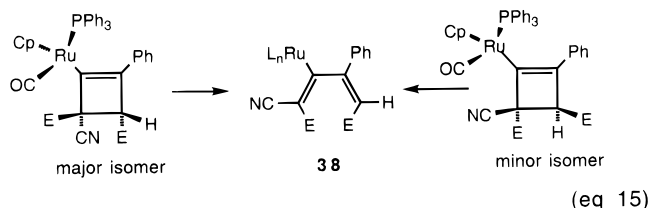
Epoxides (oxiranes) are the result of a formal [2+1] cycloaddition of an oxygen atom to an olefin. The mechanisms of transition metal-mediated stoichiometric and catalytic oxygen atom transfer reactions are still under debate. The metal species involved are predominantly oxo (O^{2-}) complexes, $L_nM=O$, of groups 6 to 8.¹⁰³ For a discussion of mechanisms and synthetic applications of olefin epoxidations refer to the reviews by Schurig and Betschinger¹⁰⁴ (*Metal-Mediated Enantioselective Access to Unfunctionalized Aliphatic Oxiranes*) and Jørgensen¹⁰⁵ (*Transition-Metal-Catalyzed Epoxidations*).

B. [2+2] Metal-Assisted Cycloaddition Reactions

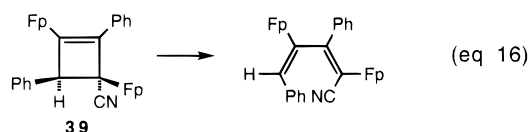
Electron-rich metal fragments can stabilize positive charge and thus allow σ -acetylides $L_nMC\equiv CR$ (**31**) to undergo stepwise [2+2] additions to electrophilic double bonds $X=Y$ (**32**) of which one terminus can accommodate a negative charge^{106–116} (Scheme 4). This type of reaction is not limited to the cyclopentadienyl complexes in Scheme 4, but has also been described for e.g. $Mn(C_2Ph)(CO)_3(dppe)$.¹⁰⁷ The in-

termediacy of the dipolar structure **33** has not only been demonstrated spectroscopically^{106,111} but is also supported by the observation of exclusively one regioisomer with the unsymmetrical olefin $(F_3C)_2C=C(CN)_2$ in **e,f,h**. [The identity of the observed species with **33** has been questioned,¹⁰⁷ however, without supporting evidence.] In the corresponding complexes **35** only the $C(CN)_2$ moiety is found in position Y. The activation barriers of the consecutive reactions in Scheme 4 and therefore the nature of observable or isolable products is strongly influenced by the metal–ligand combination. The cycloreversion of σ -cyclobutenyl to σ -butadienyl ligands as in **35** to **36** has been observed rather frequently^{107–109,112,117–120} and has in particular been investigated by Bruce et al. In case of the TCNE adducts the cycloreversion occurs very readily and often precludes the isolation of the cyclobutenyl complexes. Bruce et al.¹²¹ have reported the reaction of **31i** with the prochiral olefin *trans*-1,2-bis(carbomethoxy)-1-cyanoethene [*trans*- $C(CN)(CO_2Me)=CH(CO_2Me)$]. Two diastereomeric σ -cyclobutenyl complexes (eq 15) were

formed from attack of the *re* and *si* face of the olefin in a ratio of ca. 2:1, and the X-ray molecular structures of both isomers have been determined. Thermally, at 80 °C, they are both converted to the same σ -butadienyl complex **38**, the structure of which has again been elucidated by a single-crystal X-ray study.

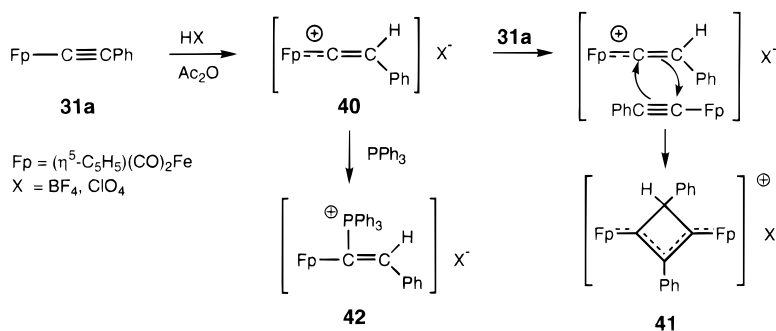


This confirms that the cycloreversion **35** to **36** occurred in a conrotatory fashion in accord with the Woodward–Hoffmann rules. The authors state that the cycloreversion reaction of the cyclobutenyldiiron complex **39** (eq 16, Fp = CpFe(CO)₂) that had earlier been reported by Kolobova et al.¹¹⁸ also had proceeded via the expected conrotatory process. In the reac-

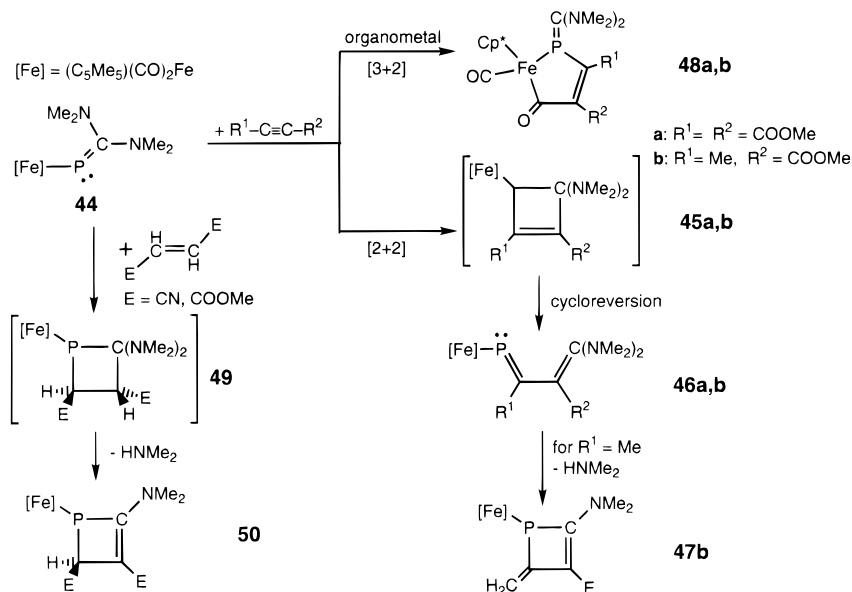


tions in Scheme 4 with ketenes as X=Y¹¹⁰ (**n–z**), it is not clear that a dipolar intermediate **33** is actually

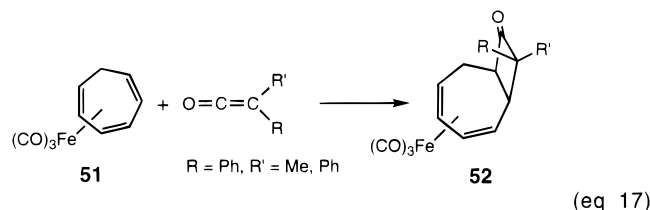
Scheme 5



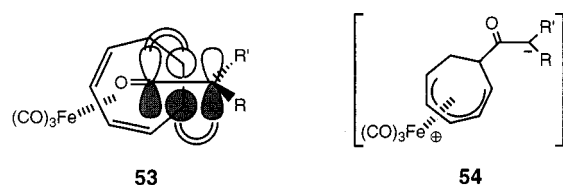
Scheme 6



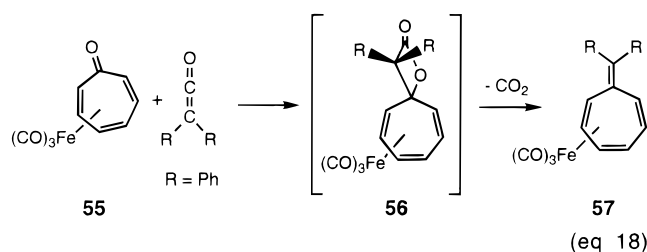
Since the (diene)Fe(CO)₃ group is also known for its ability to effectively stabilize positive charge, Goldschmidt et al.¹²⁶ investigated the stereochemistry of the [2+2] cycloaddition of unsymmetrically substituted ketene to the noncoordinated π -bond of tricarbonyl(η^4 -cycloheptatriene)iron **51** in eq 17. The



outcome, i.e., the regio- and stereospecific formation of **52** with the larger substituent (R = Ph) in the endo position confirms a concerted mechanism via transition state **53**, thus a [$\pi 2_s + \pi 2_a$] addition in the electronic notation. A deviation from the concerted pathway via the possible intermediacy of zwitterion **54** in a stepwise mechanism would have resulted in loss of stereospecificity. The [2+2] cycloaddition prod-

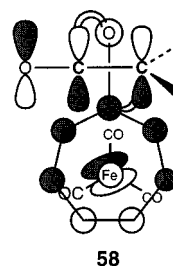


uct **52** is formed at room temperature. At elevated temperatures it undergoes a [2,2]-sigmahaptotropic rearrangement¹²⁷ to the corresponding σ, π -allylic [3+2] adduct (see following section). When, in place of **51**, troponeiron tricarbonyl **55** is used¹²⁸ (eq 18), we have a different LUMO which in transition state **58** interacts in a [$\pi 2_s + \pi 2_a$] manner via its ring-carbonyl group with the diphenylketene HOMO to give the intermediate spiro β -lactone **56** which eliminates CO₂ to give the isolated fulvene complex **57**.



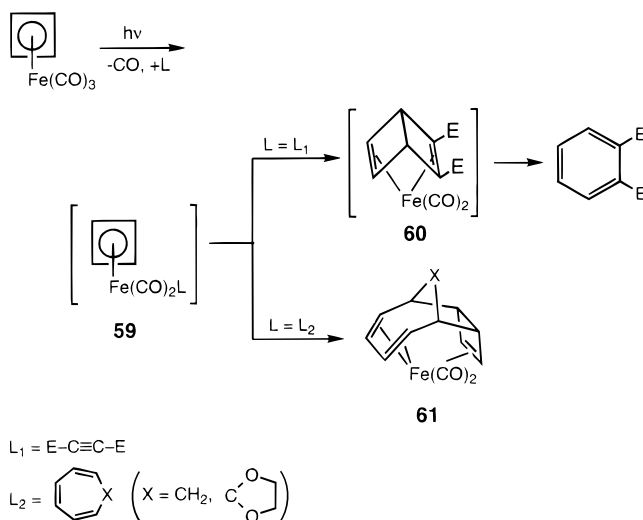
(Cyclobutadiene)Fe(CO)₃ complexes in conjunction with an oxidant such as ammonium cerium(IV) nitrate (see e.g., refs 129–135) or lead(IV) acetate^{136,137} have found extensive use in [2+2], [3+2], and [4+2] cycloaddition reactions. However, it has unequivocally been shown by Pettit¹³⁸ and others^{139–141} that the cycloaddition reactions take place with the *free* cyclobutadiene after oxidative destruction of the complexes. These are therefore not metal-assisted reactions; the Fe(CO)₃ fragment acts only as temporary storage device, and the reactions are not further discussed here. They are included in the review by Efraty on metal cyclobutadiene complexes.¹⁴² The thermally very stable complex (2,2'-bipyridine)(tetramethylcyclobutadiene)nickel¹⁴³ does not react with

added donor ligands, e.g., bipyridine or triphenylphosphine; however, CO (1 atm, 20 °C, THF) displaces the cyclobutadiene, and its [2+2] (or [4+2]) cycloaddition, octamethyl tricyclo[2.2.0.0]octadiene, is formed. It is therefore reasonable to assume that the cycloadducts that are formed with acrylonitrile, tetramethyl benzoquinone, or diphenyl acetylene, which are all good π -acceptors, are also the result of an initial displacement of the coordinated cyclobutadiene.

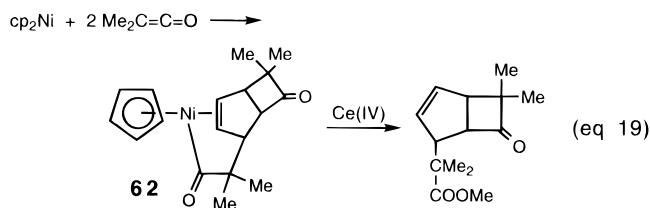


On the other hand, it has been shown that cycloaddition reactions between cyclobutadiene and other unsaturated systems can also be effected while both components are coordinated to the metal, see Scheme 7.¹⁴⁴ Through photochemical substitution of one CO

Scheme 7

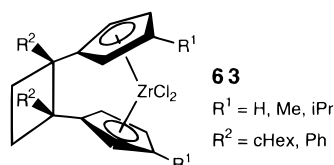


ligand in (cyclobutadiene)Fe(CO)₃ for L the reactive intermediates **59** are formed which undergo intramolecular cycloaddition reactions. The [2+2] cycloadduct with dimethyl acetylenedicarboxylate, the Dewar benzene complex **60**, is coordinatively unsaturated and decomposes to the isolated dimethyl phthalate, while the [6+2] cycloadducts with the cycloheptatrienes L₂, complexes **61**, are coordinatively saturated and stable. The reaction product of nickelocene (di- π -cyclopentadienylnickel) with dimethylketene¹⁴⁵ has been reinvestigated.¹⁴⁶ It is identified as **62** (eq 19), i.e., the reaction consists of

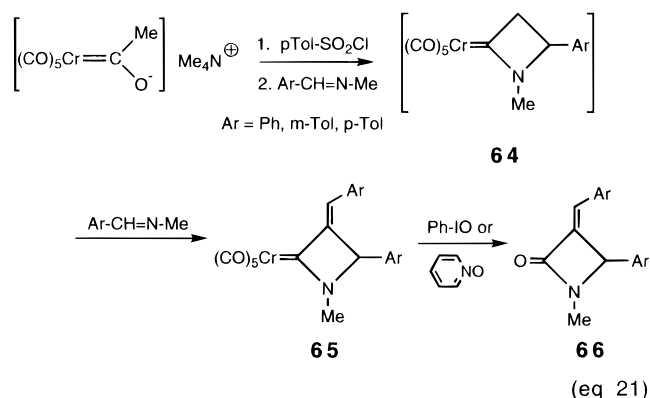
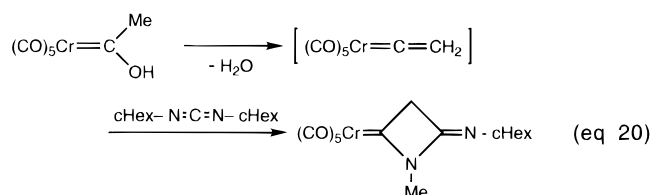


a [2+2] addition of dimethylketene to one of the coordinated Cp rings with subsequent insertion of a second ketene into a nickel–carbon bond. The organic ligand was liberated as its methyl carboxylate by oxidative degradation of **62** with ammonium cerium(IV) nitrate in methanol. [The author reports formation of the same product by degradation of **62** with sodium sulfide in methanol solution, however without experimental details.] Other examples of [2+2] additions to a coordinated Cp ring in nickelocene, e.g., of tetrafluoroethylene¹⁴⁷ and tetrafluorobenzene¹⁴⁸ have been reported. At -15°C in acetonitrile, the thermally forbidden [2+2] cycloaddition of propylene to one double bond of norbornadiene (NBD), coordinated to palladium in the dicationic complex $[\text{Pd}(\text{NBD})(\text{MeCN})_2](\text{PF}_6)_2$, to give 55% of free 3-methyltricyclo[4.2.1.0^{2,5}]nonene-7 has been observed.¹⁴⁹

A series of *ansa*-metallocenes **63** have been made by Erker et al.^{150,151} by photochemical intramolecular [2+2] cycloaddition of bis(alkenylcyclopentadienyl)-zirconium dichlorides, $[(\text{R}^1)\text{CpC}(\text{R}^2)=\text{CH}_2]_2\text{ZrCl}_2$.

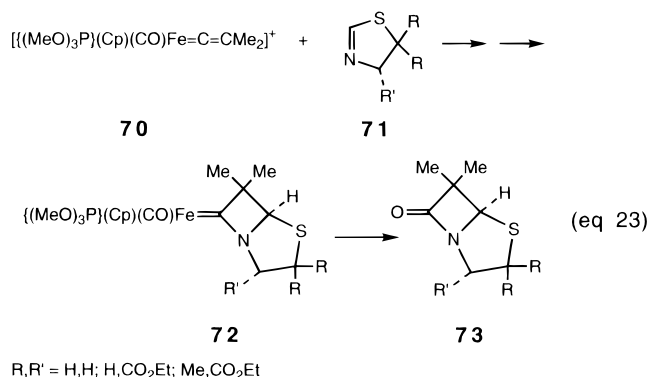
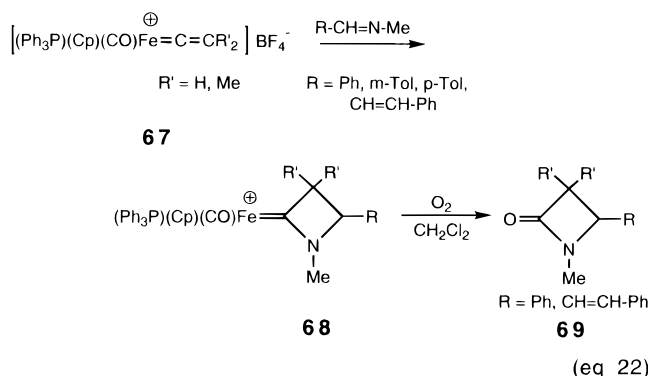


Metal vinylidene complexes, often generated in situ from carbene precursors or through prototropic rearrangement of η^2 -coordinated terminal alkynes,^{152–154} are promising reactants for β -lactam syntheses^{155–159} via [2+2] cycloaddition reactions of imines. Following a report of Fischer¹⁶⁰ (eq 20), Barrett et al.¹⁵⁵ (eq 21) could isolate complexes **65**, however in low yields.



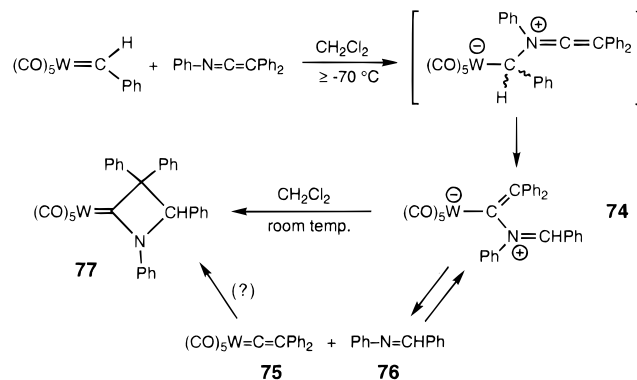
They were presumably formed through the addition or rather condensation of a second imine to the CH acidic ring methylene group in the initial adduct **64**. Oxidation of **65** with iodosobenzene¹⁶¹ or pyridine *N*-oxide¹⁶² to the β -lactams **66** is very efficient. Use of cationic iron(II) vinylidenes **67**^{156,163} (eq 22) gave

azetidinyldene complexes **68** in yields up to 52%, which in turn were oxidized again to the β -lactams **69**. High yields of 2-azetidinyldene complexes have also been obtained from the [2+2] addition of neutral vinylidenes $\text{Cp}'(\text{CO})_2\text{Mn}=\text{C}=\text{CHR}$ with imines.^{164,165} The penam derivatives **73** (eq 23) were obtained in yields of 32–52% after oxidation by iodosobenzene or tetrabutylammonium nitrite of the adducts **72** from the iron vinylidene complex **70** and the 2-thiazolines **71**.¹⁶⁶ Different from the reaction of cationic



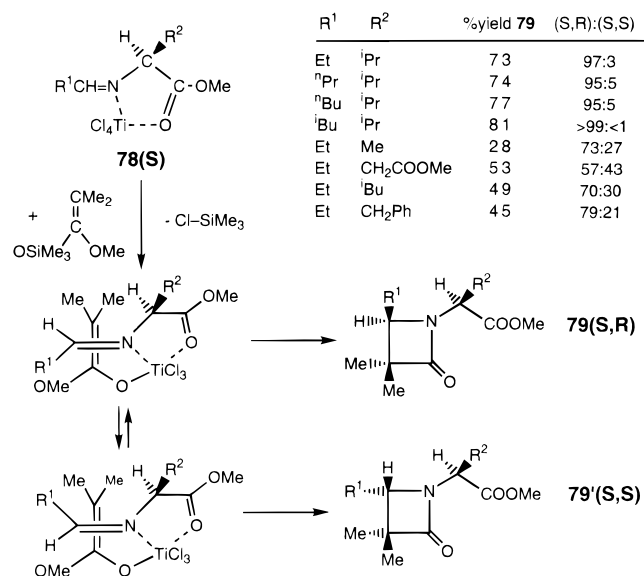
iron vinylidenes with imines in eq 21, Fischer et al.¹⁶⁷ have reported the formation of tungsten azetidinyldene complex **77** from tungsten benzylidene and triphenylketenimine according to Scheme 8. While

Scheme 8

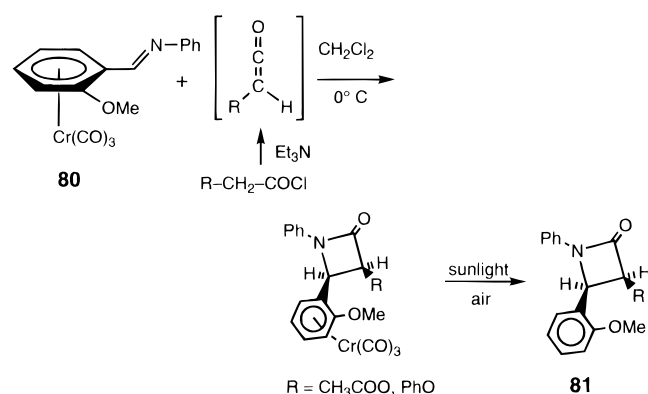


the $\text{M}=\text{C}/\text{N}=\text{C}$ metathesis products **75** and **76** are formed reversibly from the isolable zwitterionic intermediate **74**, the formation of azetidinyldene **77** is irreversible. The authors suggest that **77** is formed from **74** by an intramolecular cyclization, but they do not exclude a direct antharafacial [2+2] addition of **76** (and other imines in crossover experiments) to the $\text{C}=\text{C}$ bond in **75**.

Scheme 9

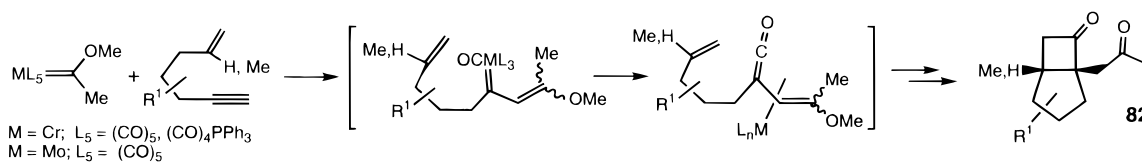


Scheme 10

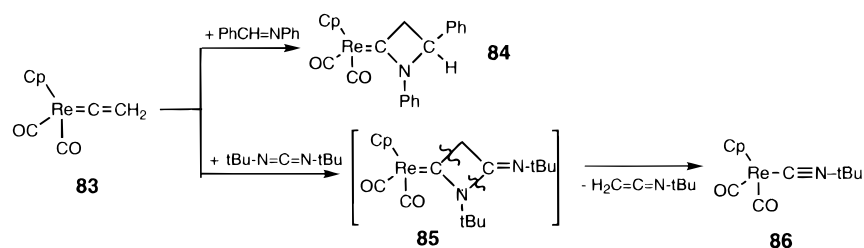


Very efficient metal-induced diastereoselectivity was observed in the asymmetric synthesis of β -lactams **79** by the stepwise [2+2] cycloaddition of dimethylketene trimethylsilyl acetal to the TiCl_4 complexes **78** of Schiff bases of chiral α -amino esters (Scheme 9).¹⁶⁸ A preparatively very attractive photochemical synthesis of β -lactams, starting from chromium or molybdenum Fischer carbene complexes and imines, oxazoles, or oxazolines has been developed by Hegedus et al.^{169–175} Mechanistically, these reactions appear to involve a [2+2] addition of an

Scheme 11



Scheme 12



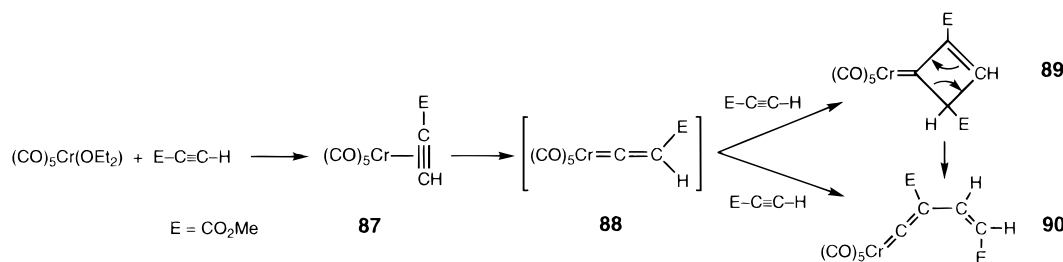
intermediate photochemically generated ketene complex.¹⁷⁶ Overall, however, they represent a stepwise multicomponent [2+1+1] addition and will be discussed in section II.F. The same holds for the analogous photochemical reaction of the Fischer carbene complexes with olefins, producing cyclobutanones.¹⁷⁷ In a stereoselective variant of the Staudinger reaction, chiral β -lactams **81** have been prepared¹⁷⁸ in high enantiomeric excesses (>98% ee) and yields (95%) by the [2+2] addition of enantiomeric pure $\text{Cr}(\text{CO})_3$ -complexed arylimines **80** to the C=C bond of ketenes, generated in situ from acid chlorides (Scheme 10).

The reaction of Fischer carbene complexes and enynes (Scheme 11) generates intermediate vinyl ketene complexes which undergo an intramolecular [2+2] addition to give bicyclo[3.2.0]heptanones **82**. Wulff et al.¹⁷⁹ have investigated the reactivity and stereoselectivity in dependence of the metal and the substitution pattern of the enyne and compared it with those of independently generated free vinyl ketenes. From the observed enhancement of rate and stereoselectivity, and the dependence on the metal and its ligands, the authors conclude, that the metal is coordinated to the vinylketene during the cycloaddition.

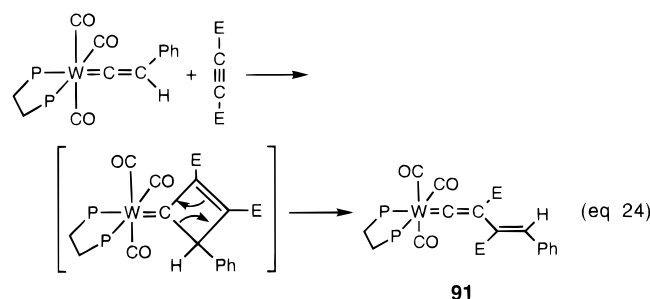
The vinylidenerhenium complex **83**, or its manganese analogue, adds its C=CH₂ double bond across the C=N double bond in $\text{PhN}=\text{CHPh}$ ^{165,180} (Scheme 12) to give the carbene complex **84**. This is analogous to the above mentioned cycloaddition of imines with vinylidene iron complexes.^{156,163,166} In the reaction of **83** with carbodiimide, the supposed initial [2+2] cycloadduct **85** undergoes a cycloreversion to the isolated isocyanide complex **86**, whereas the chromium analogue of **85**¹⁶⁰ in eq 20 was a stable compound. With benzalazine, $\text{Ph}(\text{H})\text{C}=\text{NN}=\text{C}(\text{H})\text{Ph}$, **83** does not undergo two [2+2] additions to the two C=N bonds, but rather a bicyclic product is obtained with two N–N fused five-membered rings via a “criss-cross” 1,3-dipolar [3+2] cycloaddition reaction (cf. eq 68, **246b** in section II.C.2).

There have been reports^{181–183} on the participation of the C=C bond of metal vinylidene complexes¹⁵³ in [2+2] cycloaddition reactions with alkynes. The resulting cyclobutenylidene complexes may consecutively undergo cycloreversion reactions. Berke et

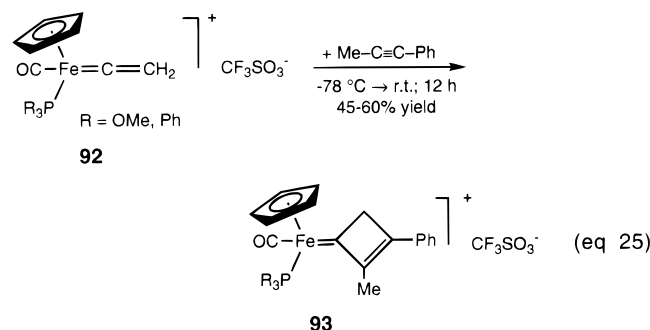
Scheme 13



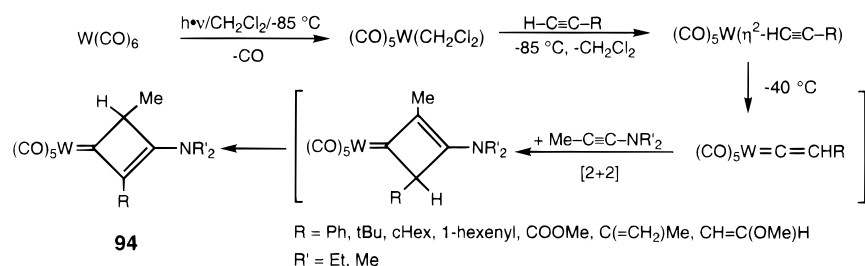
al.¹⁸² reported the isolation of compounds **87**, **89**, and **90** (cf. Scheme 13) in yields of 39%, 43%, and 8.6% after warming of $(\text{CO})_5\text{Cr}(\text{Et}_2\text{O})$ in the presence of methyl acetylenecarboxylate (MAC) and chromatographic workup at -60°C . The formation of **89** and **90** was explained via the common intermediate vinylidene complex **88** resulting from prototropic rearrangement of **87**. The [2+2] addition of **88** with a second MAC gives **89**, which is described as thermally very labile, while **90** is proposed to arise from a Michael addition of C-H acidic **88** to MAC. An alternative would have been the indicated cycloreversion **89** to **90**. Via this route the formation of vinylvinylidene complexes **91**¹⁸³ is explained (eq 24).



Without the electron-withdrawing ester groups this cycloaddition/cycloreversion sequence may not apply. Indeed, the [2+2] addition of phenylpropyne to the cationic vinylidene iron(II) complex **92** led to the first stable cyclobutenylidene complexes **93** (eq 25).¹⁸⁴



Scheme 14

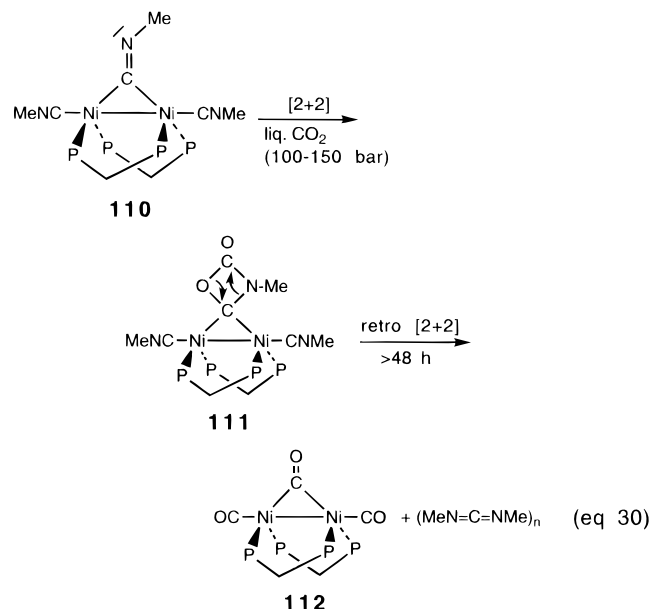


More recently, Fischer¹⁸⁵ has reported a one-pot synthesis of stable cyclobutenylidene tungsten complexes **94** according to Scheme 14. After chromatographic workup, the isolated yields of **94** are 21–37%. In a communication, Geoffroy et al.¹⁸⁶ suggest that the photoassisted polymerization of acetylene or phenylacetylene with $\text{W}(\text{CO})_6$ (eq 26) does not proceed via the addition of free acetylene to the C=C bond of the intermediately formed tungsten vinylidene complex **95**, but rather, in analogy to the related carbene complex,¹⁸⁷ via the addition of η^2 -coordinated alkyne to the $\text{W}=\text{C}$ bond, i.e., an organometal cycloaddition in a sequence as indicated between square brackets.

Reactions, as in eq 24 or 26, or the reaction of **35** to **36** in Scheme 4, where initially formed [2+2] cycloadducts consequently undergo a retroaddition by electrocyclic ring opening are not uncommon. Fischer et al. have investigated the reactions of chromium and tungsten pentacarbonyl complexes of thio, seleno, and telluroaldehydes and ketones **96**^{188–190} with yneamines (eq 27) and other donor-substituted alkynes (OR, SR, SeR).^{191–198} The cycloaddition (ΔH^\ddagger values ca. 30 kJ/mol; ΔG^\ddagger values around $-150 \text{ J}/(\text{mol K})$) is regioselective ($\text{R}^2 = \text{Me}$) and the ring opening is stereoselective ($\text{R}^1 = \text{H}$). With R^2 being NET_2 , the initial cycloadducts, thiet and selenet complexes **97**, can be observed spectroscopically because there the subsequent (rate-determining) ring opening is much slower. The thio- and selenoacrylic amides can be displaced unaltered from the ring-opened complexes **98** by CO (70–100 bar; 60–100 $^\circ\text{C}$). The thio- and selenobenzaldehyde complexes **96** ($\text{M} = \text{W}$; $\text{R}^1 = \text{H}$) react with vinyl ethers by regioselective [2+2] cycloaddition of the C=C and C=X bonds to form isolable thietane and selenetane $\text{W}(\text{CO})_5$ complexes.^{188,199} For a reaction of **98** as heterodiene in a [4+2] cycloaddition, see section II.D.2 (eq 96).

Tungsten and chromium vinylidene complexes $(\text{CO})_5\text{M}=\text{C}=\text{CR}^1\text{R}^2$, with R^1/R^2 being Ph/Ph; *t*-Bu/Et; *t*-Bu/Me, react with electron-rich alkynes ($\text{MeC}\equiv\text{CNET}_2$, $\text{Et}_2\text{NC}\equiv\text{CNET}_2$, $\text{MeC}\equiv\text{COEt}$) to give cyclobutenylidene complexes, two of which have also

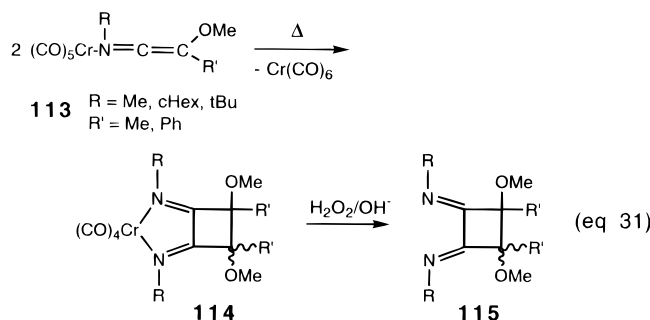
isonitrile to give **111** which has been isolated and characterized. Independent labeling experiments with $^{13}\text{CO}_2$ and $^{13}\text{C}\equiv\text{NMe}$ confirmed that the coordinated CO carbon atoms in **112** exclusively originate from the isocyanide ligands. The thermal formation



of **111** in solution under <3 atm of CO_2 only proceeds in the presence of catalytic amounts ($\sim 1/100$ equiv) of NaPF_6 . This suggests a two-step mechanism for the cycloaddition reaction via a zwitterionic carbyne intermediate which is stabilized by the Na^+ ions. Complex **111** is also formed on irradiation of a THF solution of **110** under 1 atm of CO_2 , and the photochemistry²¹³ and electronic spectroscopy²¹⁴ of **110** have been thoroughly investigated.

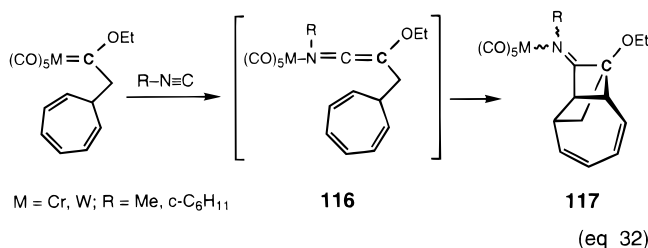
As opposed to these reactions, the metal-induced (mostly with Rh(I)), stoichiometric²¹⁵ or catalytic^{216,217} ring-opening reactions of strained cyclobutanes to the formal [2+2] cycloreversion products proceed by an oxidative addition (insertion of the metal into the strained C–C bond)/reductive elimination sequence.

Heteroatom-stabilized carbene complexes react with isocyanides to give ketenimine complexes **113**.^{218–222} On warming, complexes **113** dismutate, whereby, in a template reaction, two ketenimine ligands undergo a symmetrical (head to head) [2+2] cyclodimerization via their C=C bonds (eq 31).²²¹ The



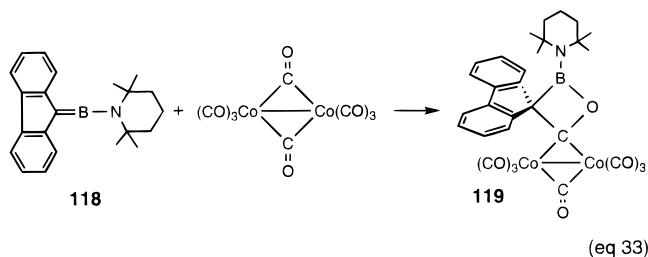
X-ray structure of one complex **114** has been reported²²³ and the 1,2-bis(imino)cyclobutanes **115** can be liberated from **114**, e.g., by treatment with $\text{H}_2\text{O}_2/\text{OH}^-$. The ketenimine complexes **116**,²²⁴ containing

a C-(4-alkenyl)ketimine fragment are formed in situ as shown in eq 32. They undergo an intramolecular



[2+2] addition, giving *syn*- and *anti*-{9-ethoxy-10-R-iminotricyclo[5.3.0.0^{2,9}]deca-3,5-diene-*N*} $\text{M}(\text{CO})_5$ (**117**) which is formed in a strictly stereospecific fashion in an orbital controlled [2_s+2_a] cycloaddition reaction.

Cycloadditions to the C=O bond of bridging carbonyl ligands are very exceptional. One such example of a metal-mediated activation of CO has been reported by Nöth et al.,²²⁵ for an example of a 1,3-dipolar cycloaddition to a μ -CO ligand see eq 73 in the last paragraph of section II.C.2. The B=C bond of (9-fluorenylidene)(2,2,6,6-tetramethylpiperidino)-borane **118** cycloadds at room temperature in toluene in [2+2] fashion to the bridging CO in $\text{Co}_2(\text{CO})_8$ to give the C-bridging oxaboretane in **119** (eq 33). The

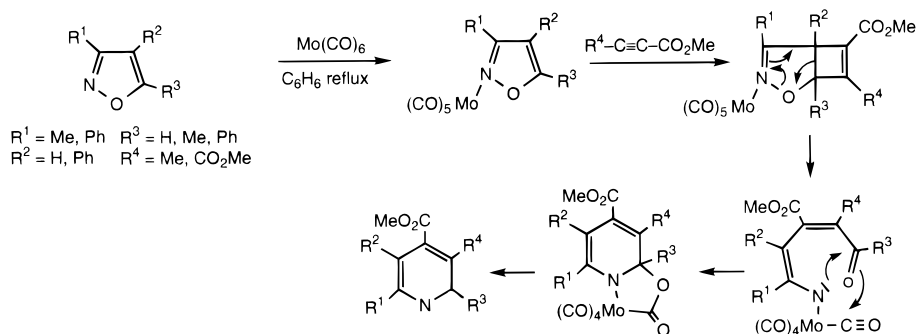


only other comparable example is a [3+2] addition of a diazoalkane reported by Dickson et al.²²⁶ (see section II.C.2).

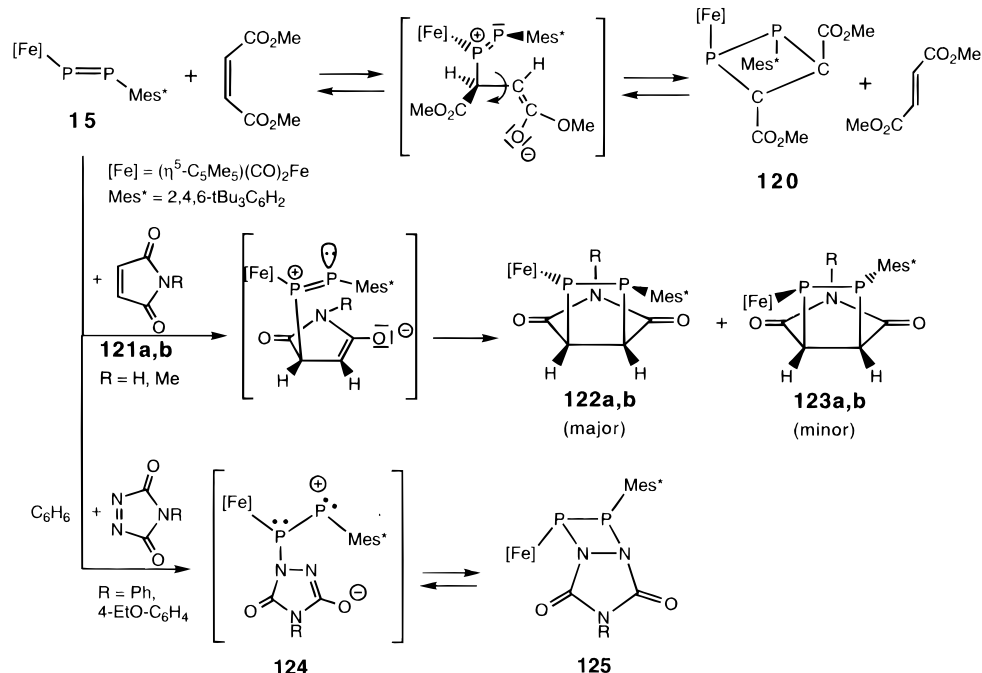
An interesting reaction sequence, starting with a molybdenum-induced [2+2] cycloaddition of acetylenic esters across the C4–C5 double bond of 3,5-disubstituted isoxazoles, has been reported by Kobayashi and Nitta²²⁷ (cf. Scheme 15). Preparatively, the reaction is not very attractive because of the low yields of isolated pyridines (11–28%) which are accompanied by comparable amounts of cyclotrimerized alkyne. However, simple isoxazoles do not undergo [2+2] cycloadditions with olefins or acetylenic esters, and the reaction clearly demonstrates the activating influence of the coordinated metal.

The diphosphenyl complex **15** undergoes a [2+2] cycloaddition reaction with electron-poor alkenes, such as fumarodinitrile, dimethyl fumarate, and dimethyl maleate, to give the all-*trans*-configured 1,2-diphosphetane complexes **120**.⁹⁰ Since a concerted [2+2] addition is symmetry forbidden, and because in the reaction with dimethyl maleate also only the *trans*-configured product **120** (and considerable amounts of dimethyl fumarate) are formed, a step-wise mechanism has been proposed, which is indicated in Scheme 16. When **15** is reacted with equimolar amounts of *N*-aryl triazolindiones in benzene solution, the [2+2] adducts **125**, analogous to **122** and **123**, precipitate.⁸⁴ When instead of apolar

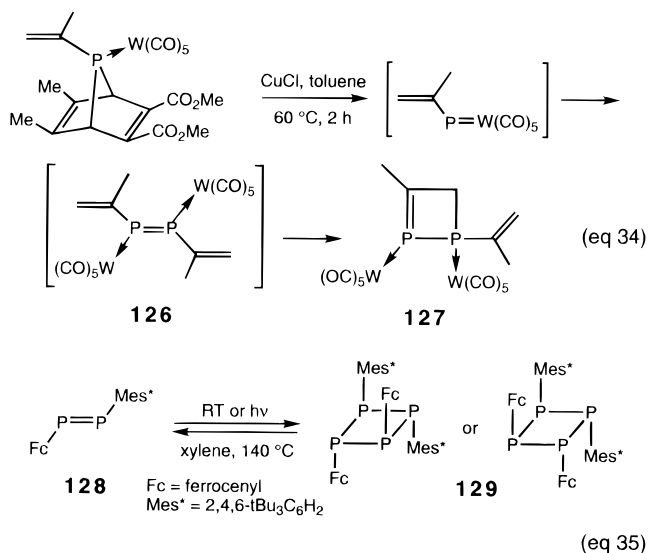
Scheme 15



Scheme 16

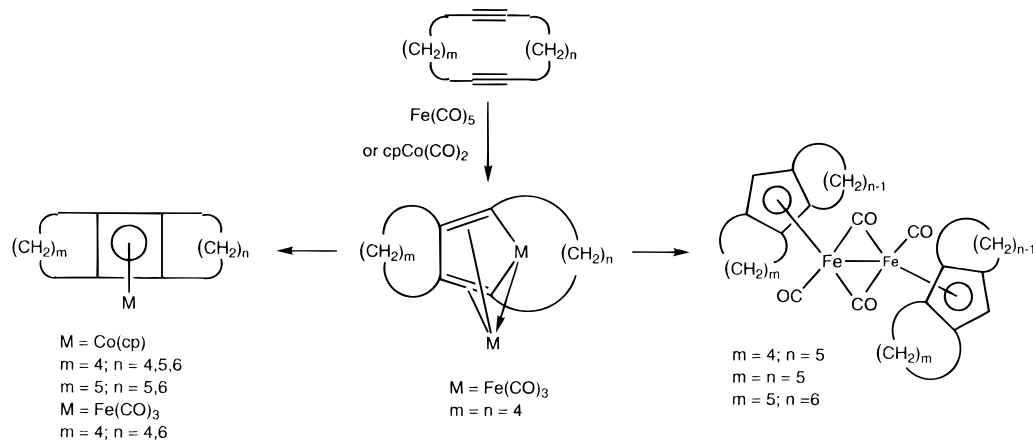


benzene, dipolar diethyl ether is used as the reaction medium, the postulated zwitterionic intermediates **124** (one of the possible resonance forms is shown) obviously become sufficiently long-lived to form a 12-membered macrocycle in a [6+6] head-to-tail cyclodimerization. These [2+2] cycloadditions of **15** contrast the behavior toward vinyl ketones and azodicarboxylates which undergo cheletropic [4+1] cycloadditions (cf. section II.E). For a concerted cheletropic [4+1] addition, a cisoid arrangement of the α,β -unsaturated carbonyl is crucial. Indeed, when it is fixed in a rigid transoid arrangement as in maleimides **121a,b**, the system escapes into the stepwise [2+2] addition, giving diastereomeric mixtures of **122a,b** and **123a,b**.⁸⁹ An intramolecular [2+2] addition of trans-divinyl-diphosphene complex **126**, giving the 2,3-dihydro-1,2-diphosphete **127** (eq 34), has been reported by Mathey et al.²²⁸ Nonprotected diphosphenes often undergo [2+2] dimerization to tetraphosphetanes (normally head-to-tail).⁸⁷ This appears also to be true for the ferrocenyldiphosphene **128** in eq 35.²²⁹ The stereochemistry of adduct **129** is not definitely established, but a head-to-head dimer is spectroscopically made plausible. More importantly, however, the ferrocenyl substituent obviously is responsible for a ready thermal cycloreversion to the original diphosphene.



King et al.^{230–233} and others²³⁴ have investigated the metal-induced intramolecular transannular cyclizations of macrocyclic alkadiynes. They proceed stepwise via dinuclear intermediates (cf. Scheme 17) and the type of isolable product depends on the metal complex and the number of methylene groups bridging each side of the pair of $\text{C}\equiv\text{C}$ bonds. These

Scheme 17



reactions, as well as the [2+2] cyclodimerization of monoacetylenes (see also²³⁵) are included in the review by Efraty.¹⁴²

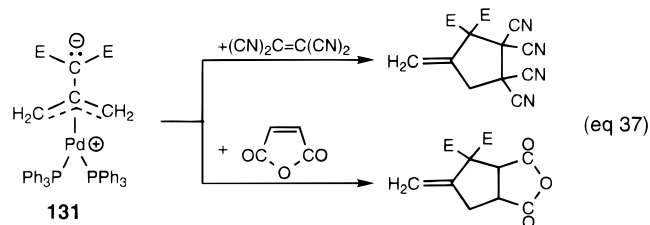
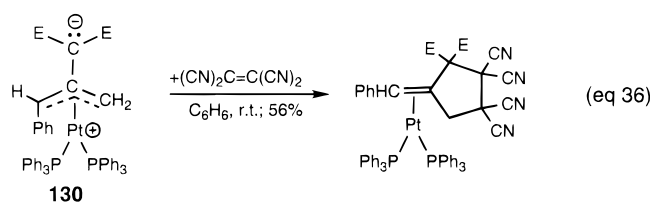
C. [3+2] Metal-Assisted Cycloaddition Reactions

1,3-Dipolar cycloaddition^{236–238} has become a classic in organic chemistry, being one of the most important tools for synthesizing heterocyclic five-membered ring compounds. As metals can induce or stabilize charge in an organic fragment, it is not surprising that there are many examples of metal-assisted 1,3-dipolar cycloaddition reactions where the metal stabilizes and activates existing 1,3-dipoles. A metal fragment can also induce 1,3-dipolar behavior in organic groups which do not originally have these properties. Furthermore, the steric bulk of an ML_n fragment attached to the 1,3-dipole or to the dipolarophile can be used to influence the stereochemical course of the reaction. Finally, metal fragments have also advantageously been used to activate the dipolarophile, or to protect reactive sites and thereby produce chemoselectivity. The examples in the following two subsections will illustrate each of these functions of the metal.

1. Activation of the 1,3-Dipole

Two reviews, by Trost,²³⁹ and by Binger and Büch,²⁴⁰ are on the synthesis of five-membered rings by [3+2] cycloaddition of (1,3-dipolar) trimethylene-methane (TMM) and synthetic equivalents (see also ref 241). Although it mainly concerns transition metal (Pd, Ni) *catalyzed* reactions, it departs from and refers to the stabilization and reactivity of TMM coordinated to tricarbonyliron.^{242–244} The Pd-catalyzed [3+2] cycloaddition reactions of TMM precursors to electron-deficient alkenes have been suggested to proceed via zwitterionic ($\eta^3\text{-TMM}$) PdL_2 complexes.^{245–250} Ten years later, the groups of Wojcik^{251,252} and Chen²⁵³ were the first to isolate and structurally characterize such species. Both, the analogous $\text{Pt}(\eta^3\text{-TMM})$ (**130**, eq 36)²⁵¹ and $\text{Pd}(\eta^3\text{-TMM})$ (**131**, eq 37)²⁵³ complexes, at room temperature readily undergo stoichiometric [3+2] cycloaddition to, e.g., TCNE and maleic anhydride.

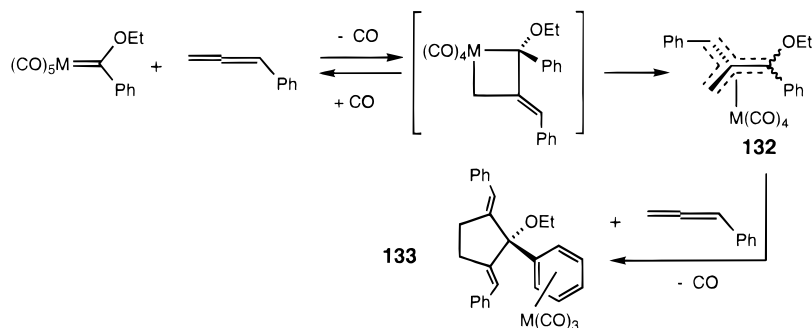
Substituted $\eta^4\text{-TMM}$ complexes **132** (Scheme 18) of Cr, Mo, or W have been obtained by Aumann et al.,²⁵⁴ presumably via metallacyclobutanes, from the



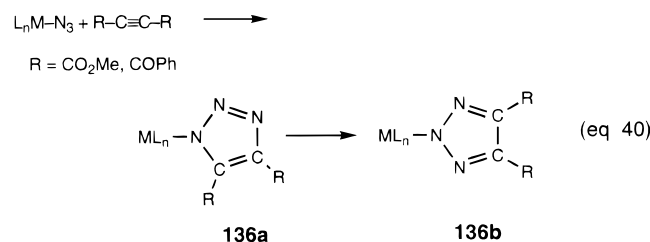
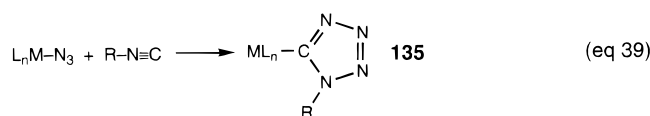
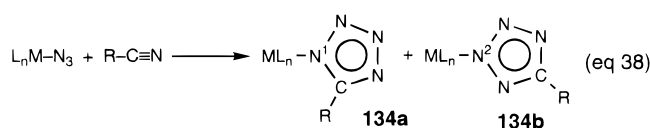
reaction of the Fischer carbene complexes $(\text{CO})_5\text{M}=\text{C}(\text{OEt})\text{Ph}$ with phenyl allene. Already at room temperature they slowly react further in [3+2] fashion with additional phenyl allene to give the carbocyclic five-membered rings **133**. Interestingly, the CO that is lost during this sequence is used up in a parallel catalytic [2+2+1] reaction which forms a cyclopentenone.

Organic azides have been frequently used as 1,3-dipoles for synthesizing heterocyclic compounds.^{255,256} Analogously, metal-coordinated azido ligands undergo 1,3-dipolar cycloaddition reactions with carbon-carbon and carbon-heteroatom multiple bonds, frequently under very mild conditions. A short review the *Chemistry of Coordinated Azides* has appeared in 1973;²⁵⁷ however, it refers to 1,3-dipolar additions only very briefly. Among others, this chemistry has most extensively been studied during the last two decades by the group of Beck. The metals involved are most often palladium(II),^{258–270} platinum(II),^{260,262,265–268,271} and cobalt(III),^{259,261,272–275} although a whole range of other transition metals (and main group metals, see e.g. refs 267 and 276–281) has been used, including nickel(II),^{258,282–284} rhodium(I),^{266,285} iridium(I),^{265,266} copper(I),^{286–288} and gold(I)^{267,288} and gold(III).^{263,267,289} With nitriles^{261,265,266,268,271,273,275,282,285,286,288,290,291} these metal azido complexes (eq 38) react to give metal- N^1 - or metal- N^2 -bonded tetrazolate complexes **134a** and **134b** respectively, a reaction which has been described²⁹² as early as 1958. A preference for N^2 -coordination of the ambidentate tetrazolate anion is sterically induced,²⁹³ but an electronic influence,

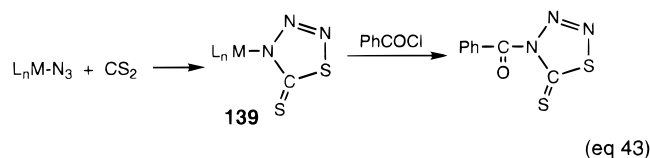
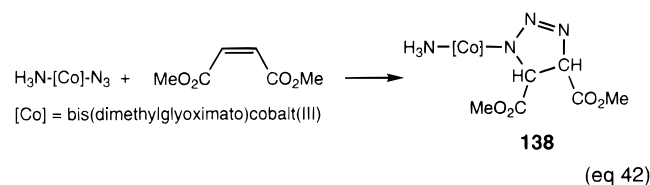
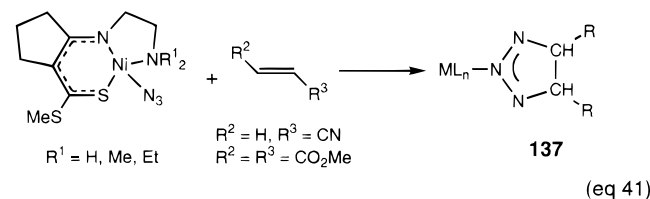
Scheme 18



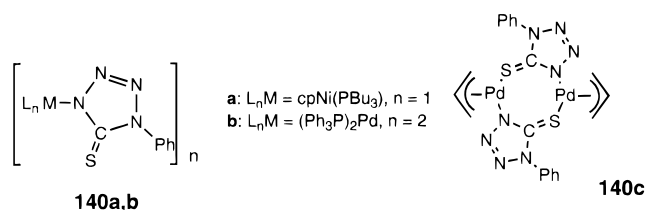
favoring the N^2 -bound isomers with electron-withdrawing substituents on the tetrazolates has also been put forward.²⁶⁹ With isonitriles^{267,274,285,289} (eq 39), the metal-carbon-bonded tetrazolates **135** are produced, and with activated alkynes^{261,265,272,273,282,285,294,295} (eq 40), the metal- N^1 -



bound triazolates **136a** are formed under kinetic control which may then isomerize to the thermodynamically stable N^2 -bound complexes **136b**. Olefins (eqs 41 and 42) are far less reactive, but a few

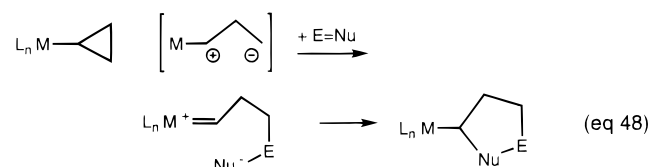
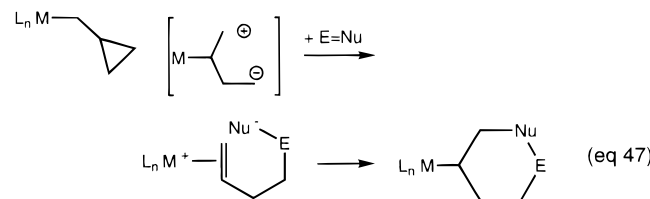
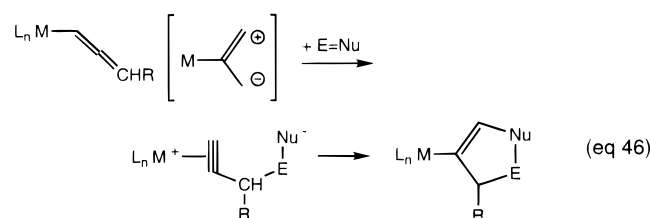
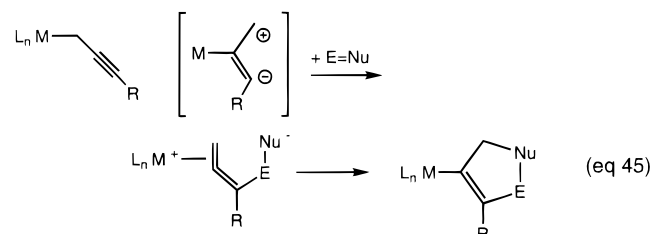
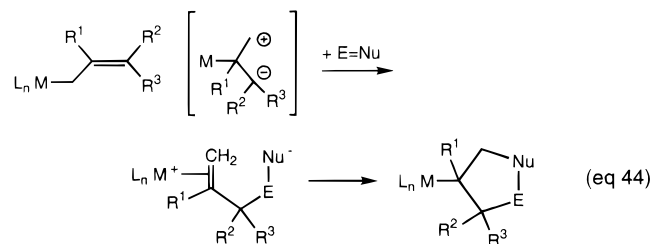


triazolinate complexes **137**^{269,282} and **138**²⁷³ have been described. Heterocumulenes such as carbon disulfide (eq 43)^{259,263,268,269,284,285,287,288} and phenyl isothiocyanate^{265,268,269,282,283} cycloadd to the metal-bound azide to give 1,2,3,4-thiatriazole-5-thiolate (**139**) and 1-phenyltetrazolate-5-thione complexes to which structures such as **140a-c** have been assigned. Although several complexes **139** could be isolated, they are thermally and photochemically very labile and often decompose to isothiocyanato complexes, sulfur, and dinitrogen.



An interesting, preparatively very useful metal-assisted [3+2] dipolar cycloaddition reaction is the reaction of (η^1 -allyl)metal and related (propargyl, allenyl, cyclopropylmethyl, cyclopropyl) complexes with various electrophilic, unsaturated substrates to yield cyclopentanoid derivatives (eqs 44–48). The reaction has been extensively studied and reviewed with respect to its scope and mechanism by the groups of Wojcicki, Rosenblum, Baker, and others.^{296–307}

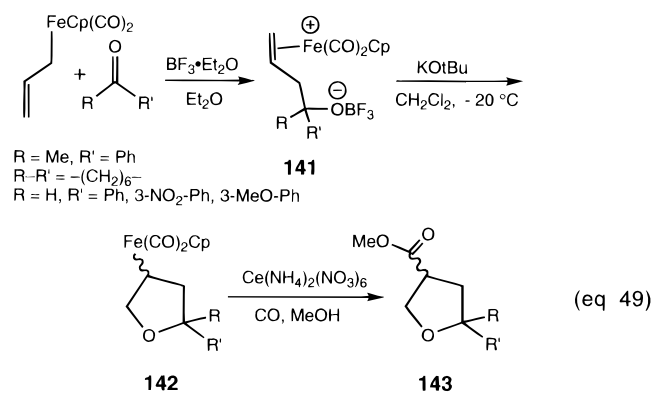
The electron-rich metal fragment L_nM induces dipolar behavior in the σ -bound organic ligand, and the dipolar equivalent of the starting complexes in eqs 44–48 is shown in square brackets. Direct evidence for the two-step path shown in the equations has been presented in the case of eq 44 when $E=Nu$ is SO_2 , where a dipolar metal- η^2 -olefin species has been detected and intercepted.^{296,301,308} The most widely used L_nM fragment is (η^5 -cyclopentadienyl)-dicarbonyliron (Fp). As the removal of an Fp group is often readily accomplished by a variety of methods (replacement by H,^{310,311} COCl or COOMe,^{311–316} halogen,^{309,311,313} or NH_2 ³¹⁷), these cycloadditions present a great potential also for organic synthesis as exemplified by the synthesis of, e.g., hydrazulenes,³¹⁸ trisubstituted cyclopentene,^{310,311} (\pm)-sarkomycin.³¹⁹ [Reference 309 gives a list of references on mechanistic, kinetic, and stereochemical investigations on the cleavage of compounds of the general formula $cpFe(CO)LR$ by electrophiles EX to yield RE and $cpFe(CO)LX$.] Table 4 gives an overview over the types of compounds used and obtained. When



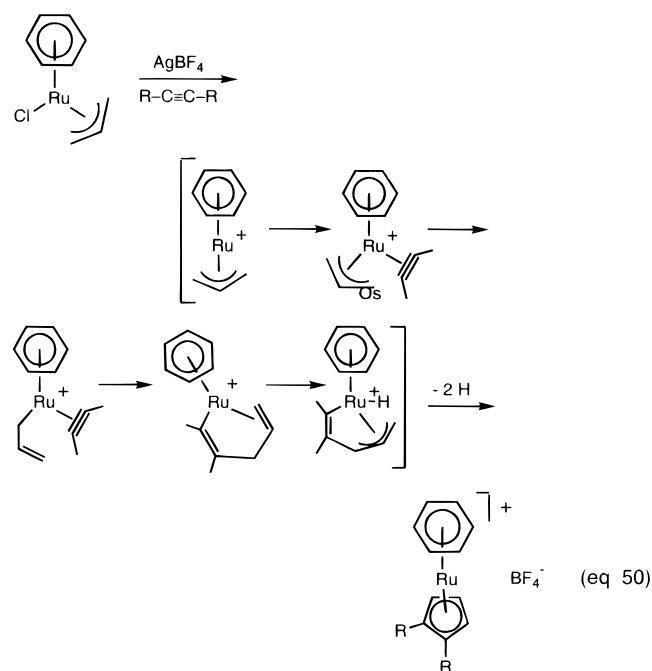
the CpW(CO)₂(η^1 -*trans*-hex-2-en-4-yn-1-yl) complex in entry 9 is reacted with 1 equiv of TCNE at 0 °C in THF,³⁵⁰ the [3+2] cycloadduct is formed as the major product (67% isolated yield after column chromatography), while [2+2] cycloaddition of TCNE to the C≡C triple bond is only a minor side reaction (5%). The L_nM(η^1 -2,4-hexadien-1-yl) complexes (L_nM = Mn(CO)₅, CpFe(CO)₂, CpMo(CO)₃) in entry 12 normally give [4 + 2] cycloaddition products with TCNE or maleic anhydride (see section II.D.2). On the other hand, they can be regarded as being a higher homologue of the allyl complexes.³³² If the ϵ -carbon of the dienyl ligand is disubstituted, as in the η^1 -5-methyl-2,4-hexadien-1-yl ligand, the Diels–Alder reaction encounters difficulties owing to the increasing intraligand steric hindrance in the required *cis*-diene conformation, and the [3+2] cycloaddition of the more typical η^1 -allyl complexes becomes competitive and is even the preferred mode of reaction.³³⁴

The carbonyl carbon atom in normal aldehydes and ketones is apparently not sufficiently electrophilic to be attacked by the metal-2-alkenyl and -2-alkynyl complexes in eqs 37 and 38, as hexafluoroacetone is the only carbonyl compound in Table 4 (entries 16 and 31). However, Turos et al.³⁵²⁻³⁵⁴ have found that by Lewis acid promotion with BF_3 -etherate, the equivalents of the spontaneously cyclizing dipolar

metal- η^2 -olefin intermediate in eq 44, i.e. **141** in eq 49, can be obtained with a series of unactivated aldehydes³⁵³ and ketones³⁵² as stable compounds. Cyclization of **141** to **142** was finally effected by addition of KOt-Bu.³⁵⁴ The sensitive, difficult to handle complexes **142** were then, under the conditions in eq 49, in situ converted to the tetrahydrofuran esters **143**.



Entry 22 differs insofar from the other examples, as the initial η^1 -cyclopentadienyl complex is not observed; hapticity change by substitution of two CO ligands directly gives the η^5 -complex. A reaction, described by Rubezhov et al.,³⁵⁵ of π -allyl- π -arene complexes of Ru and π -allyl- π -cyclopentadienyl complexes of Rh and Ir with a series of aryl- and alkyl-substituted alkynes, also leads to η^5 -coordinated substituted cyclopentadienyls. This reaction, however, obviously proceeds by a different mechanism, i.e., via an initial coordination of the alkyne to the positively charged, coordinatively unsaturated metal center. A likely course of the reaction is shown in eq 50.



A great number of substituted 7-azabicyclo[2.2.1]hept-5-ene complexes (Scheme 19) have been prepared in high yields (84–98%) by 1,3-dipolar cycloaddition of various dipolarophiles (acrylonitrile, meth-

Table 4. [3+2] Cycloaddition of Electrophilic Unsaturated Substrates E=Nu to η^1 -Allyl, Propargyl, Allenyl, Cyclopropylmethyl, and Cyclopropyl Compounds with Metal-Induced 1,3-Dipolar Behavior

| entry | starting complex | unsatd. electrophile E=Nu | product | references |
|-------|--|--|---------|---------------------------------|
| | | | | |
| 1 | <p>[M] = Fp^{a)}</p> <p>R¹ = H, Me R² = H, Me, OMe R³ = H, Me, Ph, OMe</p> | <p>R-N=C=O</p> <p>R = H, Tos^{b)}, SO₂Cl, 2,5-Cl₂-C₆H₃, Cl₃CCO</p> | | 301 320 299 |
| 2 | <p>[M] = Fp^{a)}</p> <p>R¹ = R² = H R³ = -(CH₂)_{2,3}-C_α</p> | R = Tos ^{b)} , MeOSO ₂ | | 301 320 |
| 3 | <p>[M] = Fp^{a)}</p> <p>R¹ = H, Me R² = H, Me R³ = H, Me, Ph, COⁱPr</p> | TCNE ^{c)} | | 301 311 321 322 323 |
| 4 | <p>[M] = Fp^{a)}</p> <p>R¹ = R² = H R³ = -(CH₂)_n-C_α n = 1, 2, 3, 4</p> | TCNE ^{c)} | | 301 |
| 5 | <p>[M] = Fp^{a)}</p> <p>R¹ = R² = H R³ = OMe</p> | <p>R⁴ R⁵ R⁶ CN CN CO₂Et CO₂Et CN CO₂Et CO₂Et CN CN CN CO₂Et CN CO₂Et CO₂Et H CO₂Me CO₂Me CO₂Me</p> | | 315 311 |
| 6 | <p>[M] = Fp^{a)}</p> <p>R¹ = R² = H R³ = OMe</p> | MeO ₂ C-C≡C-CO ₂ Me | | 315 324 |
| 7 | <p>[M] = cp(CO)Fe[P(OCH₂)₃CCH₃]</p> <p>R¹ = OMe R², R³ = H</p> | <p>R⁴ R⁵ R⁶ CO₂Me CO₂Me CO₂Me CO₂Me CN CO₂Me CN CN CO₂Et CN CN Ph CO₂Et CN CH₂-S-CH₂-S-CH₂-S-CH₂-S-</p> | | 310 |

Table 4 (Continued)

| entry | starting complex | unsatd. electrophile E=Nu | product | references |
|-------|--|---|---------|--------------------------|
| | | | | |
| 8 | [M] = Fp ^{a)} R ¹ = OMe R ² , R ³ = H | TCNE ^{c)} | | 316 |
| 9 | [M] = cpW(CO) ₃ R ¹ , R ³ = H; R ² = C≡C-Me | TCNE ^{c)} | | 350 |
| 10 | [M] = PtClL ₂ L = PPh ₃ , PMePh ₂ , PCy ₃ L ₂ = dppen ^{d)} R ¹ , R ² , R ³ = H [M] = Pt(C ₆ F ₅)P,P P,P = dppe ^{e)} , 2 PPh ₃ R ¹ , R ² , R ³ = H | TCNE ^{c)} | | 325 326 327 328 |
| 11 | [M] = Fp ^{a)} R ¹ , R ² , R ³ = H R ² or R ³ = Me | | | 318 329 330 |
| 12 | [M] = Fp ^{a)} , Mn(CO) ₅ , cpMo(CO) ₃ R ¹ = R ³ = H R ² = | TCNE ^{c)} | | 331 332 334 |
| 13 | [M] = C ₆ F ₅ -Pd P-P = dppen ^{d)} , dppe ^{e)} R ¹ , R ² , R ³ = H | | | 333 |
| 14 | [M] = Fp ^{a)} R ¹ , R ² , R ³ = H | | | 335 |
| 15 | [M] = Fp ^{a)} ; R ¹ = H, Me; R ² , R ³ = H, Me Mn(CO) ₅ ; R ¹ = R ² = R ³ = H | R-S(O) ₂ N=S=O R = Me, Ph | | 336 |
| 16 | [M] = Mn(CO) ₅ , cpMo(CO) ₃ ; R ¹ = R ² = H, R ³ = Ph [M] = Fp ^{a)} ; R ¹ = H, R ² = R ³ = Me; R ¹ = R ² = H, R ³ = H, Me, Ph, Cl [M] = cpW(CO) ₃ ; R ¹ = R ² = H; R ³ = H, Me | (CF ₃) ₂ C=O | | 349 |

Table 4 (Continued)

| entry | starting complex | unsatd. electrophile E=Nu | product | references |
|-------|--|--|---------|-------------------|
| | | | | |
| 17 | [M] = Fp ^a , Mn(CO) ₅ ; R = Me, Ph [M] = cpMo(CO) ₃ ; R = Ph | SO ₃ | | 337 338 339 |
| 18 | [M] = Fp ^a , Fp ^{*a} , cpMo(CO) ₃ for all [M] R = Me, Ph | | | 340 |
| 19 | [M] = Fp ^a ; R = Me, SiMe ₃ | | | 318 329 330 |
| 20 | [M] = Fp ^a ; R = Me, Ph, CH ₂ -Fp [M] = Fp ^a ; R = Me, Ph, CH ₂ -Fp [M] = cpMo(CO) ₃ ; R = Ph | R ¹ R ² C=C=O R ¹ = R ² = Ph R ¹ = ^t Bu, R ² = CN | | 342 351 |
| 21 | [M] = Fp ^a ; R = Me, Ph, CH ₂ -Fp [M] = Mn(CO) ₅ ; R = Ph | R'-N=S=O R' = Ph, p-MeC ₆ H ₄ SO ₂ | | 342 343 |
| 22 | [M] = Mn(CO) ₅ ; R = Ph | MeO ₂ C-C≡C-CO ₂ Me | | 301 |
| 23 | [M] = Fp ^a , Mn(CO) ₅ , Re(CO) ₅ R = Me | | | 300 |
| 24 | [M] = Fp ^a , cp Mo(CO) ₃ , cpW(CO) ₃ , cpMo(CO) ₂ (PPh ₃), cpMo(CO) ₂ [P(OPh) ₃], Mn(CO) ₅ , Mn(CO) ₄ (PPh ₃) R = Ph [M] = cpMo(CO) ₃ , Mn(CO) ₄ (PPh ₃) R = Me [M] = cpRu(CO) ₂ ; R = Ph | Tos-N=C=O ^b | | 299 307 |
| 25 | [M] = cpW(CO) ₃ R = Me, Ph [M] = Fp ^a , cpMo(CO) ₃ R = Me, Ph, CH ₂ -Fp, CH ₂ Mo(CO) ₂ cp | SO ₂ | | 146 345 346 |

Table 4 (Continued)

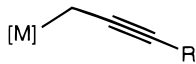
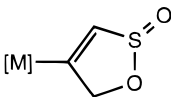
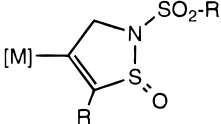
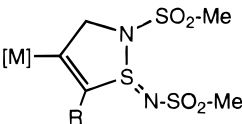
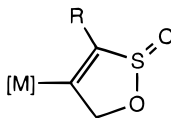
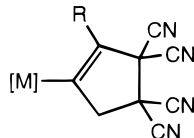
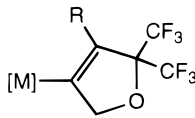
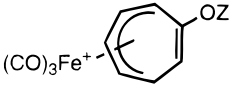
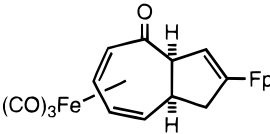
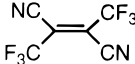
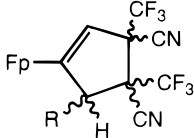
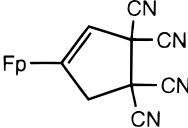
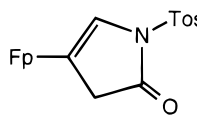
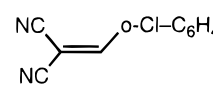
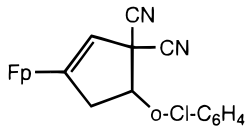
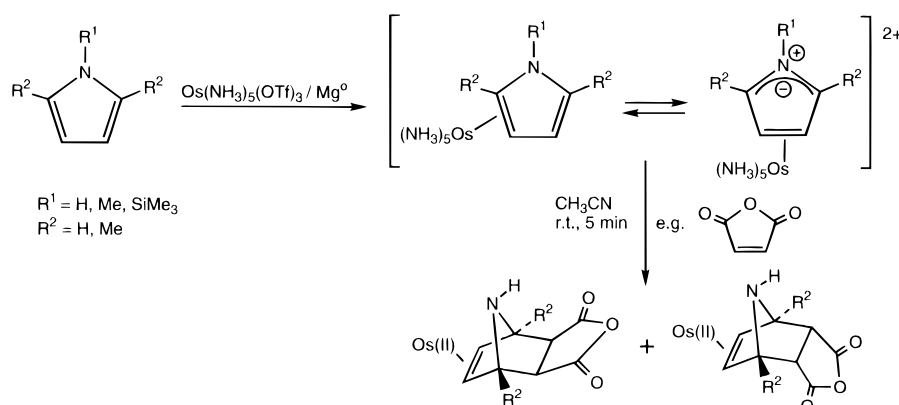
| entry | starting complex | unsatd. electrophile E=Nu | product | references |
|---|--|---|--|-------------------|
|  | | | | |
| 26 | [M] = Mn(CO) ₄ (PPh ₃) R = H | SO ₂ |  | 347 |
| 27 | [M] = Fp ^a , cpMo(CO) ₃ R = Me, Ph | R'S(O) ₂ N=S=O R' = Me, Ph |  | 336 |
| 28 | [M] = Fp ^a , cpCr(CO) ₃ , cpW(CO) ₃ , Mn(CO) ₅ ; R = Ph [M] = Mo(CO) ₃ ; R = Me, Ph | [MeS(O) ₂ N] ₂ S |  | 336 |
| 29 | [M] = Co(CO) ₃ (PPh ₃) R = Me, Ph, CH ₂ Cl | SO ₂ |  | 341 |
| 30 | [M] = Co(CO) ₃ (PPh ₃) R = Me, Ph, CH ₂ Cl [M] = cpRu(CO) ₂ ; R = Ph | TCNE |  | 341 307 |
| 31 | [M] = Mn(CO) ₅ , Fp ^a ; R = Me, Ph [M] = cpMo(CO) ₃ ; R = Ph | (CF ₃) ₂ C=O |  | 349 |
| [M]-CH=C=CHR | | | | |
| 32 | [M] = Fp ^a ; R = H |  Z = SiMe ₃ , BBu ₂ |  | 318 329 330 |
| 33 | [M] = Fp ^a ; R = H, Me |  |  | 300 |
| 34 | [M] = Fp ^a ; R = H | TCNE ^c |  | 348 |

Table 4 (Continued)

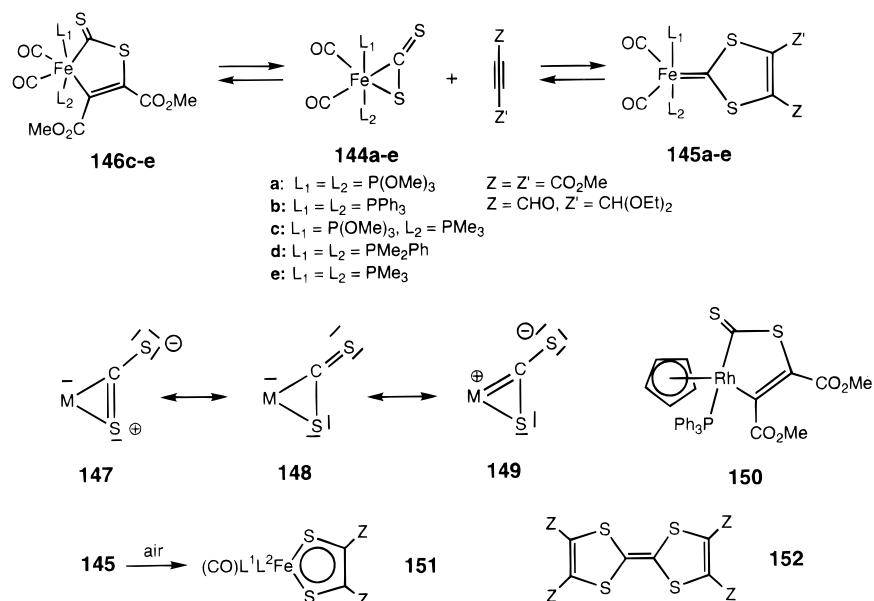
| entry | starting complex | unsatd. electrophile E=Nu | product | references |
|----------------|------------------------|---|--|------------|
| $[M]-CH=C=CHR$ | | | | |
| 35 | $[M] = Fp^a$; $R = H$ | $Tos-N=C=O^b$ |  | 348 |
| 36 | $[M] = Fp^a$; $R = H$ |  |  | 348 |

a) $Fp = (\eta^5-C_5H_5)Fe(CO)_2$, $Fp^* = (\eta^5-C_5Me_5)Fe(CO)_2$; b) $Tos = p-CH_3-C_6H_4-SO_3$; c) TCNE = tetracyanoethylene; d) $dppen = Ph_2P-CH=CH-PPh_2$; e) $dppe = Ph_2P-CH_2-CH_2-PPh_2$

Scheme 19



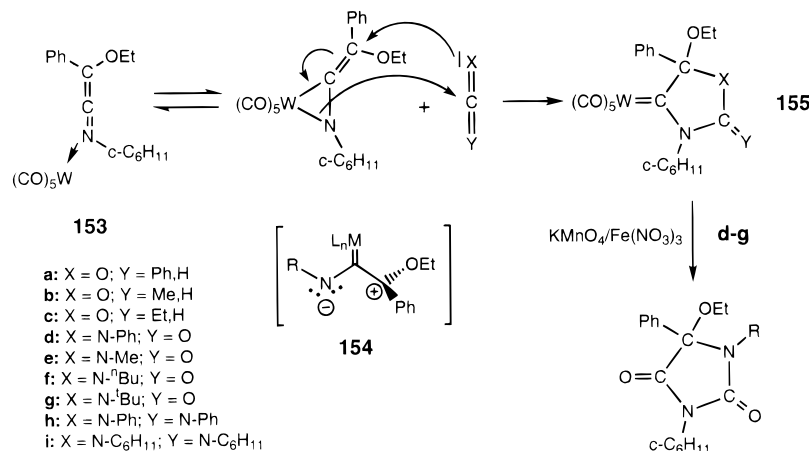
Scheme 20



yl acrylate, α -methylene- γ -butyrolactone, dimethyl maleate, dimethyl fumarate, *N*-phenylmaleimide, cyclopentene-1,2-dicarboxylic acid anhydride, (*E*)- and (*Z*)-methyl 3-(3'-pyridyl)acrylate) to substituted pyrroles, which by coordination of $[Os(NH_3)_5]^{2+}$ across C3 and C4 are effectively transformed into azomethine ylides,^{356,357} which in turn dramatically enhances their reactivity toward 1,3-dipolar cycloaddition.

(η^2-CS_2) iron complexes **144a,b** (Scheme 20) have been reported to cycloadd dipolarophilic alkynes to give 1,3-dithiocarbene complexes **145**.^{358,359} This can be visualized via canonical form **147**. Earlier, Wakatsuki et al.³⁶⁰ had isolated complex **150** from the reaction of $CpRh(\eta^2-CS_2)(PPh_3)$ with dimethyl acetylenedicarboxylate. This would be the result of an organometal [3+2] cycloaddition via canonical form **149**. Analogous carbonylmanganese complexes $Cp-$

Scheme 21

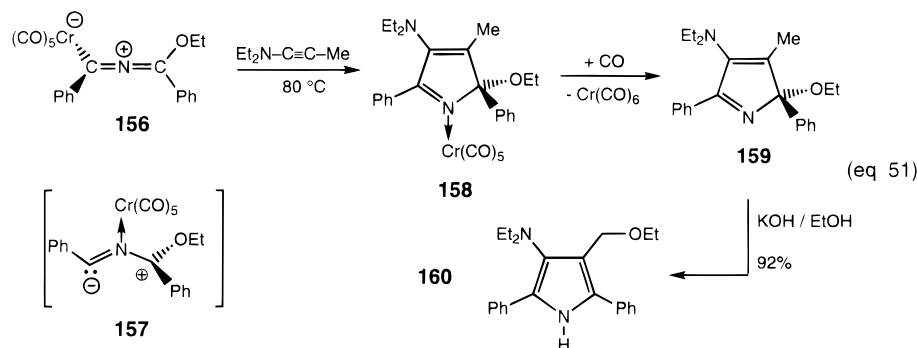


Mn(CO)(η^2 -CS₂)L (L = P(OMe)₃, PMe₂Ph, PMe₃),³⁶¹ on the other hand, reacted again via canonical form **147** to give the 1,3-dithiocarbene complexes as in **145**. 1,3-Dithiocarbene complexes analogous to **145** have also been obtained³⁶² from the reactions of (η^2 -CS₂)-(diphosphine)W(CO)₃ with electron-deficient alkynes. Investigation of the reaction of the extended series of complexes **144a–e** with dimethyl acetylenedicarboxylate has indicated³⁶³ that the formation of **145** is a reversible process. The more strongly basic phosphorus ligands destabilize **145**, the initially formed product, and give rise to an isomerization into **146**. The isomerization rate was found to depend on the concentration of **145**, ruling out an intramolecular pathway. The reaction of **144d** with **145e** gave **144e** and **145d**, indicating the reversibility of the reaction, and suggesting that the isomerization **145** to **146** proceeds via cycloreversion **145** to **144** and 1,3-dipolar addition **144** to **146** from canonical form **149**. The type of product formed can therefore be rationalized by the ability of the L_nM fragment to release electrons (stabilizing canonical form **149**) or to accept electrons (stabilizing canonical form **147**). On the basis of extended Hückel calculations and qualitative MO theory, Mealli, Hoffmann, et al.^{364,365} have recently discussed the reactivity of alkynes toward M(η^2 -CS₂) metal complexes in great detail. However, with respect to the preferential formation of either structure **145** or **146** they conclude that “the semiempirical method used is not sufficiently reliable to monitor the electronegativity effects of the substituents on the ligands, so as to predict which isomer (**145** or **146**) is favored in which case. However the Mullikan analysis of charge distribution is consistent with the experimental trends reported.” The car-

bene–iron complexes **145** are decomposed by air to give dithiolene complexes **151** in 22–46% yields.³⁶⁶ Complexes **145a,b** can be used to prepare tetrathiofulvalene **152** in yields of up to 83%, either via thermolysis or by reaction with iodine.³⁶⁷

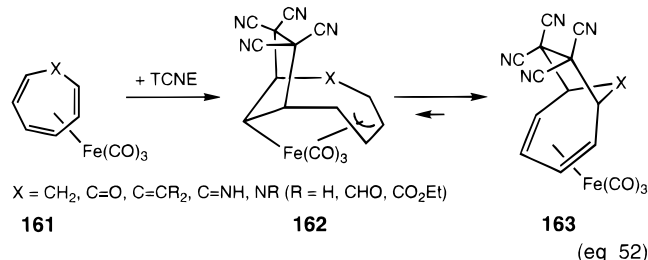
A reaction analogous to the formation of **145** has been described by Aumann et al.³⁶⁸ (see Scheme 21). Tungsten–ketenimine complexes **153**, obtained by insertion of aliphatic isonitriles into the metal–carbon double bond of Fischer carbene complexes,^{218,369,370} react with the C=O and C=N groups of aldehydes, isocyanates or carbodiimides to give oxazolidine or imidazolidine complexes **155**. Oxidative decomposition of **155d–g** with KMnO₄/Fe(NO₃)₃ (1:1) in acetone/water gave the corresponding hydantoines in high yields. With manganese,³⁷¹ one-pot reactions at room temperature of the carbene complex (CO)₂(MeC₅H₄)Mn=C(OEt)Ph with methyl isocyanide and a variety of polar C=X bonds (X = O, S, NR) gave the respective analogues of **155**, from which the heterocyclic ligands could be easily displaced by transformations of the Mn=C into Y=C bonds (Y = O, S, Se). The intermediate ketenimine complexes, which are formed in the rate-determining step, have not been isolated. A review by Aumann on the use of ketenimine complexes as building blocks for four-, five-, and six-membered ring carbo- and N-heterocyclic compounds has been published in 1988.³⁷²

While the 1,3-dipolar reactivity of ketenimine complexes **153** can be represented by **154**, the isomeric 2-azaallenyl complex **156** shows a reactivity that corresponds to the 1,3-dipolar structure **157**.^{373,374} With 1-(diethylamino)propyne, **156** reacts according to eq 51 to give the 2*H*-pyrrole **159**. The intermediate Cr(CO)₅ complex **158** has also been isolated, al-

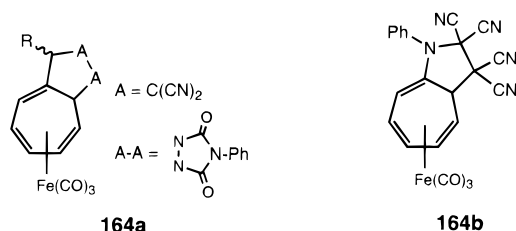


though, under the reaction conditions, most of it is directly converted to **159**. On base catalysis (EtOH/KOH, 80 °C, 15 h), **159** smoothly isomerizes to the pyrrole **160**.

The cycloaddition reactions of cyclic triene complexes **161** (eq 52) related to (η^4 -cycloheptatriene)-Fe(CO)₃ or (COT)Fe(CO)₃ with reactive dienophiles such as tetracyanoethylene (TCNE), 4-phenyltriazoline-3,5-dione (NPTD), or hexafluoroacetone (HFA) have been studied by several groups.^{375–396}

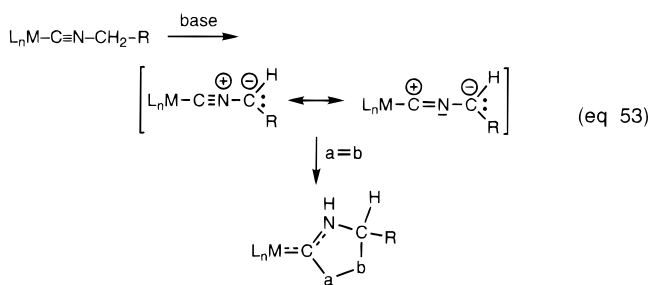


Experimentally, the reactions with TCNE (eq 52), TCNE always attacking from the exo side, away from the metal, usually yield mixtures of the [3+2] (**162**) and [6+2] adducts (**163**). In the case of (η^4 -cycloheptatriene)Ru(CO)₃,³⁹⁷ the [3+2] adduct with TCNE equilibrates via a [4,4]-sigmatropic rearrangement with the less stable [6+2] adduct, which decomposes under the reaction conditions to the demetalated [6+2] adduct. It is concluded that σ,π -allylic adducts are in general more stable than their isomeric η^4 - π counterparts. The concerted [3+2] addition, classified by Mingos et al.³⁹³ in the electronic notation as symmetry-allowed [$(\pi 2_a + \sigma 2_a) + \pi 2_s$] reaction, has been investigated kinetically,^{378–381,398} and by extended Hückel calculations,^{375,377,378} and it has been shown that even in cases where also the [5+2] adduct would be accessible via an allowed concerted pathway,³⁷⁵ the kinetically labile [3+2] adduct **162** is the initial product formed, which then rapidly undergoes a facile pericyclic [3,3]-sigmatropic rearrangement^{383,384} to give **163**. While noncoordinated electron-poor cycloheptatrienes with electron-withdrawing substituents at the end positions of the conjugated system, e.g., 1,6-bis(methoxycarbonyl)cycloheptatriene, do not react with either TCNE or NPTD, they are strongly activated by η^4 -coordination to Fe(CO)₃.³⁹⁹ While [1,6-bis(methoxycarbonyl)- η^4 -cycloheptatriene]Fe(CO)₃ readily reacts with TCNE ($\Delta G^\ddagger = 17.4$ kcal/mol) to give a quantitative yield of the [3+2] adduct, the reaction with NPTD gives a mixture of the [3+2], [4+2], and [5+2] adducts. In the case of complexes **161** with an exocyclic double bond^{377,379,381,400–404} [**a**, X = C=CRR' (Ph, Me; Ph, Ph; Me, Me; Me, Et; -(CH)₆-) or C=CHR (R = H, Me, OMe, Ph, *p*-Tol); **b**, X = C=NPh], TCNE and NPTD apparently add across the 1,8-positions to give **164a,b** which, in the electronic notation, corresponds to an allowed [8 π +2 π] cycloaddition reaction, as it is found with uncoordinated heptavulvenes. It has therefore been stated⁴⁰⁰ that "Fe(CO)₃ complexation did not alter the periselectivity of the cycloaddition as compared to the noncomplexed heptafulvenes". However, also here, conclusive evidence could be obtained^{377,379,381} that the exocyclic double bond is not involved in the initial



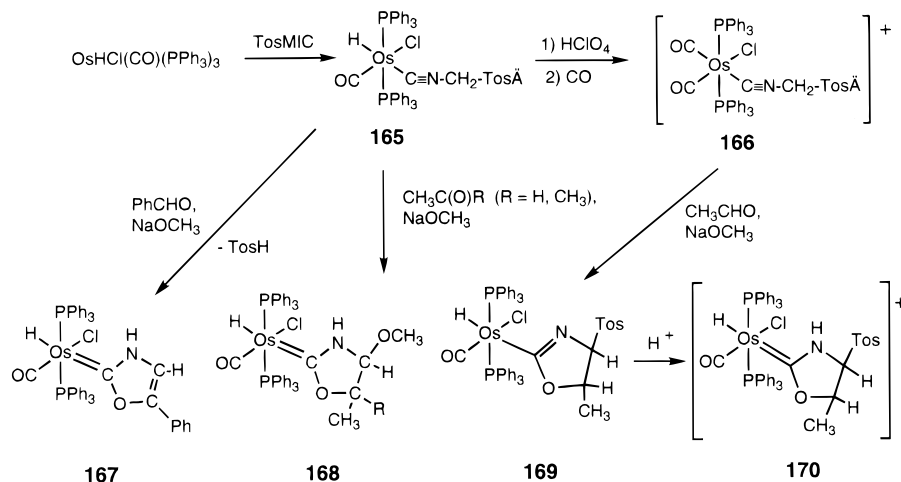
cycloaddition, but rather structure **162** from the 1,3-addition mode is originally formed, which then, directly or via **163**, irreversibly rearranges to **164**. Substitution of a CO ligand in (tropone)Fe(CO)₃ (**161**, X = C=O) for a phosphine leads to strongly enhanced rates for cycloadditions with normal (with NPTD and TCNE to the initial kinetic 1,3-adduct, cf. **162**) and inverse electron demand [[4+2] cycloaddition with 3,6-bis(methoxycarbonyl)-1,2,4,5-tetrazine (**302** in Scheme 44, section II.D.1)], and of sigmahaptotropic rearrangement.³⁹⁶

Deprotonation of metal-coordinated C-H acidic isocyanides (C \equiv NCH₂R with R = *p*-tosyl,^{405,406} CO₂Et,^{406–409} PPh₃^{410,411}) leads to metal-stabilized 1,3-dipoles, metallonitrile ylides, which react with a variety of dipolarophiles to give heterocyclic carbene complexes (eq 53). A first example with TosMIC

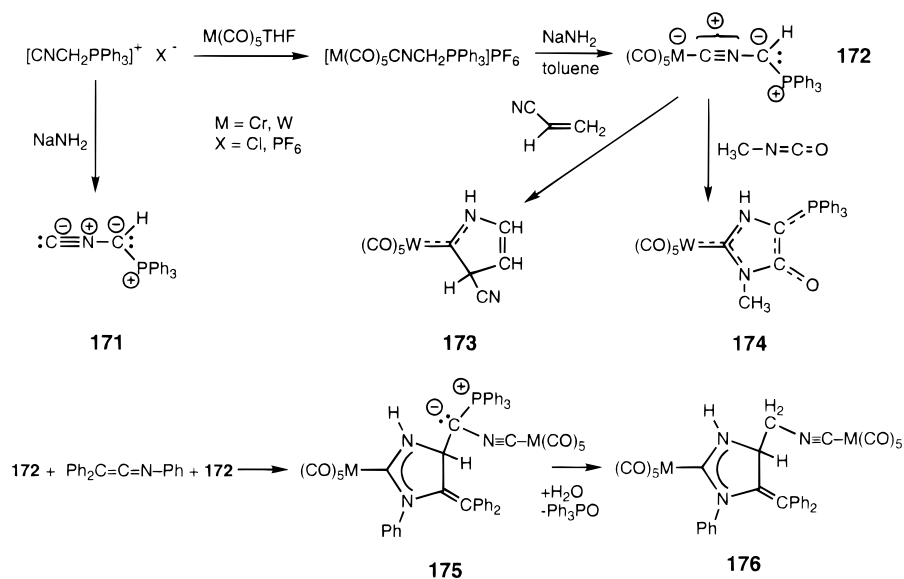


(tosylmethyl isocyanide) coordinated to osmium(II) in complexes **165** and **166** has been reported by Grundy and Roper⁴⁰⁵ (Scheme 22), where oxazol-2-ylidene (**167** and **170**), oxazolidin-2-ylidene (**168**), or oxazolidin-2-yl (**169**) complexes are obtained through addition of aldehydes or acetone in the presence of sodium methoxide. A broad scope of this type of reaction has been demonstrated by Fehlhammer et al. for metallonitrile ylides of Cr, W, Pt, and Pd, generated in situ from the C-H acidic isocyanide complexes mostly using Et₃N as base, but also by *t*-BuOK or *n*-BuLi. As dipolarophiles they used carbon disulfide,^{409,411} iso(thio)cyanates,^{406,408,411} aldehydes, acetylenic esters, acrylonitrile, or trifluoroacetonitrile.^{406,407} Particularly interesting is a comparative study⁴¹¹ of the reactivity of free, **171**, and M(CO)₅-coordinated (M = Cr, W), **172**, (isocyanomethylene)triphenylphosphorane⁴¹⁰ (cf. Scheme 23). Complexes **172**,⁴¹¹ where the ylidic part is further stabilized through the triphenylphosphino substituent, were the only examples where the 1,3-dipolar metallonitrile ylide could be isolated and characterized. They cycloadd heteroallenes, nitriles, acetylenes, and olefins in [3+2] fashion to give M-C-bonded heterocycles with (e.g. formation of **173**) or without (e.g. formation of **174**) elimination of triphenylphosphine. With respect to their reactivity, they thus resemble more closely organic nitrile oxides or nitrilimines rather than alkyl- or aryl-substituted

Scheme 22

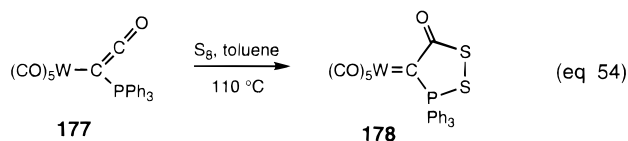


Scheme 23



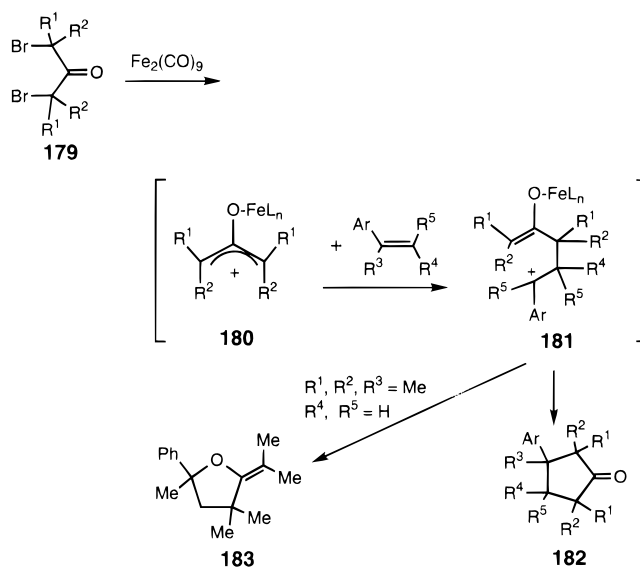
nitrile ylides. The reaction of **172** with triphenylketenimine⁴¹² gave an unexpected result. The unobserved initial carbenoid [3+2] cycloaddition product, analogous to **174**, had undergone a C–C coupling reaction with a second molecule of **172**, giving **175** which on chromatography in CH_2Cl_2 or with intentionally added water readily hydrolyzed to **176** and triphenylphosphine oxide.

In an attempt to eliminate triphenylphosphine as triphenylphosphine sulfide, Lindner⁴¹³ reacted ylide complex **177** (eq 54) with cyclohexasulfur. Instead of the expected carbonylmethylene complex $(\text{CO})_5\text{WC}_2\text{O}$ they obtained carbene complex **178** via the [3+2] addition of two sulfur atoms.

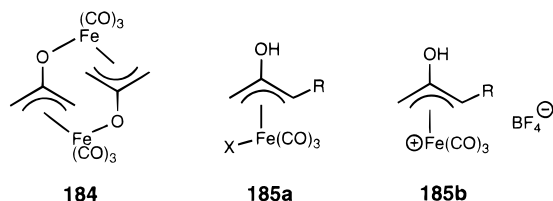


An interesting example of a metal-induced [3+2] cycloaddition where a cationic two-electron three-atom component is generated and stabilized by an ironcarbonyl fragment has been developed by Noyori et al.^{414–421} (Schemes 24 and 25). Starting from an

Scheme 24



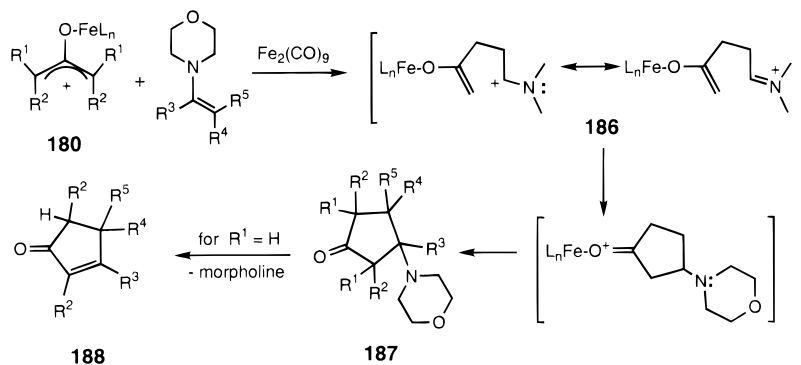
α,α' -dibromo ketone, **179**, the crucial intermediate **180**, a cationic oxyallyl–Fe(II) species,⁴¹⁷ is generated with $\text{Fe}_2(\text{CO})_9$. The structure of **180** has been debated, and the related complexes **184**⁴²² and **185a,b**⁴²³



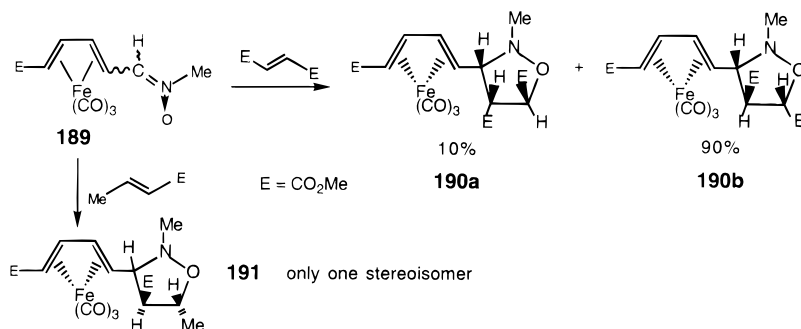
have been prepared and isolated; however, they fail to cycloadd to furan. In the actual cycloaddition reaction between **180** and the olefin, two two-electron components are involved, i.e., in the electronic notation a $[\pi 2 + \pi 2]$ process, which is thermally forbidden. Consequently, the reaction proceeds stepwise via carbocation **181**. Ring closure normally gives the 3-arylcyclopentanones **182** in high yields. When the carbon terminus of the enolate moiety of **181** is sterically crowded, however, ring closure at the oxygen terminus to give enol ethers, e.g. **183**, can compete with the normal cyclization. The aryl substituent in the olefinic part is important to stabilize the positive charge at carbon in **181**, making it a benzylic position. This stabilization can also be effected by heteroatoms (cf. **186**), and a great many reactions have been done with enamines⁴¹⁹ as olefinic component (Scheme 25). If the carbon terminus of the enolate moiety in **186** bears at least one hydrogen, morpholine is eliminated from the initial cyclization product **187** to give the substituted cyclopentenones **188**. α, α' -Bis(sulfonyl) ketones have been explored as alternative precursors for the metal stabilized oxyallyl cations **180**.⁴²⁴ With TiCl_4 as Lewis acid and $\text{Fe}(\text{CO})_5$, $\text{Fe}_2(\text{CO})_9$, or $\text{Co}_2(\text{CO})_8$ as metal carbonyls, good yields of cyclopentanones **182** were obtained with styrenes and *trans*-stilbene as olefins, while phenyl- and diphenylacetylenes gave the corresponding β, γ -cyclopentenones in high yields.

Influence of a pendant butadiene-irontricarbonyl group on the stereochemistry of the classic 1,3-dipolar

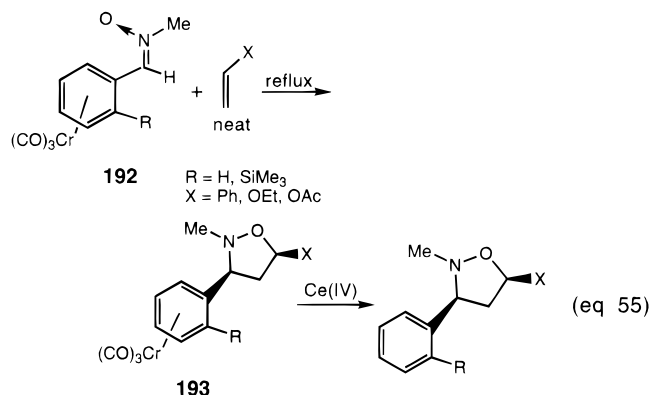
Scheme 25



Scheme 26

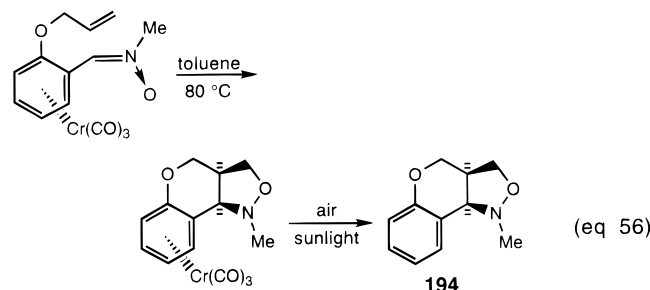


cycloaddition of dimethyl fumarate or methyl crotonate to the nitron moiety in **189** has been demonstrated by Grée et al.⁴²⁵ (cf. Scheme 26). With dimethyl fumarate, of the two possible isoxazolidines, **190b** is preferred by a ratio of 9:1 over **190a**. With methyl crotonate, **191** is the only diastereomer observed. The reactions have been carried out with racemic **189**, although the authors⁴²⁶ have developed a very efficient method to optically resolve its precursor aldehyde complex ($\eta^4\text{-MeO}_2\text{CCH=CHCH=CH-CHO}$) $\text{Fe}(\text{CO})_3$. An efficient, highly stereo- and regio-selective synthesis (eq 55) of *cis*-3,5-disubstituted



isoxazolidines **193** has been developed by Hanaoka et al.^{427,428} The racemic $\text{Cr}(0)$ -complexed nitrones **192** react with electron-rich olefins in a completely stereocontrolled way to the $[3+2]$ cycloadducts **193**. The 5-aryl nitrones were consecutively decomplexed by cerium(IV) ammonium nitrate in isolated overall yields of 65–96%. The stereocontrol is lost when either uncomplexed nitron or electron-deficient olefins ($\text{X} = \text{SiMe}_3$, CN , 4- BrC_6H_4) are employed. Starting from the optically active complexed nitrones (+)- and (–)-**192**, the respective chiral (–)- and (+)-

isoxazolidines were obtained in enantiomeric excesses of 96% to >98%. This methodology has been applied in an intramolecular fashion⁴²⁹ (eq 56) to the com-

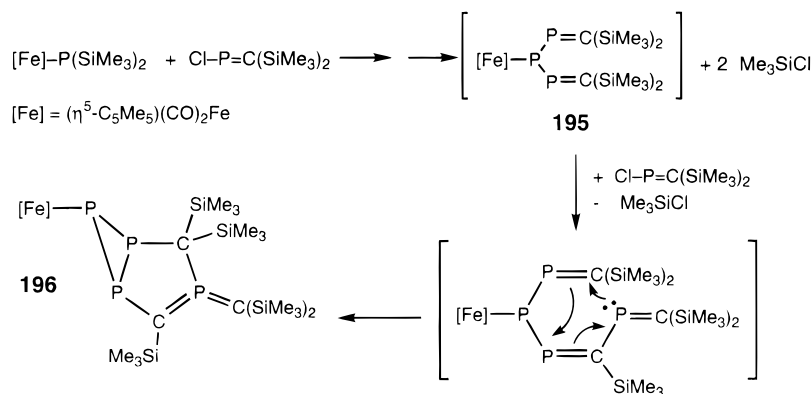


pletely enantioselective synthesis of the tricyclic isoxazolidine derivative **194** which was quantitatively decomplexed by exposure to air and sunlight.

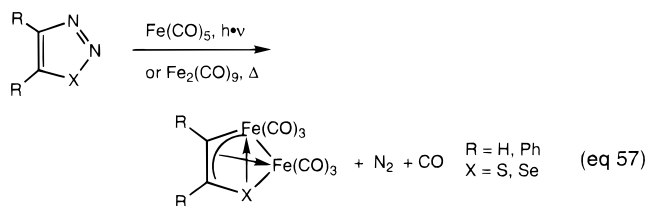
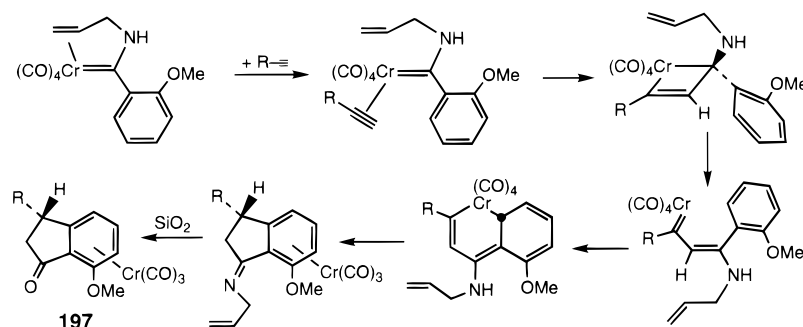
An unexpected intramolecular [3+2] cycloaddition has been reported by Weber et al.⁴³⁰ during the attempted synthesis of the metalated 2,3,4-diphosphapenta-1,4-diene **195** (Scheme 27) which resulted in the unusual 3-methanediyl-1,3,5,6-tetraphosphabicyclo[3.1.0]hex-2-ene system **196**.

There are a few examples where inherently reactive free 1,3-dipoles are stabilized through complexation to a transition metal. The diphenyldiazomethane complex (Ph₂CN₂)Ni(*t*-BuNC)₂ has been reported.⁴³¹ The complex decomposes with regeneration of the diazoalkane on reaction with oxygen or triphenylphosphine. Hexacarbonyldiiron complexes of thio- and selenoketocarbenes have been prepared⁴³² according to eq 57. The complexed 1,3-dipoles form σ - and π -bonds with the iron carbonyl fragments and exhibit low residual reactivity, undergoing cycloaddition reactions with alkynes only on thermolysis.

Scheme 27



Scheme 28

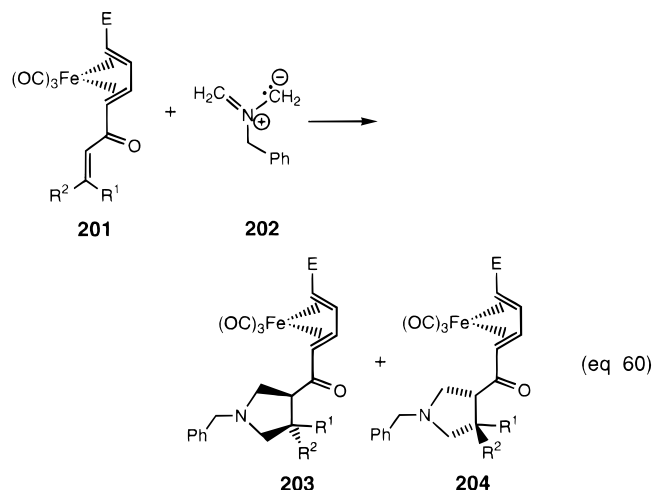
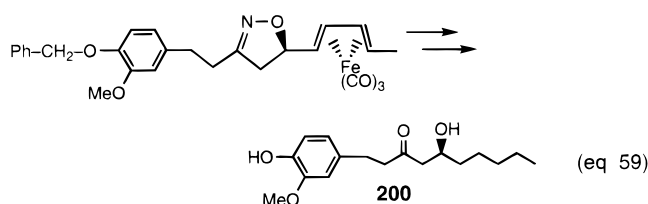
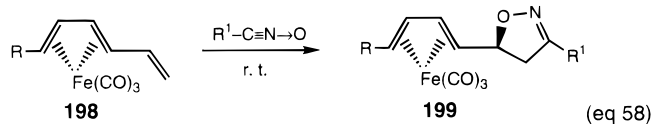


The annealed cyclopentenone in complex **197** in Scheme 28⁴³³ is not formed in a 1,3-dipolar cycloaddition, but the mechanism is related to the Dötz reaction which normally follows a [3+2+1] pattern. Here, however, the one-carbon fragment, supplied by CO insertion, is omitted. For references to related examples see section II.F.

2. Activation of the Dipolarophile

The cycloaddition of nitrile oxides R¹-C≡N→O (R¹ = Me, Et, *t*-Bu, Ph) as 1,3-dipoles to the pendant vinyl group of (η^{1-4} -triene)Fe(CO)₃ complexes **198** (eq 58),⁴³⁴⁻⁴³⁶ giving Δ^2 -isoxazolines **199**, is complementary to the reaction shown in Scheme 26. The nitrile oxide attacks the pendant vinyl group in **198** anti to the bulky Fe(CO)₃ group, and diastereoselectivities of ca. 90:10 are observed throughout, favoring attack of the dipole at the vinyl group in *s*-trans arrangement. The nature of R and R¹ does not affect the diastereoselectivity. The major diastereomers, the configuration of which is indicated in eq 58, have been isolated in 65–75% yields. Since Δ^2 -isoxazolines are useful intermediates in the synthesis of β -hydroxy ketones, the reaction in eq 58 was used as the key step in a short synthesis of (+)-(*S*)-[6]-gingerol **200** (eq 59).⁴³⁶ 1,3-Dipolar cycloaddition of azomethine ylide **202** (eq 60) to the pendant double bond of the η^4 -coordinated cross-conjugated polyenone

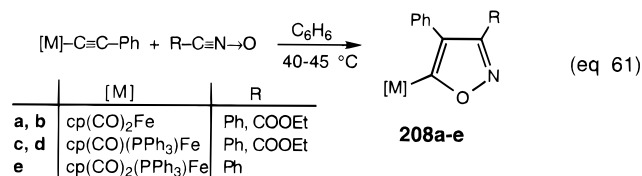
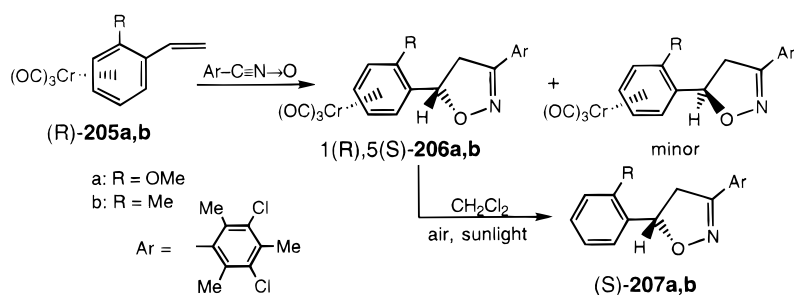
in **201** gave 70:30 mixtures of the diastereomeric adducts **203** and **204**.⁴³⁷



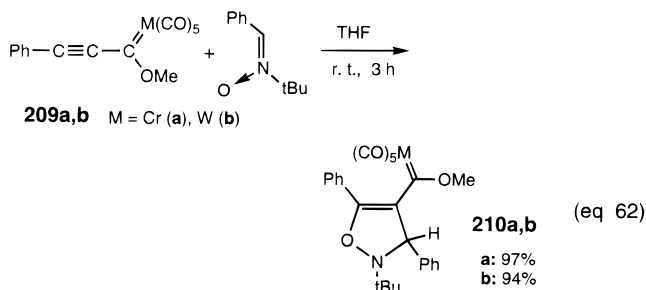
Optically active Δ^2 -isoxazolines (*S*)-**207a,b** (Scheme 29) have been made from the enantiomerically pure complexes (*R*)-**205a,b** in 63% and 98% ee, respectively.⁴³⁸ The enantiopure starting complexes (*R*)-**205a,b** were made by Wittig reaction of the corresponding resolved benzaldehyde complexes. Optically pure (*S*)-**207a,b** were obtained after initial chromatographic separation of the diastereomers of **206a,b** and consecutive decomplexation. Kalinin⁴³⁹ reported the synthesis of the σ -metal-bonded isoxazoles **208a-e** (eq 61). The [3+2] cycloaddition of nitrile oxides (R^1 = Ph, 2,4,6-Me₃C₆H₂) to (η^1 -allyl)iron complexes (Cp)(CO)(L)FeCH₂CH=CH₂ (L = CO, P(OCH₂)₃-CCH₃, PPh₃) has been described by Malisch et al.⁴⁴⁰ They obtained 5-ferriomethyl-substituted isoxazolines (Cp)(CO)(L)FeCH₂CHCH₂-C(*R*)=NO in yields ranging from 61% to 91%. With the chiral, P-substituted complexes, the diastereomer ratios were 59:41 to 93:7.

The [3+2] addition of many differently substituted nitrones to the triple bond of alkynyl Fischer carbene

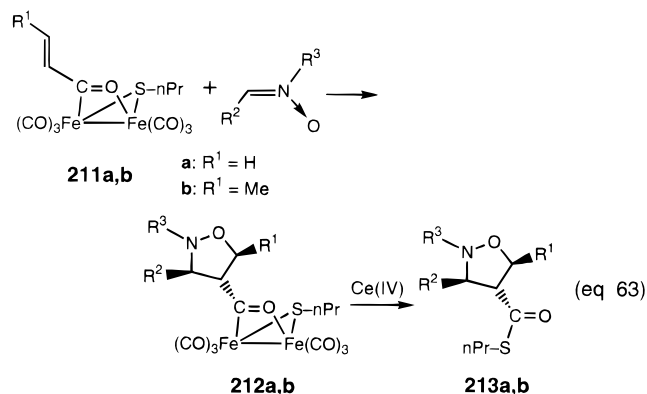
Scheme 29



complexes **209a,b** (eq 62) has been reported to give 2,3-dihydroisoxazole carbene complexes **210a,b** in excellent yields.^{441,442} The M(CO)₅ group in **210a,b** can be readily exchanged for oxygen through the usual oxidative cleavage by stirring the complexes at room temperature in DMSO solution (**a**, 96%; **b**, 59%).



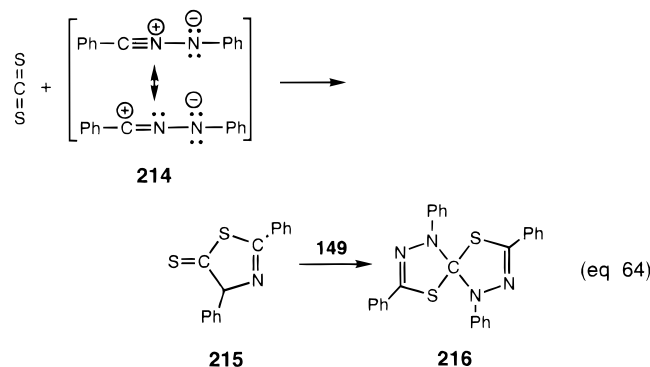
The diiron-acyl complexes **211a,b** (eq 63) cycloadd a variety of differently substituted nitrones in a very regio- and stereoselective manner, giving the 4-substituted isoxazolidine complexes **212a,b** in high yields and with high endo selectivities from which the thioesters **213** can be liberated with ceric ammonium nitrate.⁴⁴³ With a methyl group in α -position of the double bond (2-propenylacyl), the thioester group ends up in the 5-position of the isoxazolidine.



In the beginning of section II.C.1, the addition of RC≡N as dipolarophile to coordinated azide, giving metal-N¹ (**134a**)- or metal-N² (**134b**)-bonded tetra-

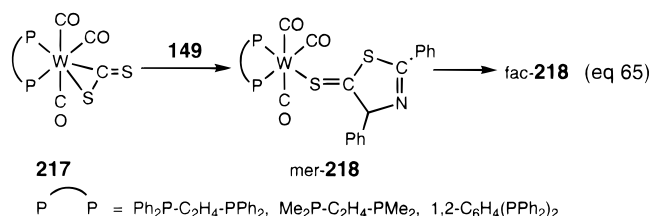
zolato complexes, has been mentioned. The complementary cycloaddition of azide ion to the $\text{RC}\equiv\text{N}$ triple bond of coordinated nitriles in pentaamminecobalt(III) complexes is also known and gives the same types of products.^{444,445} There is a considerable rate enhancement for azide ion attack on coordinated vs free organonitrile.⁴⁴⁴ The formation of 5-methyltetrazole from sodium azide and acetonitrile requires a reaction time of 25 h at 150 °C compared to only 2 h at ambient temperature for coordinated acetonitrile. Similarly, for benzonitrile the conditions are 3 h reaction time at 100 °C in dimethylformamide vs 15 min at ambient temperature for free and coordinated benzonitrile, respectively. The inverse of the reactions forming the metal–carbon-bonded tetrazolato complex **135** in eq 39, i.e., the reaction of the isocyanide complexes $[(\text{PPh}_3)_2\text{Pt}(\text{CNMe})_2][\text{BF}_4]_2$ and $[\text{diphosPt}(\text{CNMe})_2][\text{PF}_6]_2$ with azide ion, giving $[(\text{PPh}_3)_2\text{Pt}(\text{CNMe})(\text{CN}_4\text{Me})][\text{BF}_4]$ and $\text{diphosPt}(\text{CN}_4\text{Me})_2$ has also been described.⁴⁴⁶

Equation 64 shows the classic 1,3-dipolar cycloaddition of Huisgen⁴⁴⁷ between diphenylnitrilimine **214** and carbon disulfide. Organic thiocarbonyl com-



pounds, e.g., thioketones, thioesters, or thioamides, easily add to 1,3-dipoles. The symmetrical heteroallene CS_2 does so much less readily because its HOMO has a nodal plane at the central carbon. The reaction in eq 64 therefore mostly gives the spiro compound **216**, because the $\text{C}=\text{S}$ bond in the initially formed monoadduct **215** is much more reactive than in CS_2 . This has been taken into account by Schenk et al.,⁴⁴⁸ who furnished a particularly nice and instructive example, which is shown in eq 65, and where a metal fragment successively acts as an activating and protecting group. Coordination of CS_2 to tungsten in **217** thus changes its reactivity in two ways. First, the initial cycloaddition is facilitated, i.e., CS_2 is strongly activated. Coordination of the metal fragment raises the CS_2 HOMO in energy and destroys

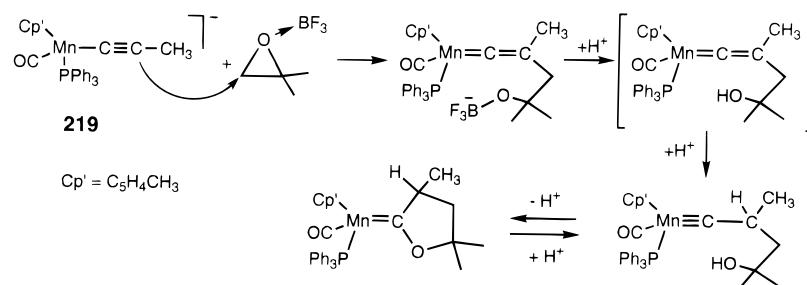
the symmetry such that the coefficient at carbon becomes different from zero. Second, due to the strong $\text{W}-\text{S}$ bond in **218**, the coordinated metal fragment now acts as a protecting group, effectively inhibiting the second addition.



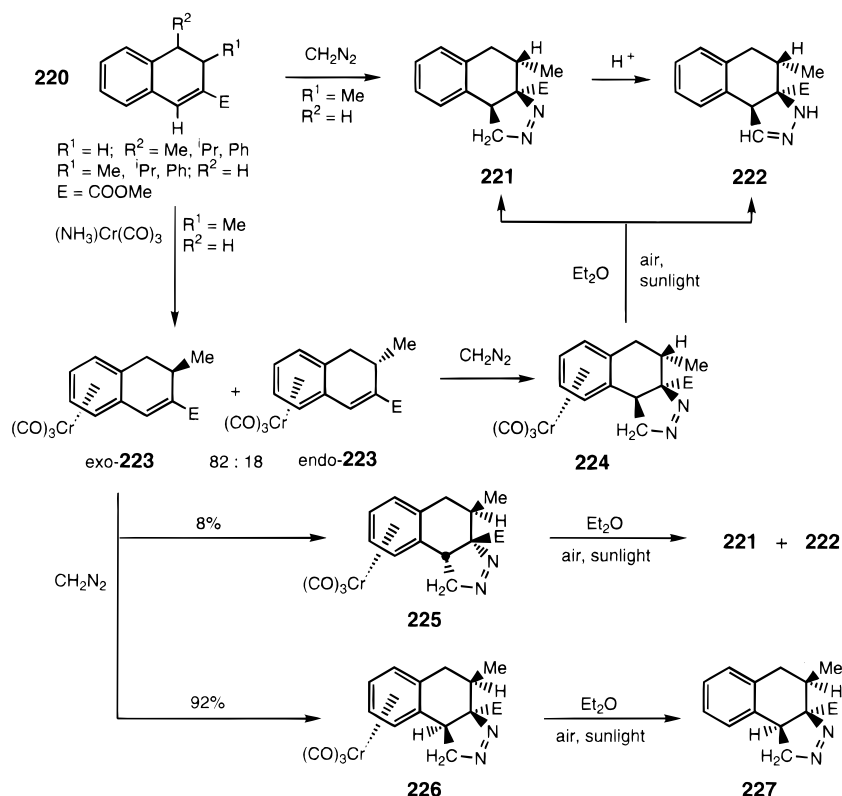
Besides the normal reactions with electrophiles to give vinylidene complexes,¹⁵⁴ the anionic, highly nucleophilic alkynyl complex **219** undergoes a unique [3+2] addition with epoxides in the presence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$.⁴⁴⁹ [It might be mentioned here that the anionic alkynyl complex **219** in Scheme 30, in the presence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$, besides with oxiranes, also reacts with 3,3-dimethyloxetane in an analogous stepwise fashion to give a tetrahydropyranidene complex.] However, since in the stepwise mechanism (Scheme 30) a σ -bond is broken, it is not a genuine cycloaddition reaction according to the rules of Huisgen.²

A nice example of stereocontrol in a 1,3-dipolar cycloaddition reaction through temporary coordination of the dipolarophile to a metal fragment has been provided by Carrié et al.⁴⁵⁰ The regio- and diastereospecific cycloaddition of diazomethane to 1,2-dihydro-3-carbomethoxynaphthalenes bearing alkyl or phenyl groups in 1- or 2-position (**220**) gives pyrazolines **221** in high yields, cf. Scheme 31. The importance of conformational factors during the cycloaddition has been discussed theoretically in order to rationalize the regioselectivity and the stereochemistry, i.e., the exclusive formation of **221/222** with the methyl substituent in cis position to the ester group. Coordination of the dipolarophile **20** to $\text{Cr}(\text{CO})_3$ gives the diastereomers *exo-223* and *endo-223*, the structures of which have been established by X-ray crystallography.⁴⁵¹ The highly diastereoselective reaction of *endo-223* with diazomethane, via **224**, gives pyrazoline **221**, the same isomer as in the uncomplexed case. The less diastereoselective reaction of diazomethane with *exo-223*, on the other hand, produces, via complex **226**, mainly pyrazoline **227** with the methyl substituent in trans position to the ester group, which cannot be obtained from uncomplexed **220**. High diastereoselectivity ($\geq 98\%$ de) has been reported⁴⁵² for the [3+2] cycloaddition of tosylmethyl isocyanide to racemic $\eta^6\text{-Cr}(\text{CO})_3$ -complexed

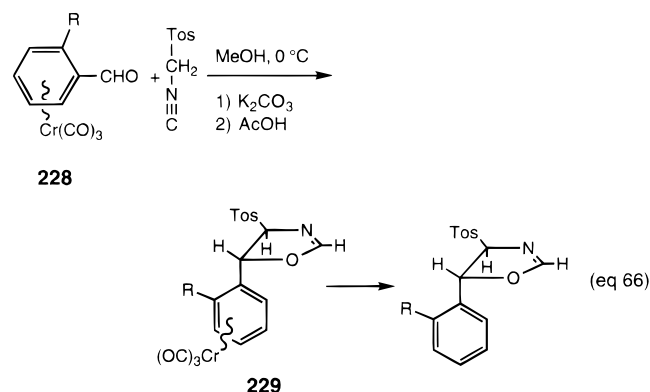
Scheme 30



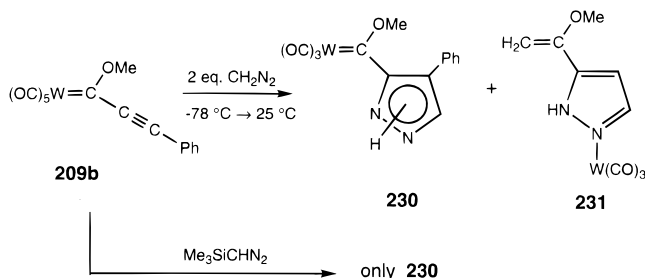
Scheme 31



benzaldehydes (**228**, eq 66). At 0 °C exclusively the trans isomers of oxazoline complexes **229** could be detected which after decomplexation and reduction with LiAlH_4 would lead to optically pure (*R*)-amino alcohols. The same reaction with the uncomplexed aldehydes gave *cis/trans* ratios of 2:1 ($\text{R} = \text{Me}$) and 3:7 ($\text{R} = \text{OMe}$).



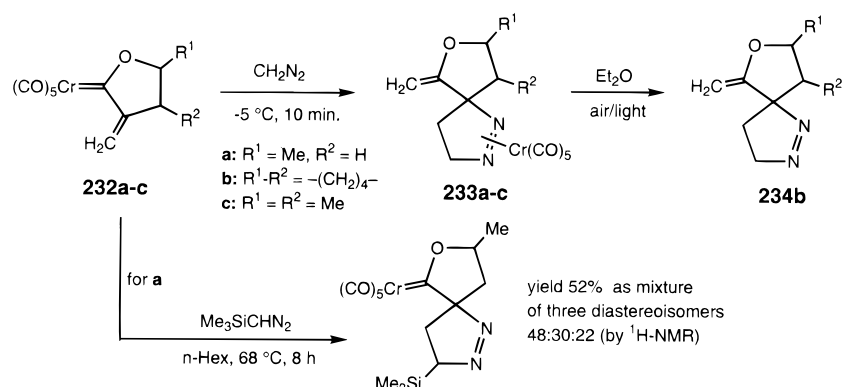
Scheme 32



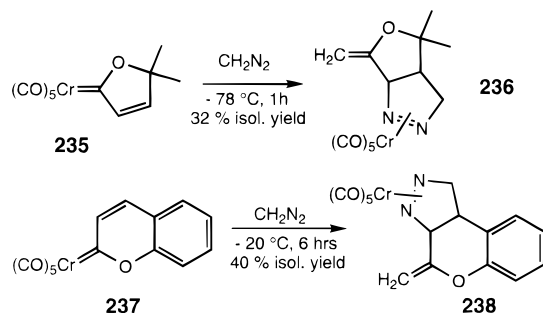
same ring as the carbene carbon atom (**235** and **237**, Scheme 34),⁴⁵³ again no chemoselectivity is found, and the diazomethane adds across the $\text{M}=\text{C}$ and $\text{C}=\text{C}$ bonds.

Diazoalkanes as 1,3-dipoles are added to tropone tricarbonyliron **55** as dipolarophiles to give pyrazolines^{457–460} (cf. Scheme 35), whereby the metal fragment not only serves as protecting group for the diene unit to give periselective addition to only one double bond, but also induces stereoselectivity in the case of unsymmetrically substituted diazoalkanes. A comparison of the dipolarophilic reactivities of tropone and (tropone)tricarbonyliron toward diphenylnitrilimine (DPNI) has been made,⁴⁶¹ the latter being more reactive. Combined electronic and steric reasons are held responsible for the strong preference for **239** over its regioisomer **240** (cf. eq 67). While the carbonyl group in **55** is not attacked by DPNI, the $\text{C}=\text{N}$ bond of tropone–imine complexes **241** readily reacts with DPNI to give cycloadducts **242**, which after decomplexation undergo sigmatropic rearrangement to give **243** and **244**, which latter are also

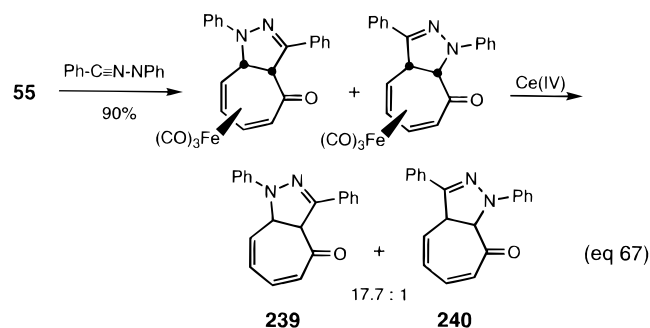
Scheme 33



Scheme 34

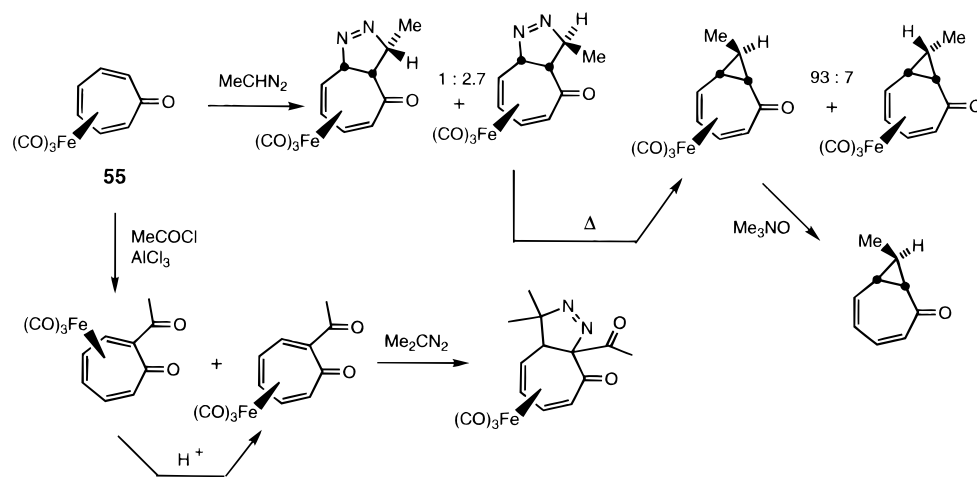


obtained in the reaction of uncoordinated tropone imines with DPNI⁴⁶² (Scheme 36).



A very interesting "criss-cross" reaction between benzalazine and the C=CH₂ double bond of the in

Scheme 35

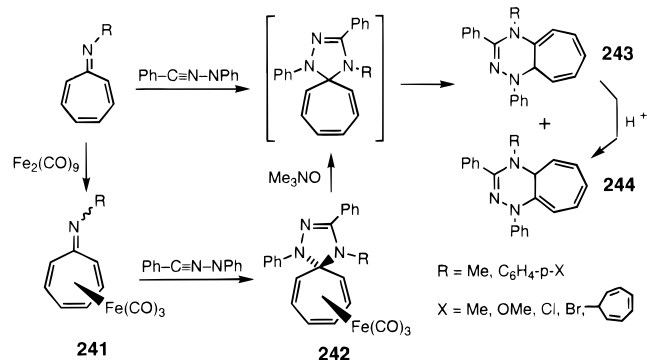


situ formed vinylidene complexes **245a,b** has been described by Geoffroy et al.,^{165,180} cf. eq 68. Whereas with isolated imine groups a [2+2] addition is observed (cf. section II.B), here the C=CH₂ double bond in **245a,b** behaves as a very reactive dipolarophile and consecutively cycloadds across both N=N=C fragments to give exclusively the *RR/SS* enantiomeric pair (not the meso form) of **246a,b** with the two phenyl groups on the same side of the fused five-membered rings.

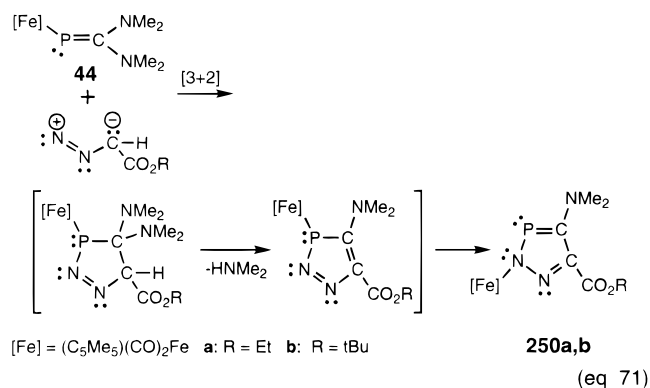
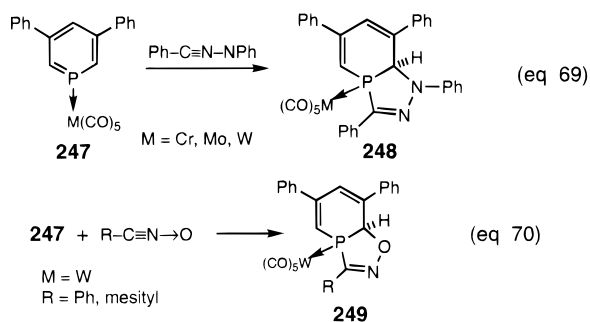
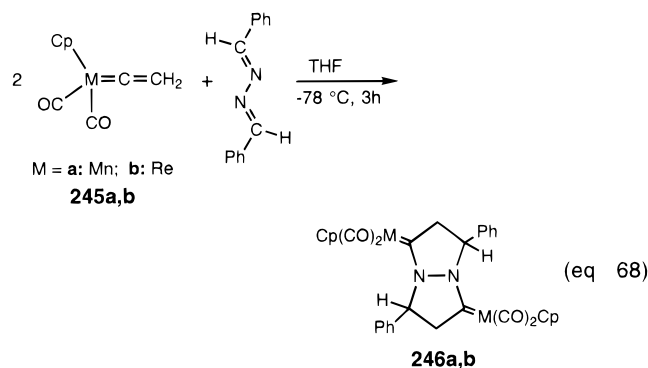
The PC double bond of (3,5-diphenyl-λ³-phosphinine)M(CO)₅ **247** (eq 69)⁴⁶³ reacts with DPNI to give the [3+2] adducts **248**. The same adducts are obtained without a metal coordinated to phosphorus, i.e., an activation of the dipolarophile is not necessary. However, with nitrile oxides (eq 70) as 1,3-dipoles, coordination of the phosphorus is essential in order to obtain cycloadducts **249**, because in case of the uncoordinated λ³-phosphinine, oxidation of the λ³o²-phosphorus by the nitrile oxide seems to prevail.⁴⁶³ The potent 1,3-dipoles ethyl and *tert*-butyl diazoacetate readily cycloadd to the P=C double bond of the metallophosphaalkenes **44**. The isolated metallo-2*H*-1,2,3-diazaphospholes **250a,b** (eq 71)⁴⁶⁴ result from consecutive [3+2] cycloaddition, elimination of dimethylamine, and sigmatropic 1,2-shift of the metal fragment from phosphorus to nitrogen.

The Fe(CO)₃ group in **251** (eq 72) not only prevents isomerization of the organic ligand to the thermodynamically more stable, aromatic 4-methylanisole,

Scheme 36

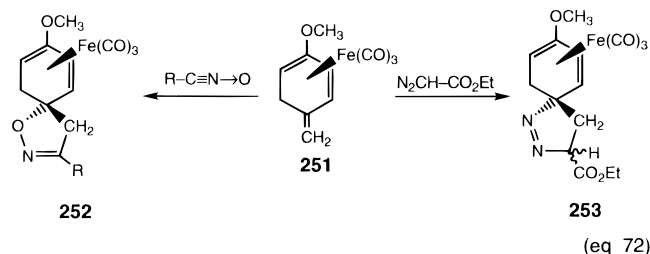


i.e., it protects the free exocyclic double bond, but also provides a high degree of chemo- and stereoselectivity

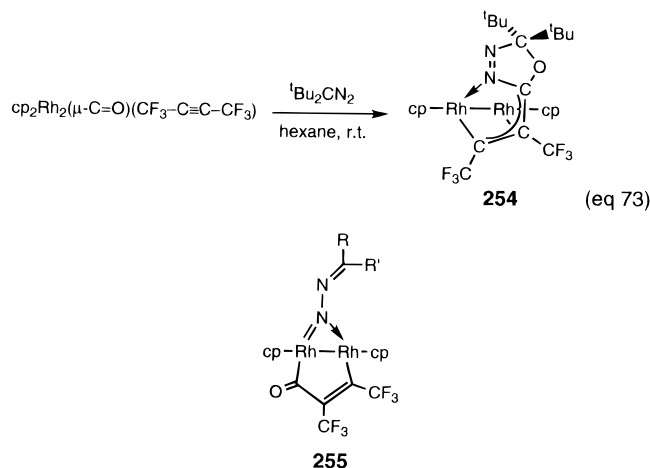


in the formation of the spiro[4.5]decatrione systems in **252** and **253**.⁴⁶⁵

A remarkable [3+2] cycloaddition of bis-*tert*-butyldiazomethane to the bridging CO in a binuclear rhodium complex (eq 73) has been reported by Dickson et al.²²⁶ The reaction is unique to *t*-Bu₂CN₂, and complex **254** is thermally stable at its melting



point of 184 °C. With mono- or unsubstituted diazomethanes rapid loss of N₂ takes place,^{466–468} while for the products with other disubstituted diazoalkanes structure **255** is proposed.



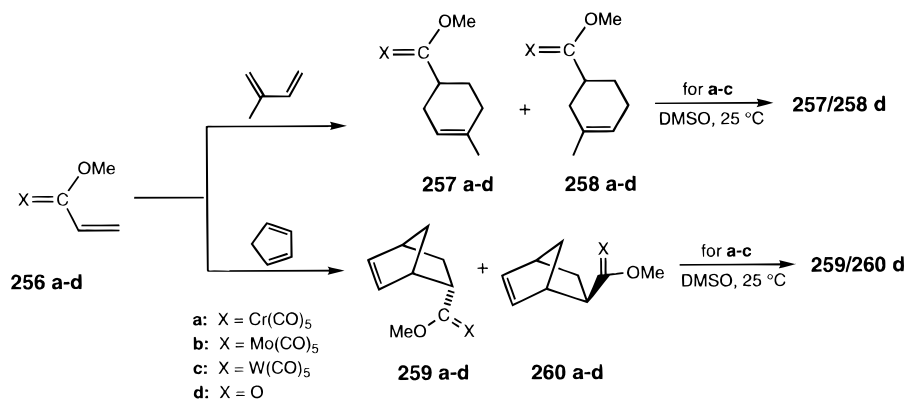
D. [4+2] Metal-Assisted Cycloaddition Reactions

In the purely organic realm, the Diels–Alder [4+2] cycloaddition is older than its electronically equivalent [3+2] dipolar counterpart. But, while the literature abounds of metal-assisted [3+2] cycloaddition reactions (previous section), examples of metal-assisted [4+2] cycloaddition reactions are less frequent. Nevertheless, also here, the metal can be present in either the two-electron component (dienophile), or the four-electron component, the diene.

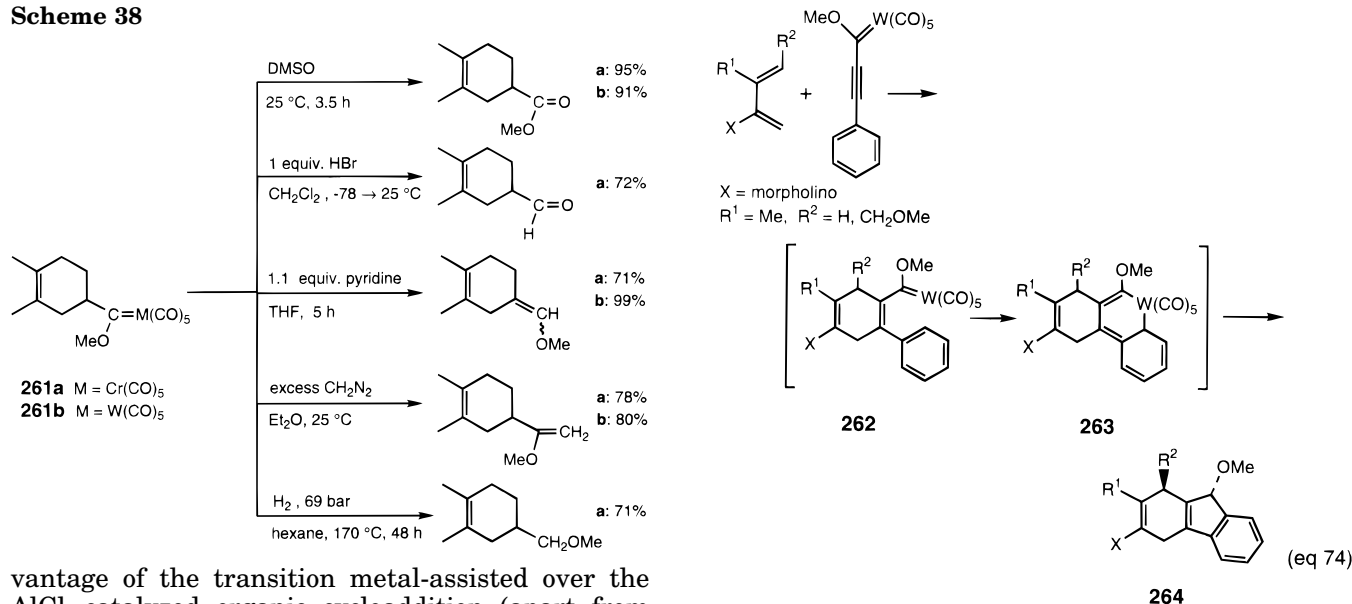
1. Activation of the Two-Electron Component (Dienophile)

Among the most widely used organic dienophiles are alkenyl and alkynyl esters such as acrylate, maleate, fumarate, and propynoate or acetylenedicarboxylate. Applying the isolobal relation^{469,470} between a d⁶-metal pentacarbonyl fragment and an oxygen atom, vinyl and alkynyl Fischer-type carbene complexes have been used as dienophiles in inter- and intramolecular Diels–Alder reactions by the groups of Wulff^{39,471–479} and Dötz^{480–486} (with respect to ref 483, see also Scheme 44 in the following section). It has been shown,⁴⁷¹ that the methoxy(vinyl)carbene complexes **256a–c** (Scheme 37) react with a variety of dienes with rate accelerations of greater than 10⁴ over that of the isolobally related methyl acrylate **256d**; concurrently the regioselectivity toward isoprene is increased (**257a:258a** = 92:8 vs **257d:258d** = 70:30), and a high endo/exo stereoselectivity with cyclopentadiene is found (**259a:260a** = 94:6 vs **259d:260d** = 78:22). The rates and selectivities observed with the methoxy(vinyl)carbene complexes very closely equal those of the AlCl₃-catalyzed organic reactions. A great synthetic ad-

Scheme 37



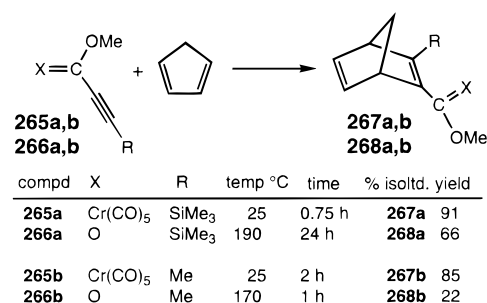
Scheme 38

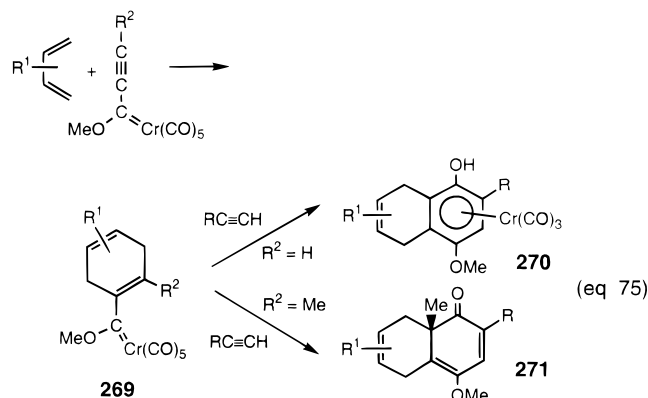


vantage of the transition metal-assisted over the AlCl_3 -catalyzed organic cycloaddition (apart from slightly higher yields) lies in the fact that the resulting Fischer carbene cycloadducts (e.g., **261a,b**, obtained from **256a,b** with dimethyl butadiene in 75% and 80% yields⁴⁷¹) can be readily converted to a variety of organic functional groups by employing known reactions of Fischer carbene complexes (cf. Scheme 38). A detailed study on the rates of [4+2] additions of [methoxy(vinyl)carbene] $\text{W}(\text{CO})_5$ with various dienes, and their dependency on the solvent, has been published by Sauer et al.⁴⁸⁷ Barluenga et al.^{488,489} have reported on the stereoselectivity in [4+2] cycloaddition reactions between [methoxy(vinyl)carbene] $\text{W}(\text{CO})_5$ and chiral 2-aminobuta-1,3-dienes derived from (*S*)-2-(methoxymethyl)pyrrolidine. See also the review by de Meijere⁴⁹⁰ on β -amino-substituted α,β -unsaturated Fischer carbene complexes as chemical multitailents. In the reaction of 2-aminobuta-1,3-dienes with (phenylethynyl)tungsten carbene complexes (eq 74),⁴⁹¹ the initial [4+2] cycloadduct **262**, which has been identified at low-temperature by NMR spectroscopy, consecutively undergoes an annulation reaction to give the dihydrofluorene **264** via the metallacycle **263**, reductive elimination and rearomatization by {1,2}-H shift. Great improvements in reactivity and yields were also found in the cycloaddition of cyclopentadiene to the alkynyl carbene complexes **265a,b** as compared to the respective esters **266a,b**⁴⁷² (cf. Scheme 39). The synthesis and some reactions, including [4+2] cy-

cloaddition of the parent acetylenic Fischer carbene complexes $(\text{CO})_5\text{M}=\text{C}(\text{NMe}_2)\text{C}\equiv\text{CH}$ ($\text{M} = \text{Cr}, \text{W}$) to cyclopentadiene, have been described by Wulff et al.⁴⁷⁷ The products of Diels–Alder reactions of alkynylcarbene complexes with dienes, such as **267a,b**, have a double bond in conjugation with the chromium–carbene carbon bond and are of particular synthetic value. These complexes of the general form **269** have been found⁴⁷² to undergo annulation reactions with acetylenes to give the chromium tricarbonyl complexed phenols **270**, when $\text{R}^2 = \text{H}$, or cyclohexadienones **271**, when $\text{R}^2 = \text{Me}$ (eq 75, see also the Dötz reaction, eq 140, section II.F). The reactions can also be carried out with the alkynylcarbene complex, the diene, and the acetylene all in one pot. Fischer-type iron alkynylcarbene complexes $(\text{CO})_4\text{Fe}$

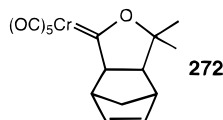
Scheme 39





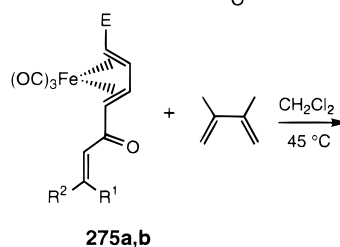
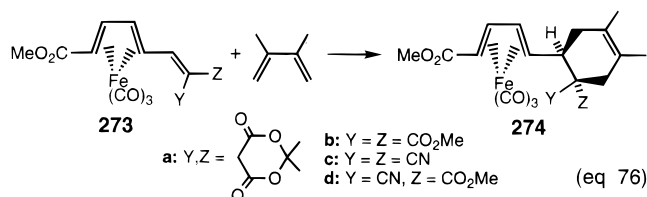
$\text{Fe}=\text{C}(\text{OEt})\text{C}\equiv\text{CR}$, analogous to **265a**, have also been prepared and reacted ($\text{R} = \text{SiMe}_3$) with 2,3-dimethyl-1,3-butadiene and cyclopentadiene.⁴⁹²

While it has been mentioned in section II.C.2, that **235** (Scheme 34) is attacked by the 1,3-dipole diazomethane as well at the exocyclic $\text{M}=\text{C}$ bond as at the $\text{C}=\text{C}$ double bond, cyclopentadiene exclusively adds across the $\text{C}=\text{C}$ bond to give a mixture of the exo- and endo-Diels–Alder adducts **272**.⁴⁵³



As in 1,3-dipolar cycloaddition (cf. section II.C.2, eq 58⁴³⁴), the pendant double bond (as dienophile) in **273a–d** (eq 76) is very selectively attacked by the diene (2,3-dimethyl-1,3-butadiene) from the face anti to the metal.⁴⁹³ Complexes **274a–d** are obtained as single isomers, however **c** and **d** in only 8–10% yield. The diastereomers **276a,b** and **277a,b** (eq 77) were obtained in almost quantitative yields from the addition of dimethylbutadiene to **275a,b** ($\text{E} = \text{CO}_2\text{Me}$; **a**, $\text{R}^1 = \text{R}^2 = \text{CO}_2\text{Me}$; **b**, $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{COPh}$). The mixture of diastereomers (**276a**:**277a** = 55:45; **276b**:**277b** = 64:36) could be easily separated by silica gel chromatography.⁴³⁷

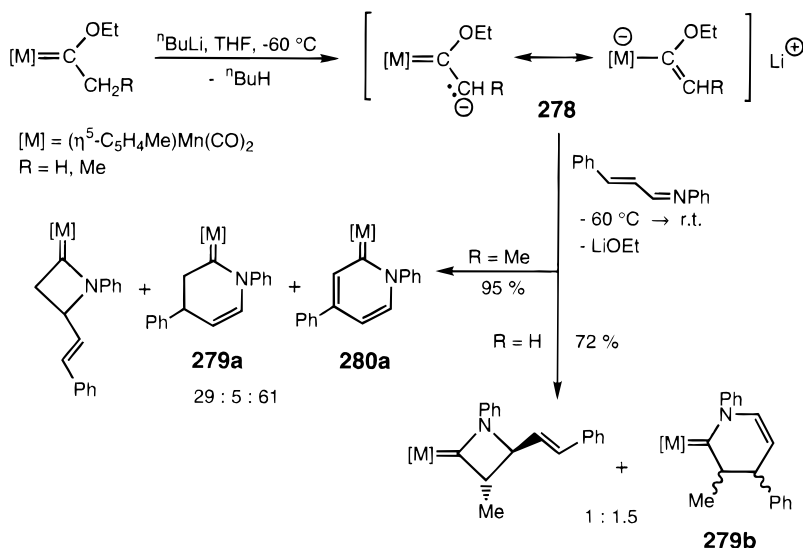
Geoffroy et al.¹⁶⁴ have compared the reactivity of cationic carbyne $[\text{Cp}'(\text{CO})_2\text{Mn}=\text{CCH}_2\text{R}]^+$ ($\text{R} = \text{H}, \text{Me}$),

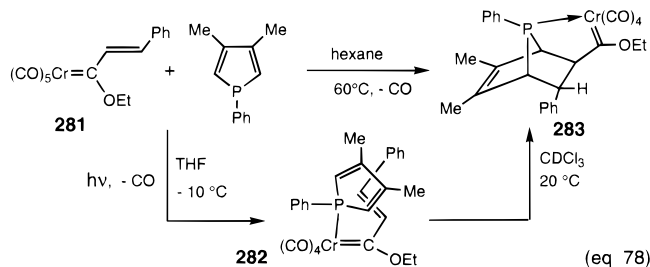


neutral vinylidene $\text{Cp}'(\text{CO})_2\text{Mn}=\text{C}=\text{CHR}$, and anionic carbene $[\text{Cp}'(\text{CO})_2\text{Mn}=\text{C}(\text{OEt})\text{CHR}]^-$ complexes (**278**, Scheme 40) toward 1,4-diphenyl-1-azabutadiene. While the former give high yields of 2-azetidinylidene complexes upon [2+2] cycloaddition (cf. section II.B), the latter undergo predominantly, although not exclusively, [4+2] cycloaddition reactions to afford primarily 2-tetrahydropyridinylidene complexes **279**. Under the basic reaction conditions, **279a** is effectively dehydrogenated to **280a**.

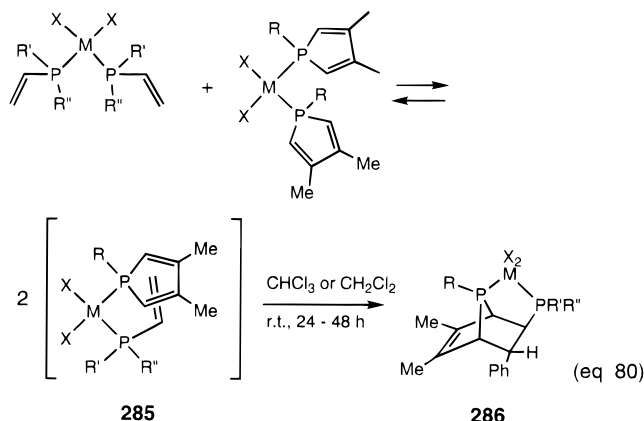
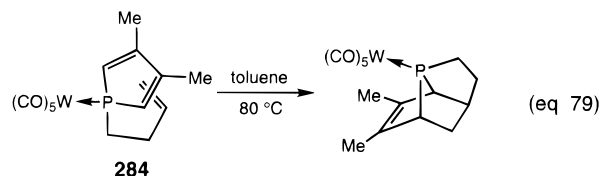
The stereochemical control in intramolecular Diels–Alder reactions of Fischer carbene complexes with an all-carbon tether between the diene and dienophile has been evaluated.⁴⁷⁶ An intramolecular [4+2] cycloaddition (eq 78) between a vinylcarbene and a phosphole, both coordinated to tetracarbonylchromium in **282** has been shown by Mathey⁴⁹⁴ to take place, when the vinylcarbene chromium complex **281** and the phosphole are heated in hexane. Intermediate **282** could be prepared independently by

Scheme 40





photolytic CO substitution at -10°C in THF, and it then thermally transformed to **283**. Earlier, Mathey⁴⁹⁵ had already reported the topologically related intramolecular [4+2] addition of [1-(3-butenyl)-3,4-dimethylphosphole]W(CO)₅ (**284**, in eq 79). Another related reaction has been described by Nelson et al.⁴⁹⁶ (eq 80). They observed facile intramolecular [4+2]

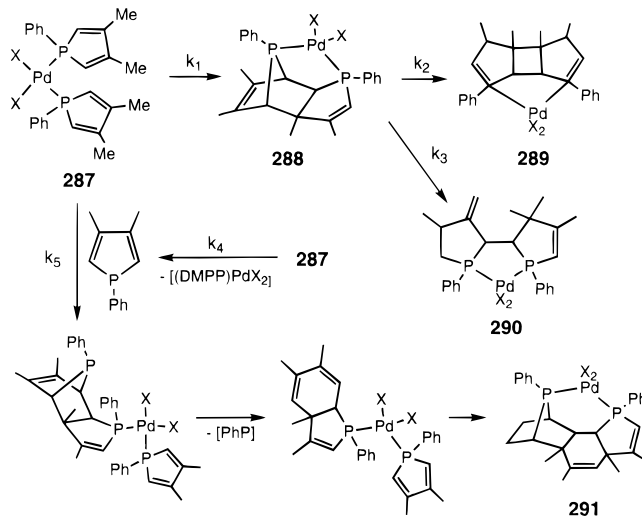


X = Cl, Br, I
 M = Pt; R' = -CH=CH₂, R'' = Ph; R = Ph, -CH₂Ph
 M = Pd; R' = R'' = Ph; R' = -CH=CH₂, R'' = Ph; R = Ph, tBu

when R' ≠ R''
 only one diastereomer

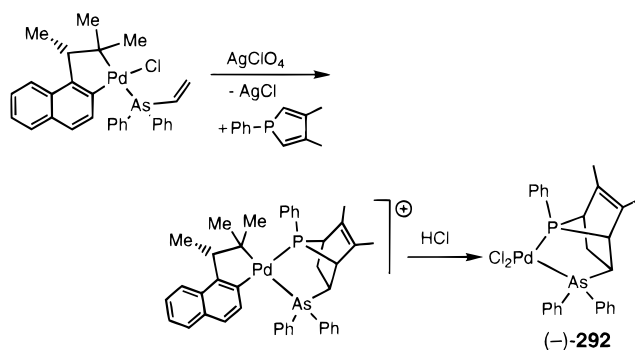
Diels–Alder reactions in mixed phosphole–vinylphosphine complexes of platinum and palladium **285** to give the dihalo[2-(R'R'')-phosphino]-5,6-dimethyl-7-R-7-phosphabicyclo[2.2.1]hept-5-ene complexes **286** of palladium(II) and platinum(II). Nelson et al. have also reported several other intramolecular versions^{494,497–505} of these cycloadditions to the coordinated phosphole. They state⁵⁰⁴ that the scope of these reactions is metal dependent and that the diastereoselectivity is generally thermodynamically controlled and is a primary function of steric effects within the metals' coordination sphere. Both *cis*-(DMPP)₂PdCl₂ and *cis*- or (after *trans/cis* isomerization) *trans*-(DMPP)₂PdBr₂ [DMPP = 1-phenyl-3,4-dimethylphosphole] undergo thermal coupling reactions of their coordinated phosphole ligands (Scheme 41).⁵⁰⁶ In their kinetic investigation the authors conclude with respect to the mechanism, that of the four types of products formed, i.e., **288** to **291**, the first three result from a unimolecular pathway, the [4+2] adduct **288** being the first observable product from which in turn the stable [2+2] adduct **289** and the *exo*-methylene product **290** are formed. Complex

Scheme 41



291 is formed in a parallel bimolecular reaction which follows a slow dissociation of phosphole from the starting complexes **287**. This contrasts the thermolytic behavior of the analogous platinum complexes *cis*-(DMPP)₂PtX₂ where only the analogues of **288** to **290** are formed, and the analogues of **288** and **289** are both ultimately converted to **290**.⁵⁰⁷ For their implications in enantioselective synthesis, the group of Leung^{508–517} is pursuing the synthesis and coordination chemistry of chiral resolved bidentate As/S,^{508,509} P/S,^{510,511,513,516} P/O,⁵¹⁵ P/P,^{512,517} and P/As⁵¹⁴ ligands. The ligand in **292**⁵¹⁴ was obtained enantio-merically pure in high yield by the totally diastereo-selective intramolecular [4+2] cycloaddition of diphenylvinylarsine and DMPP at palladium (Scheme 42). The authors state that no Diels–Alder reaction

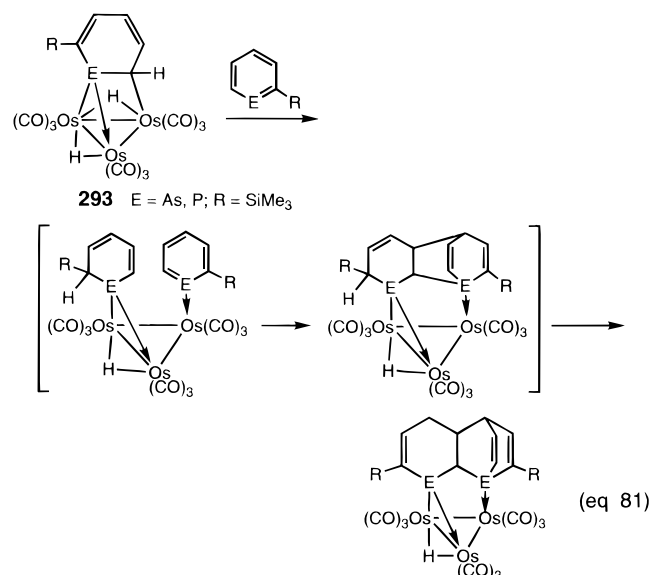
Scheme 42



is observed between free diphenylvinylarsine and free DMPP.

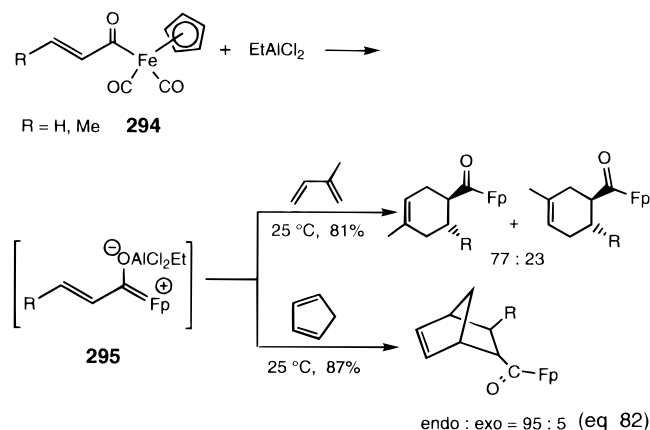
A rather unusual intramolecular [4+2] addition takes place, when a second 2-(trimethylsilyl)arsa- or phosphabenzene is reacted with the triosmium clusters **293** (eq 81).⁵¹⁸

Puddephatt et al.⁵¹⁹ have prepared a series of complexes [ML_n(Ph₂PC₁₀H₁₀PPh₂)] (ML_n = PtCl₂, PdCl₂, Mo(CO)₄, Mo(CO)₆) which resulted from a rapid intramolecular cyclodimerization of two *cis*-positioned PPh₂(C₅H₅) ligands. Diphenyl(cyclopentadienyl)phosphine itself does not undergo dimerization by Diels–Alder addition of the cyclopentadienyl rings, and also the complex [Fe(CO)₄{PPh₂(C₅H₅)}] does not readily (intermolecularly) dimerize. The

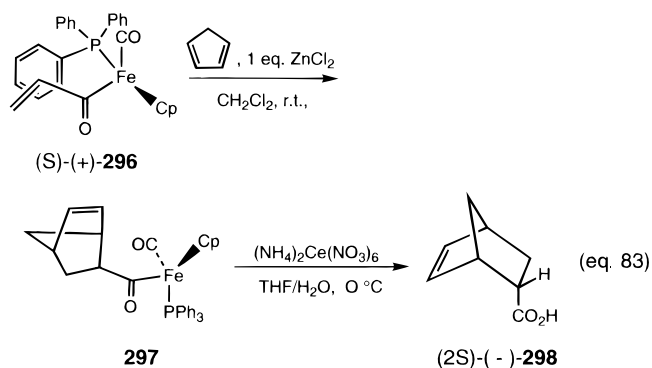


authors state that a template effect is responsible for the rapid cyclodimerization since the entropy term is usually a major component of the activation energy for Diels–Alder reactions, which have a highly ordered transition state.

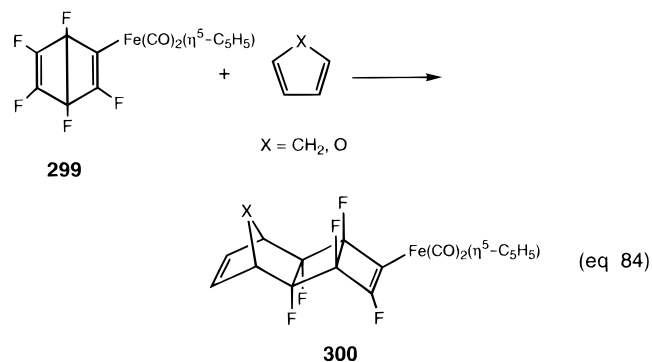
Herndon⁵²⁰ described a reaction (eq 82) that has some relation to the above mentioned reactions of the methoxy(vinyl)carbene complexes of chromium (vide supra, Scheme 37). The (η^1 -acryloyl)(η^5 -cyclopenta-



dienyl)dicarbonyl iron complexes **294**, under Lewis acid catalysis by ethylaluminum dichloride, give high yields of [4+2] cycloadducts with a variety of alkyl-substituted butadienes (only two typical examples are shown in eq 82), under mild conditions, and in many cases with very high regio- and stereoselectivity. On addition of EtAlCl₂ to the solution of complexes **294**, a species is produced giving a ¹³C NMR signal of the acyl carbon atom at 306 ppm. This is typical for a heteroatom-substituted carbene carbon and lends support to the suggested structure of the reactive intermediate **295**. An asymmetric version of the same type of reaction has been reported in the same year (eq 83).⁵²¹ The dienophile **296**, (S)-(+)-[(η^5 -C₅H₅)Fe(CO)(PPh₃)COCH=CH₂], was reacted with cyclopentadiene in the presence of one equivalent of ZnCl₂. The resulting cycloadduct complex **297** (88% yield) was oxidatively degraded in aqueous THF with ammonium cerium(IV) nitrate to yield predominantly



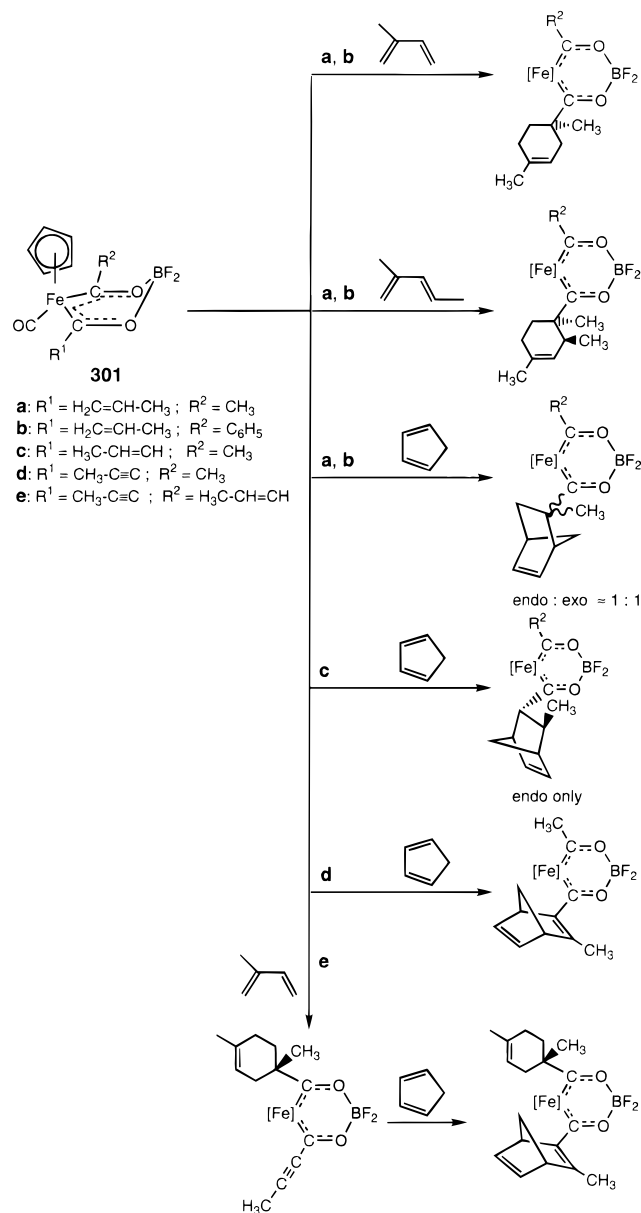
(2S)-(-)-bicyclo[2.2.1]hept-5-ene-2-endo-carboxylic acid (**298**). Two minor diastereomers (overall ratio 21:3:1) were detected by NMR. In 1975, Hazeldine⁵²² published the cycloaddition of cyclopentadiene and furan to the perfluoro complex **299** (eq 84) to give the exo-exo cycloadducts **300**. The reaction there takes place at the double bond away from the Fp moiety.



A (Cp)FeCO moiety is also present in the dienophilic alkenyl.⁵²³ and/or alkynyl-substituted⁵²⁴ (ferro- β -diketonato)BF₂ complexes **301a–e** of Lukehart et al. in Scheme 43. The dienes that have been used include isoprene, 2,3-dimethylbutadiene, *trans*-2-methyl-1,3-pentadiene, and cyclopentadiene. For the reaction of complex **301b** with dimethylbutadiene a rate enhancement by a factor of ca. 50 over the reaction of dimethylbutadiene with methyl methacrylate under similar reaction conditions is reported. The regioselectivity with the unsymmetrically substituted dienes is very high and follows the regiochemistry exhibited by methyl methacrylate in analogous Diels–Alder reactions. The unusually high stereoselectivity when diastereomeric adducts are formed, is ascribed to the highly asymmetric Fe moiety within the methacrylate dienophile. If there is a choice between an alkenyl and an alkynyl moiety in the dienophile, such as in **301e**, the reactivity of the former seems to be higher (bottom reaction in Scheme 43).

The dinuclear tetra- μ -carboxylato complexes [Mo₂(μ -O₂CHC=CH₂)₄]·0.5H₂O, [Cu₂(μ -O₂CHC=CH₂)₄]·2H₂O, [Ru₂(μ -O₂CHC=CH₂)₄Cl]·2HO₂CHC=CH₂, and [Ru₂(μ -O₂C(CH₃)C=CH₂)₄Cl]⁵²⁵ react at room temperature in methanol with cyclopentadiene to give the tetra-(bicyclo[2.2.1]hept-5-ene-2- μ -carboxylato) complexes in 51%, 56%, 96%, and 76% yields. The mild conditions with the 2-methylpropenoate complex are particularly remarkable because the purely organic Diels–Alder reaction requires rather forcing condi-

Scheme 43

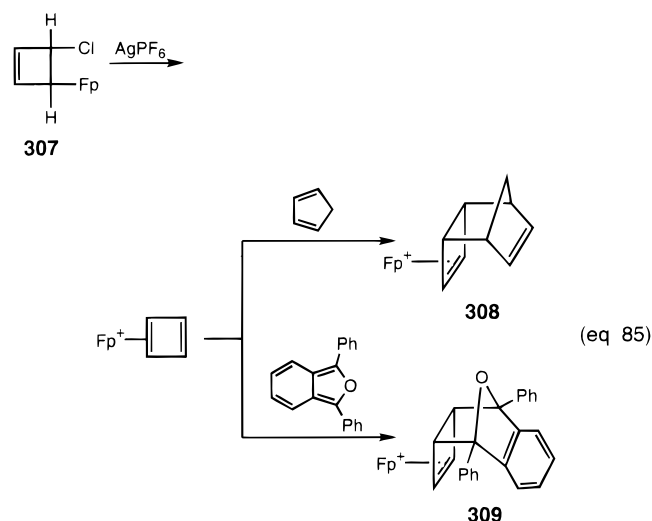


tions. Besides beneficial inductive effects, the authors ascribe the increase in reactivity to entropic advantages of having the four dienophiles coordinated to the metals. In view of the negative volume of activation for the [4+2] cycloaddition, this confinement should help to raise the ground-state energy of the dienophiles relative to the transition state, thereby lowering the activation energy.

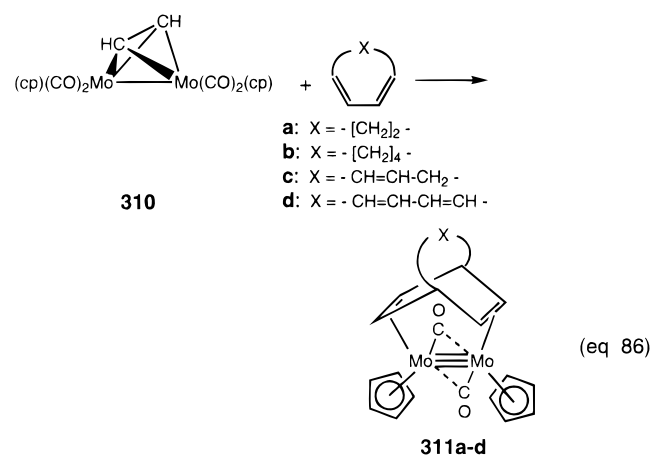
Not unexpectedly, many reactive dipolarophiles are also good dienophiles and vice versa, because the reactivity in either case relates to the ring-forming interaction with a four-electron counterpart. η^4 -Coordinated cyclic polyolefins have already been mentioned in the previous section (cf. eqs 52 and 67 and Schemes 35 and 36). Complexes **161**⁵²⁶ in Scheme 44 periselectively cycloadd the dienes **302**–**304** to the uncoordinated C(2)–C(3) positions, and the dienes obviously can approach the ring only from the side opposite to the metal. Whereas the initial cycloadducts with dienes **302** and **303** immediately eliminate N_2 and SO_2 , respectively, in the former case followed by a {1,3} hydrogen shift from the bridge-

head position to nitrogen, the cycloadduct with **304** is stable and does not eliminate CO_2 . Substitution of a CO ligand in **161c** for a phosphine leads to strongly enhanced rates for the cycloaddition with **302**.³⁹⁶ Rigby⁵²⁷ has explored reactions of **161c** characteristic of an electron deficient enone. Besides conjugate additions of typical Michael nucleophiles, Diels–Alder additions with 1-oxygen-substituted 1,3-dienes **305** under high-pressure conditions gave the expected regioisomers of the cycloadducts **306A,B** in high isolated yields. When cyclopentadiene as diene is reacted with **161c**, not only the expected Diels–Alder addition at the uncoordinated double bond of the tropone ligand is observed,⁵²⁸ but also a [6+4] addition across the 2,7-positions of tropone to give tricyclo[4.4.1.1^{6,7}.1¹⁰]dodeca-2,4,8-trien-11-one.

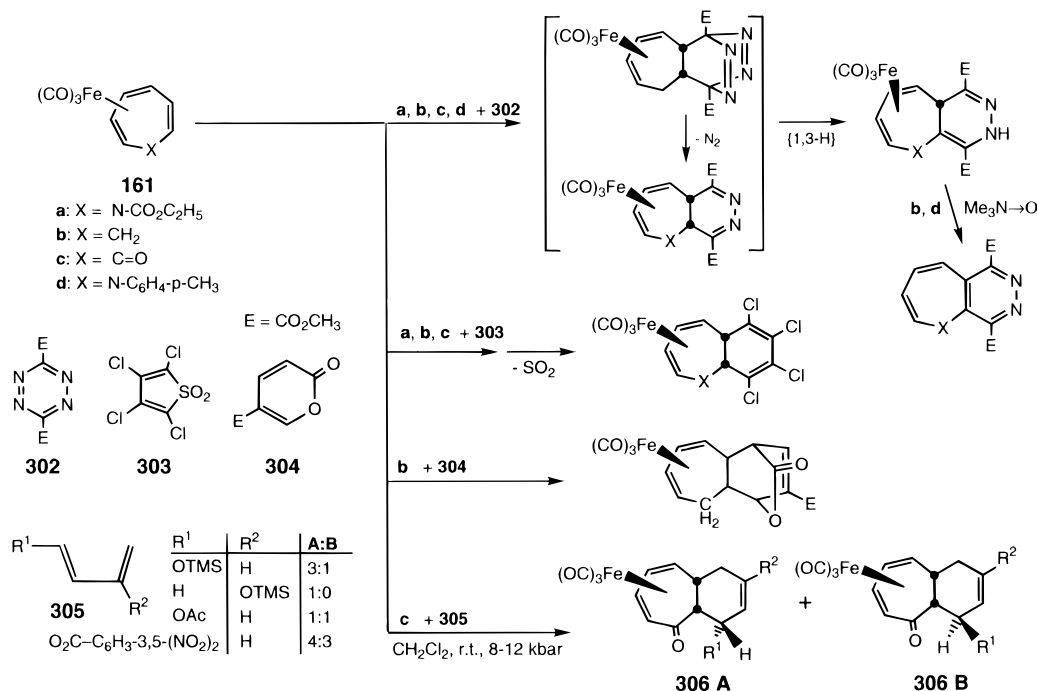
(η^2 -Cyclobutadiene) Fp^+ has been inferred⁵²⁹ as the reactive intermediate when (η^1 -3-chlorocyclobut-4-enyl)(η^5 -cyclopentadienyl)dicarbonyliron (**307**) is treated with $AgPF_6$. In the presence of cyclopentadiene and 1,3-diphenylisobenzofuran, it was trapped in the form of the respective Diels–Alder adducts **308** and **309** (eq 85). The coordinated olefinic cycloadducts could be very effectively liberated by reductive demetalation with $NaFp$, giving Fp_2 and the free olefin.



The cyclic dienes cyclohexa-1,3-diene, cycloheptatriene, cycloocta-1,3-diene, and cyclooctatetraene react in [4+2] fashion with the bridging acetylene in the dimolybdenum complex **310**^{402,530} according to eq

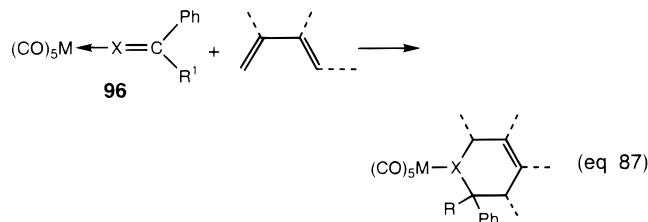


Scheme 44



86. For the formation of **311**, the authors propose a stepwise mechanism rather than a concerted process.

The heavier oxygen homologues (S, Se, Te) of benzaldehyde and diaryl ketones are not stable as monomeric compounds. Some have been trapped in situ by dienes. However, coordination to transition metals (e.g., Cr, Mo, W, Ru) stabilizes thiobenzaldehyde,^{531,532} selenobenzaldehyde,⁵³³ diaryl seleno-

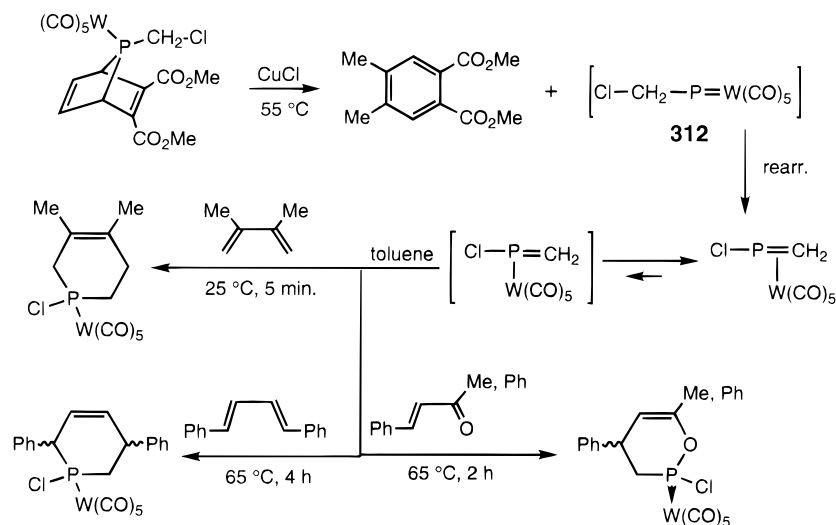


tones,⁵³³ tellurobenzaldehyde,⁵³⁴ and diphenyl telluroketone.⁵³⁵ The extreme reactivity of the free ligands is attenuated, and the complexes **96** can be

easily handled. They have been used as convenient sources of C=S, C=Se, and C=Te bonds to synthesize heterocyclics via [4+2] cycloaddition reactions with a variety of open chain and cyclic dienes.^{532,534,536-541} An example is given in eq 87. When unsymmetrically substituted dienes are used,⁵⁴² both isomeric cycloadducts are obtained with regioselectivities ranging from 2.4:1 to 19:1. The kinetics have also been studied.⁵³⁸ While free thio- and selenobenzaldehydes, in situ prepared in the presence of conjugated cyclic dienes, such as cyclopentadiene or cyclohexa-1,3-diene, selectively are cycloadded in endo fashion, this stereoselectivity is reversed when the heterodienophile is coordinated to a metal fragment.⁵⁴⁰ The cycloadducts of **96** (M = Cr, W; X = S, Se; R = H) with cyclopentadiene have exo/endo ratios of ≤7.1:1 and with cyclohexadiene ≤15:1.

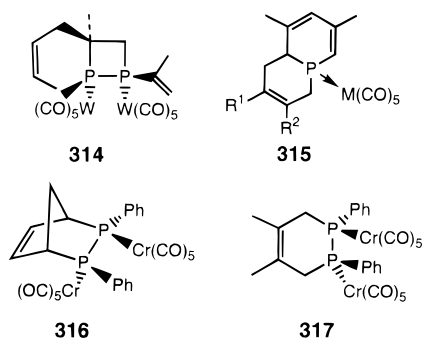
When transient [ClCH₂P=W(CO)₅] (**312**, Scheme 45) was generated from the respective 7-phosphanorbornadiene complex (cf. sections II.A and II.D.2)

Scheme 45



at 55 °C in the presence of CuCl, it rearranged^{74,543} into stable (η^2 -CH₂=PCl)W(CO)₅ (**313**), which could be characterized spectroscopically in solution. The η^2 -coordination of the P=C double bond, which was unequivocally established through the spectroscopic results, obviously very effectively stabilizes the molecule. However, this π -coordination does not deactivate the reactive P=C bond with respect to [4+2] cycloaddition to conjugated dienes and enones. This is explained by the indicated equilibrium between σ -P and η^2 -P=C coordination, which has been described earlier for Pt-phosphaalkene complexes,^{544–546} and which in the present case is shifted totally to the side of η^2 -P=C coordination.

The 2,3-dihydro-1,2-diphosphete ring in **127** (cf. eq 34) undergoes a selective [4+2] addition of 2,3-dimethylbutadiene to the P=C double bond from the less hindered side, giving **314**. While the P=C double bond of (3,5-diphenyl- λ^3 -phosphinine)M(CO)₅ **247** readily underwent [3+2] cycloadditions with nitrilimines and nitriloxides (cf. eqs 69 and 70), rather drastic reaction conditions are necessary to obtain [4+2] cycloadducts with 2-, and 2,3-substituted butadienes, i.e., **315** (R¹ = R² = Me, OSiMe₃; R¹ = H(Me), R² = Me(H); R¹ = H, R² = OSiMe₃).⁴⁶³ The P=P double bond in **22** (eq 12) is also a very reactive dienophile toward cyclopentadiene and 2,3-dimethylbutadiene.⁹⁶ The respective Diels–Alder adducts **316** and **317** are thermally stable, and a cycloreversion, which is normally observed with the adducts of cyclopentadiene and uncoordinated diphosphene, is not observed below 170 °C. The ferrocenyldiphosphene **128** (cf. eq 35)²²⁹ also forms the expected [4+2] cycloadduct with cyclopentadiene.



2. Activation of the Four-Electron Component (Diene)

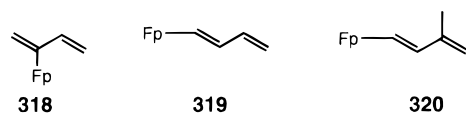
The activating influence of the Fp group, (η^5 -C₅H₅)-Fe(CO)₂, in (η^1 -allyl)metal complexes toward [3+2] additions, and the versatile transformations of Fp into organic functionalities, have already been mentioned in section II.C.1. ML_n- η^1 -pentadienyl or ML_n- η^1 -2,4-hexadien-1-yl (ML_n = Fp,^{547,548} Mn(CO)₅,^{332,549} (Cp)Mo(CO)₃,^{332,550}), being considered higher homologues of the η^1 -allyl complexes,³³² did not undergo the expected [3+2] cycloaddition reactions, but instead gave [4+2] cycloadducts with TCNE and maleic anhydride.^{332,334} With the η^1 -5-methyl-2,4-hexadien-1-yl ligand, however, the requisite s-cis conformation of the diene for a [4+2] addition is sterically disfavored, and for all three metals the [3+2] adducts are formed^{332,334} (cf. Table 4, entry 12).

Attachment of Fp to the 1- or 2-positions of 1,3-butadiene (**318–320**)^{551–553} results in a strong activa-

Table 5. [4+2] Cycloadditions to 2-Fp-1,3-butadiene (Fp = (Cp)(CO)₂Fe)

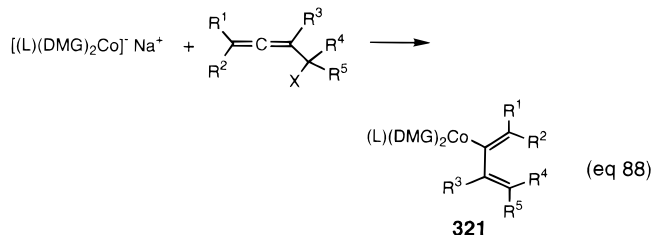
| Reactants | Product | % yield |
|--|---------|---------|
| 318 , TCNE | | 93 |
| 318 , p-quinone | | 85 |
| 318 , maleic anhydride | | 77 |
| 318 , dimethyl acetylenedicarboxylate | | 90 |
| 318 , p-toluenesulfonyl isocyanate | | 88 |
| 318 , dimethyl fumarate | | 70 |
| 318 , nitrosobenzene | | 88 |
| 318 , diethylazodicarboxylate | | 91 |

tion of these dienes toward a series of electrophilic dienophiles, and they react in nonpolar Diels–Alder fashion under mild conditions with high yields.⁵⁵⁴



They failed, however, to react with most monosubstituted electrophilic alkenes. A selection of products and yields is given in Table 5. Qualitatively, complexes **318–320** were found equally reactive. Due to the instability of the cycloadducts derived from **319** and **320**, and problems with their purification, **318** was used in most reactions. The second-order rate constants for the reactions between **318** and dimethyl acetylenedicarboxylate have been determined in solvents of different polarity. There is only an insignificant variation in the rate constant between cyclohexane and acetonitrile or nitromethane as solvents. By competition experiments it has been shown⁵⁵⁴ that **318** is at least 2 orders of magnitude

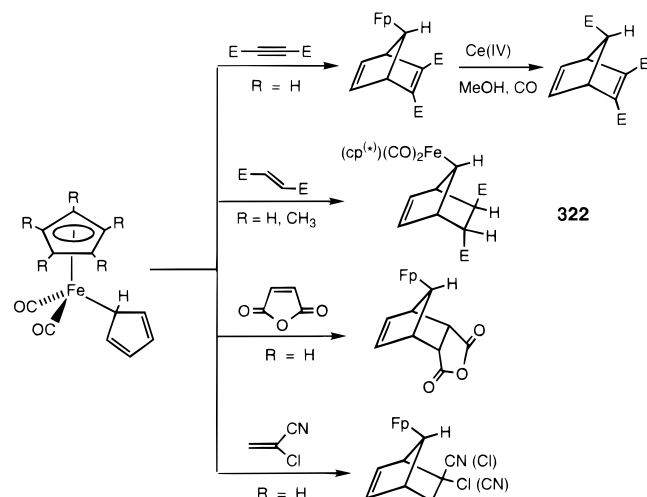
more reactive toward tetracyanoethylene than 2-(trimethylsiloxy)-1,3-butadiene. Comparable work has been reported by Tada⁵⁵⁵ with an activating cobaloxime substituent in 2-position of 1,3-butadiene. Welker et al.^{556–559} have prepared extensive series of these same air-stable, crystalline complexes, [1,3-butadiene-2-yl(pyridine)bis(dimethylglyoximate)]-cobalt(III), **321** by reaction of cobaloxime anions [(py)(DMG)₂Co][−] with allenic electrophiles (eq 88).



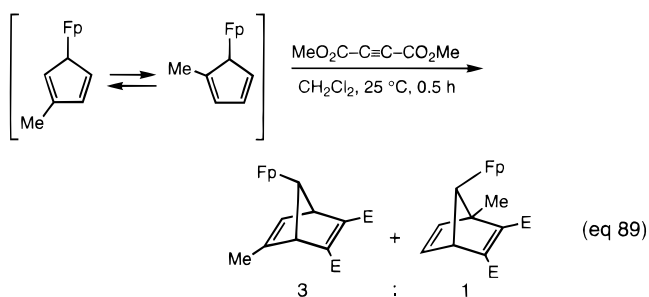
Complexes **321** are very reactive toward a range of dienophiles in highly exo-selective Diels–Alder reactions. The authors report various methods, by which the metal can be cleaved in a reusable form from the cycloadducts, maintaining the stereochemical integrity of the latter. Depending on the choice of the demetalation reaction, the 2-position of the former diene can be further functionalized in the cycloadduct. The preparation of tin and zirconium analogues of **318** and **319** as prospective reactive dienes has also been reported.^{560,561}

The addition of dimethyl fumarate^{562,563} and other reactive dienophiles to (η⁵-C₅H₅)Fe(CO)₂(η¹-C₅H₅)^{301,314,317,562–565} and (η⁵-C₅Me₅)Fe(CO)₂(η¹-C₅H₅)⁵⁶² to give, e.g., **322** (cf. Scheme 46) has been studied by

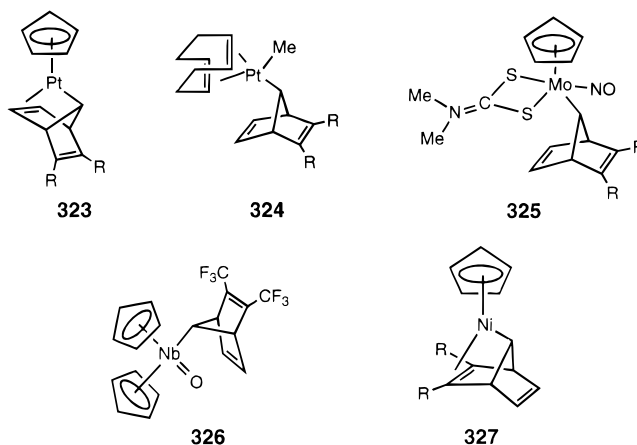
Scheme 46



several groups. As the dienophile always attacks the η¹-Cp ring at the face away from the metal, the Fp group in 7-position of the bicyclo[2.2.1]adducts always ends up syn with respect to the double bond in the former Cp ring. This is also the case when Fp(η¹-C₅H₄CH₃) is reacted with DMAD, the selectivity with respect to the position of the methyl group however is rather low (eq 89).⁵⁶⁶ The reaction has also been considered in terms of a stepwise [3+2] cycloaddition,^{314,562} comparable to the (cyclic) allyl moieties in entries 2 and 4 of Table 4. However, the appearance of the resulting bicyclo[2.2.1]adducts suggests a Di-

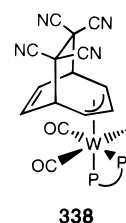


els–Alder reaction. Stereochemical investigations with fumaro- and maleonitrile have confirmed a concerted [4+2] mechanism.⁵⁶³ Analogous reactions of various dienophiles with η¹-Cp in complexes such as (COD)(η¹-Cp)₂Pt, (COD)(η¹-Cp)Pt(CH₃),^{567–569} (η⁵-Cp)(η¹-Cp)Mo(NO)(η²-S₂CNMe₂),⁵⁷⁰ or (η⁵-Cp)₂(η¹-Cp)₂Nb,⁵⁷¹ (Cp)₂MCl₂ (M = Ti, Zr)⁵⁷² have also been described, giving cycloadducts such as **323–326**, respectively. Nickelocene, (η⁵-Cp)₂Ni, has also been shown to give, besides binuclear compounds with bridging acetylene, low to moderate yields of formal Diels–Alder products **327**,^{573,574} however, the mech-

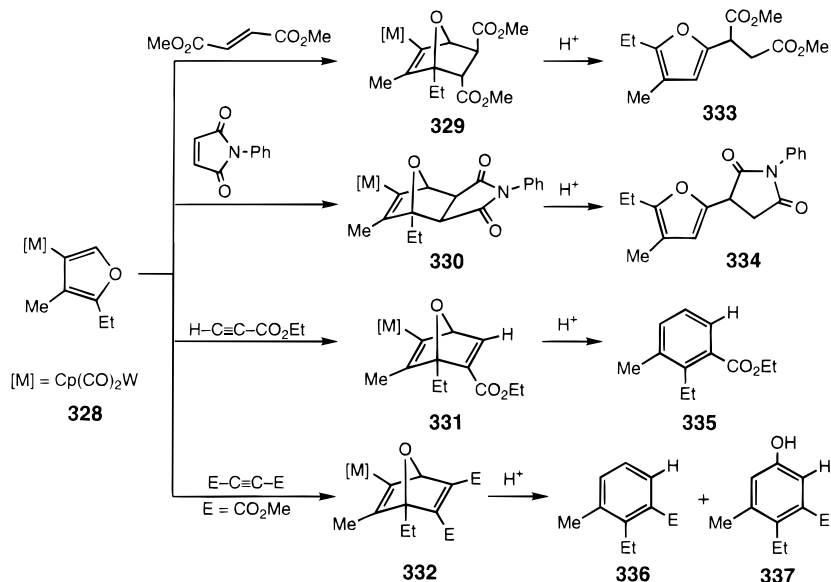


anism by which these are formed is not clear. Like CpFe(CO)₂, the CpW(CO)₃ group can be considered as electron donating. It activates the furan ring in **328** (Scheme 47) toward [4+2] cycloadditions with electron-deficient alkenes and alkynes.⁵⁷⁵ The adducts with dimethyl fumarate and *N*-phenylmaleimide, **329** and **330**, are formed as single isomers. On treatment with acid, cycloadducts **329–332** are demetalated with unusual accompanying C–C bond scissions, and deoxygenation, to give 2-alkylated furans **333** and **334** and benzenes **335–337**.

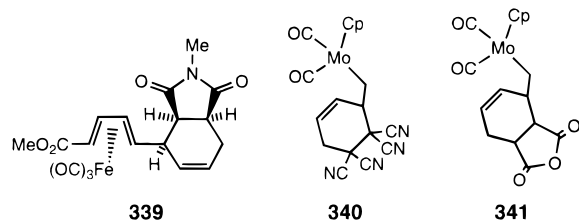
The uncoordinated diene system of the η³-cycloheptatrienyl ring in the tungsten bisphosphine complexes (Ph₂P(CH₂)_nPPh₂)(CO)₂(η³-C₇H₇)W (n = 1, 2) at 0 °C in dichloromethane cycloadd TCNE in [4+2] fashion to give complexes **338**.⁵⁷⁶



Scheme 47

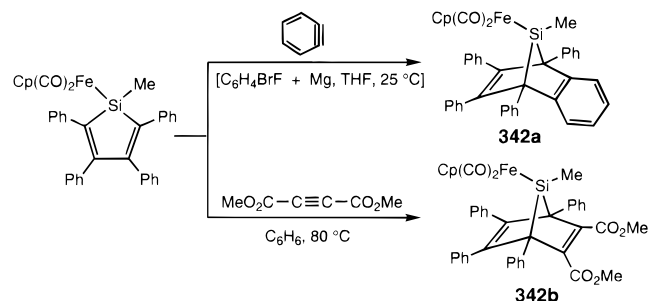


As has been mentioned before in sections II.C.2 (eq 58) and II.D.1 (eqs 76, 77), a (η^4 -1,3-diene) $\text{Fe}(\text{CO})_3$ group tethered to a reactive $\text{C}=\text{C}$ bond induces stereoselectivity by directing the incoming reactant to the face anti to the metal. This is also the case with a pendant dienyl group.⁴⁹³ Complex **339** is the exclusive product formed from (methyl η^{2-5} -nonatetraenoate) $\text{Fe}(\text{CO})_3$ and *N*-methylmaleimide. Likewise, $\text{CpMo}(\text{CO})_3(\eta^1$ -2,4-pentadien-1-yl) cycloadds the dienophiles TCNE and maleic anhydride in Diels–Alder fashion to give a single stereoisomer of **340** and **341**, respectively.⁵⁷⁷

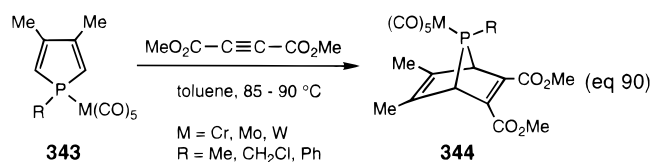


Clearly related to the reactions of η^1 -Cp complexes (vide supra) are the metal assisted [4+2] cycloaddition reactions of metal bound silole⁵⁷⁸ (Scheme 48),

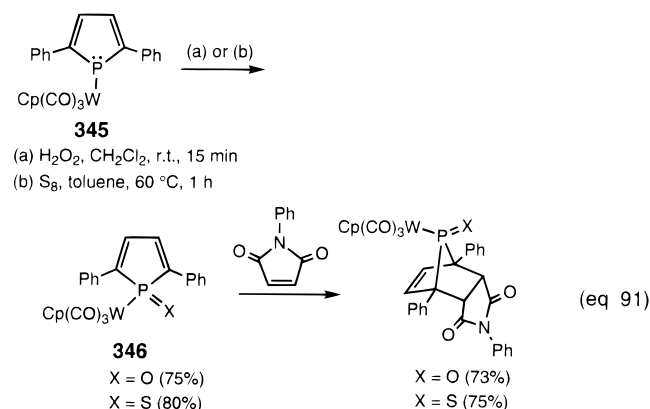
Scheme 48



and phosphole^{74,515,516,579} (e.g., **343** in eq 90, cf. also **285** in eq 80), giving, e.g., complexes **342** and **344**. The metal fragment not only increases the propensity of the phosphole to undergo [4+2] Diels–Alder cycloadditions with dienophiles⁴⁹⁷ but most importantly, it stabilizes the resulting 7-phosphanor-



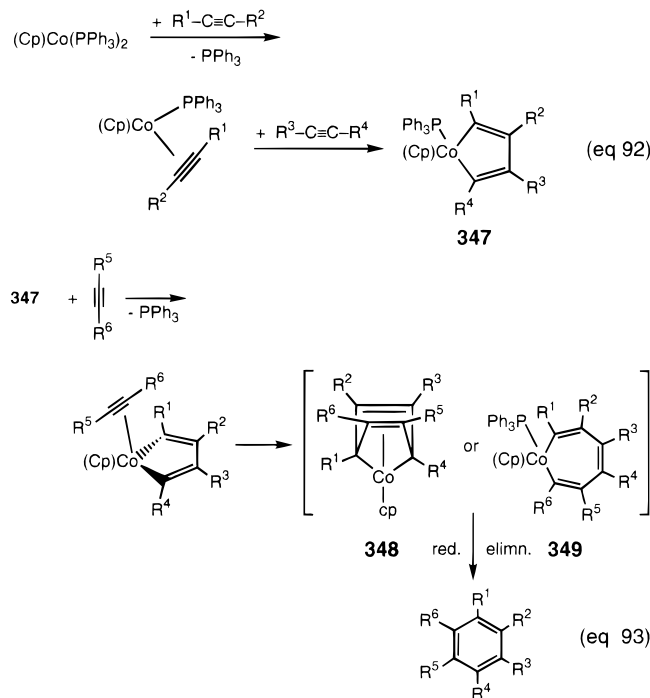
bornadiene^{579,580} with respect to loss of the phosphorus bridge. One aim in the preparation of the 7-heteronorbornadiene complexes **342** or **344** was to generate (via elimination of a benzene derivative by a retro-Diels–Alder reaction⁵⁸¹) and to stabilize, or to intercept and trap the reactive silylenes and phosphinidenes. Silylene from thermolysis of **342b** has been successfully trapped by several reagents,⁵⁷⁸ but the existence of free silylene under these conditions could not unequivocally be established. Phosphinidene transfer reactions starting from 7-phosphanorbornadienes have already been mentioned in section II.A. In compounds **343**, the phosphole phosphorus atom is coordinated to the metal fragment via donation of its lone pair. In contrast, in **345** (eq 91),



the metal fragment is a σ -bonded substituent on phosphorus, and Mathey et al.⁵⁸² have studied the influence on the reactivity of the interplay between the phosphorus lone pair, the dienic system, and the P–metal bond. The reactivity of **345** is dominated by the high nucleophilicity of their phosphorus lone

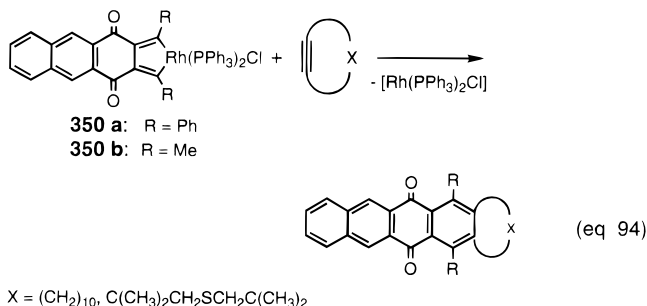
pairs, while the diene system is rather unreactive. Electron-poor alkynes do not give Diels–Alder adducts, but rather undergo an organometal [3+2] cycloaddition, yielding spirocyclic compounds containing a PC=CC(O)W ring. Only the *P*-oxides or -sulfides **346** are able to undergo clean [4+2] additions with dienophiles such as *N*-phenylmaleimide.

Cobaltacyclopentadiene complexes **347** are readily prepared according to eq 92.^{583–585} Following coordination of a third molecule of alkyne (eq 93), benzenes are produced either catalytically or stoichiometrically, whereby it is not clear whether they are formed via a genuine [4+2] cycloaddition of the alkyne (intermediate **348**) or via an insertion reaction (intermediate **349**), see also Scheme 73.



Cyclododecyne and 3,3,6,6-tetramethyl-1-thiacycloheptyne readily cycloadd to the rhodacyclopentadiene complex **350** (eq 94). This represents the last

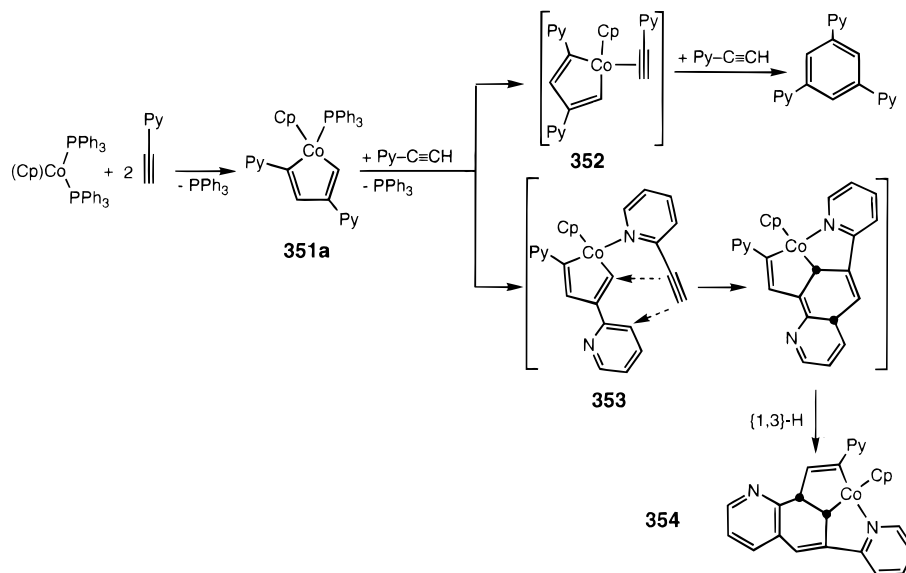
step in the [2+2+2] multicomponent cycloaddition reaction termed “diyne-reaction” by Müller⁵⁸⁶ (cf. section II.F).



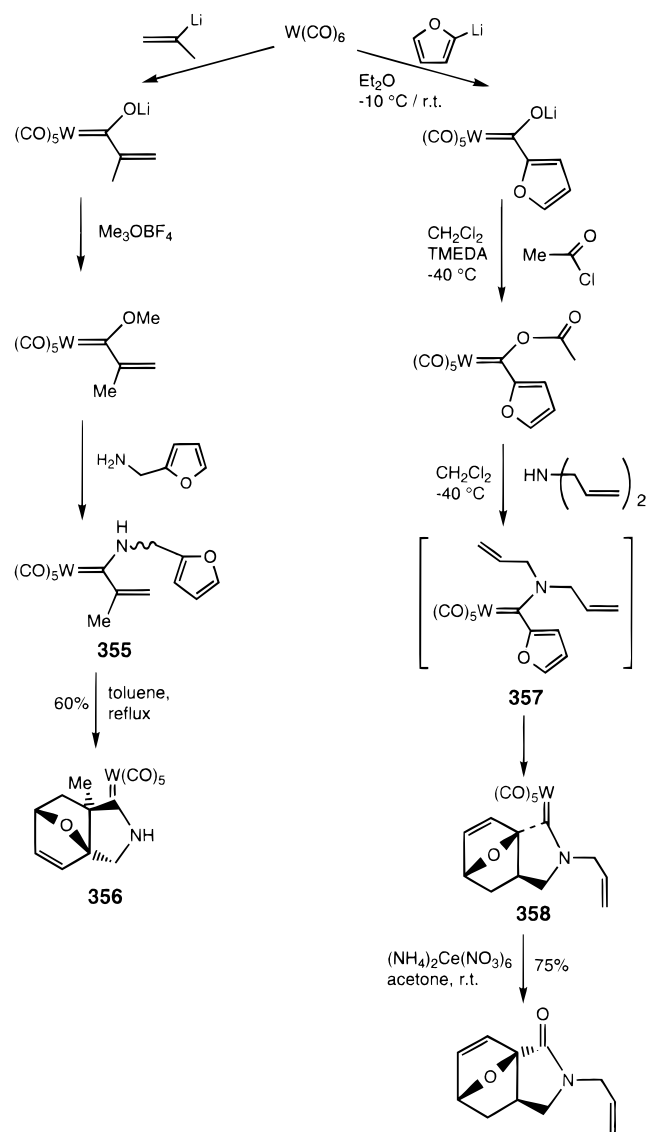
When 2-ethynylpyridine was used as alkyne in the reaction with $\text{CpCo}(\text{PPh}_3)_2$ (Scheme 49),⁵⁸⁷ four products were isolated, namely the two expected regioisomeric cobaltacyclopentadiene complexes **351a** and **351b** (not shown), 1,3,5-tri-2-pyridylbenzene, and complex **354**. Since an analogous complex is not observed in the reaction with phenylacetylene, the authors suggest that coordination of the pyridine nitrogen (**353**) instead of the alkyne triple bond (**352**) also plays an important role. In **353**, the acetylene is placed in a position that it cannot cycloadd to the 1,3-diene moiety within the metallacyclopentadiene, but rather to one double bond of the latter and one double bond in the pyridine ring. The reaction is concluded by a 1,3-hydrogen shift to regain the aromaticity of the pyridine ring.

Dötz et al.⁴⁸³ describe the role of carbene complexes in *intramolecular* Diels–Alder reactions, whereby either the diene or the dienophile functionality can be activated through direct bonding to the carbene carbon atom. In Scheme 50 the preparation and cycloaddition reaction of one example of either type is illustrated. Compound **355** is representative of an activated two-electron component (see also section II.D.1), while in **357** the four-electron component is activated. Compound **357** is so reactive that under the conditions of its formation (-40°C , CH_2Cl_2) the Diels–Alder adduct **358** is directly obtained as a

Scheme 49



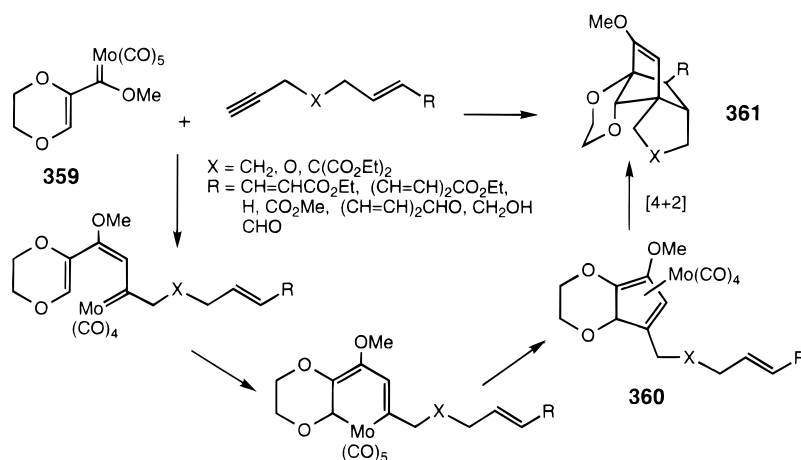
Scheme 50



single diastereomer. Trans-fused decalins have also been prepared in good yields with high diastereofacial selectivity by intramolecular Diels–Alder reactions of α,β -unsaturated Fischer carbene complexes.⁵⁸⁸

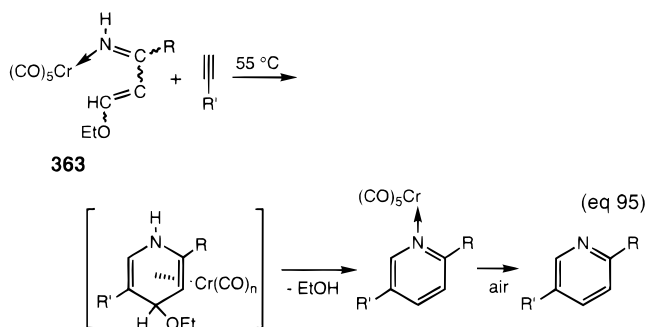
Harvey⁵⁸⁹ described the reaction of dioxenylmolybdenum carbene complex **359** (Scheme 51) with various enynes. The tetracyclic products **361** are suggested to be formed in an intramolecular [4+2] cycloaddition

Scheme 51

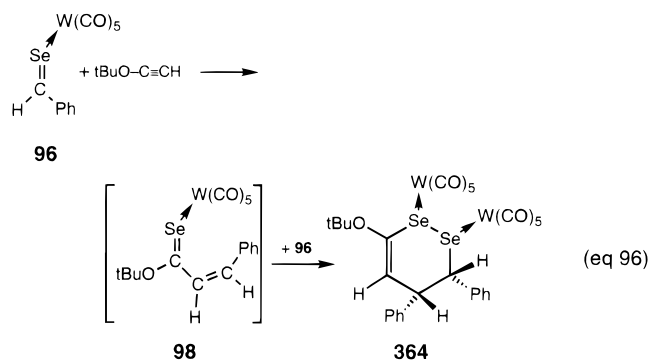


of the intermediate trialkoxycyclopentadiene complex **360**.

The 1-hetero 1,3-diene fragments in complexes **362**^{590,591} and **363**⁵⁹² are sufficiently activated to undergo hetero-Diels–Alder reactions with alkyne (Scheme 52 and eq 95). As has been mentioned in

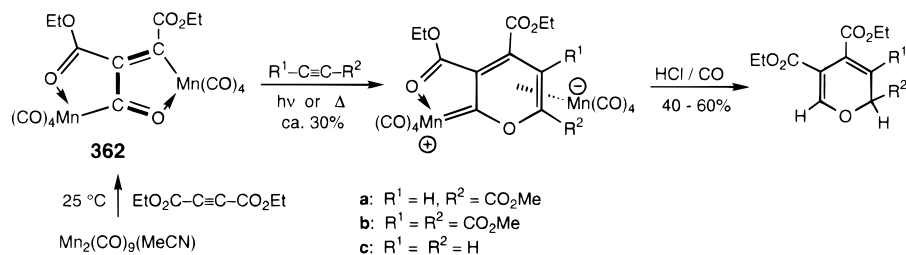


section II.B (eq 27), selenobenzaldehyde complexes **96** react with N-, O-, and S-donor-substituted alkynes by [2+2] addition and cycloreversion, i.e., formal insertion of the $C\equiv C$ into the $Se=C$ bond, to form the α,β -unsaturated selenocarboxylic acid complexes **98**, which are comparable to **363**. With *tert*-butoxyethyne as the alkyne, complex **98** (eq 96) is an

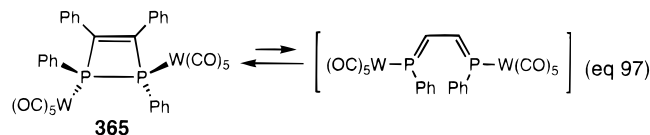


unobservable intermediate which, as heterodiene, immediately undergoes a highly regioselective [4+2] addition with the $Se=C$ bond of a second molecule of **96** to give **364**.¹⁹⁷ Via conrotatory ring opening, the 1,2-dihydro-1,2-diphospha-1,3-diene structure (eq 97),⁵⁹³ which can be trapped by the dienophiles maleic anhydride, *N*-phenylmaleimide, acrylonitrile, and benzaldehyde, giving the [4+2]

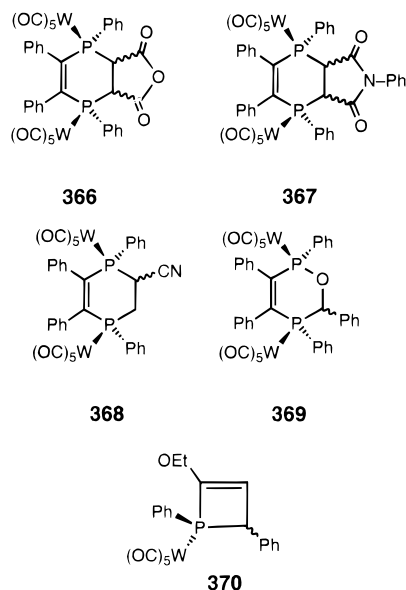
Scheme 52



adducts **366–369**, respectively. The same sort of equilibrium, and the corresponding reactivity as

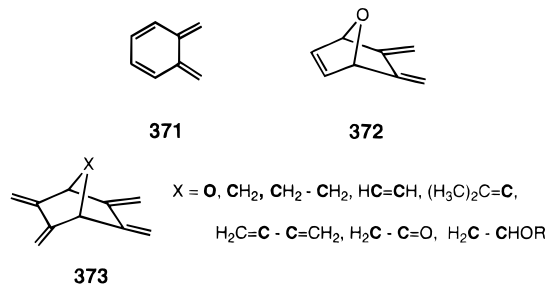


1-hetero-1,3-diene, has also been shown for the 1,2-dihydrophosphete **370**.⁵⁹⁴



The osmium-assisted formation of 7-azabicyclo[2.2.1]hept-5-ene complexes (cf. Scheme 19) from substituted pyrroles and olefins superficially looks like a Diels–Alder reaction, however, as has been shown in section II.C.1, it is in fact a 1,3-dipolar [3+2] cycloaddition.^{356,357}

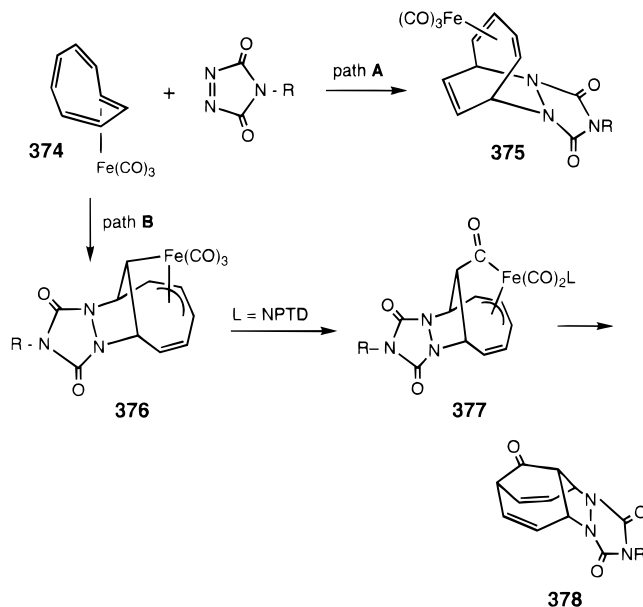
Investigations on the influence of coordinated metal fragments on the reactivity of “remote”, uncoordinated 1,3-diene moieties in cycloaddition reactions have been performed by several groups. Vogel, Roulet, et al.^{595–599} have prepared extensive series of stereochemically well-defined mono- and bis-metal-coordinated complexes of (poly)cyclic polyenes with exocyclic *s-cis*-butadiene groups, such as **371–373**. The rates,^{600–603} stereo- and regioselectivities⁶⁰³ of the free and differently (exo/endo) metal complexed polyenes in Diels–Alder additions with symmetrical and unsymmetrical dienophiles have been studied. The influence of the metal carbonyl fragments $[\text{M}(\text{CO})_5]$, $\text{M} = \text{Cr}, \text{W}$; $[\text{M}(\text{CO})_4]$, $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$; $[\text{M}(\text{CO})_3]$, $\text{M} = \text{Mo}, \text{W}, \text{Fe}$ on the rates is explained by statistics (blocking of one of several available sites), steric bulk and electronic influences. All contribute to a more



or less pronounced decrease in the reaction rates as compared to the free polyenes.

Olsen³⁹² has reinvestigated the reaction (Scheme 53) of $(\eta^4\text{-cyclooctatetraene})\text{Fe}(\text{CO})_3$ **374** with 4-

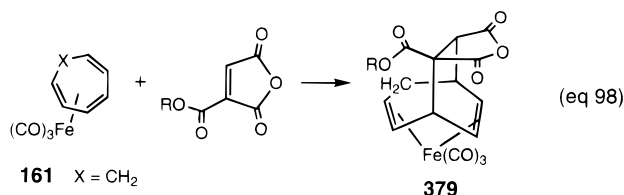
Scheme 53



phenyltriazoline-3,5-dione (NPTD) and compares it to the analogous reaction between NPTD and free COT. Obviously, the coordinated COT ligand in **374** does not undergo the Diels–Alder addition from its bicyclo[4.2.0]octa-2,4,7-triene valence isomeric structure, as does free COT.⁶⁰⁴ [This has been attributed to the considerably greater reactivity of the planar diene moiety in the bicyclic structure as opposed to the twisted geometry in the monocyclic valence isomer.] As opposed to Green and Wood,³⁹¹ Olsen not only finds the Diels–Alder adduct **375**, but also the barbaralone derivative **378**, implying that besides [4+2] addition also [3+2] addition (**376**, path B) with consecutive CO insertion (**377**) and reductive elimination takes place. This alternative reaction mode has already been discussed with TCNE as two-electron component in section II.C.1, and structure

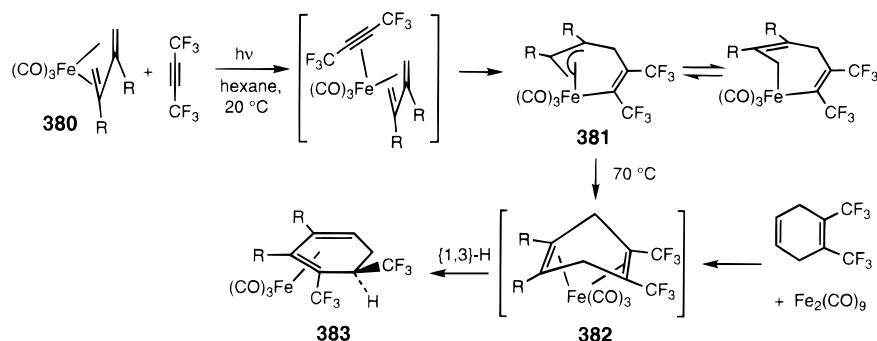
376 is equivalent to **162** in eq 52 (with $X = \text{CH}=\text{CH}$). Paquette et al.³⁹⁴ have also reported a case of [4+2] addition of chlorosulfonyl isocyanate to **374**, as opposed to the [3+2] addition mode of TCNE.

Goldschmidt et al.⁶⁰⁵ have compared the cycloaddition reactions of (η^4 -cycloheptatriene)Fe(CO)₃ (**161** with $X = \text{CH}_2$) and of free cycloheptatriene with (carbomethoxy)maleic anhydride (CMA). Just as COT, free cycloheptatriene undergoes Diels–Alder reactions with a wide variety of dienophiles from its bicyclic norcaradiene valence isomeric structure (see also ref 382 where a competition experiment with a free and a coordinated cycloheptatriene within the same molecule is carried out). The latter valence isomer is not available in the Fe(CO)₃ complex. While in all other cases (η^4 -cycloheptatriene)Fe(CO)₃ reacts with strong dienophiles (such as TCNE, cf. discussion of eq 52 in section II.C.1) by [3+2] addition, the reaction with CMA (eq 98), in a highly regioselective and stereospecific manner, exclusively gives **379**, one of the four stereoisomeric [4+2] Diels–Alder adducts expected upon CMA attack anti to the metal bonded face. Goldschmidt et al. conclude that the [4+2] addition should therefore in the electronic notation *not* be classified as a symmetry forbidden [$(\pi 2_a + o 2_s + \pi 2_a) + \pi 2_s$] reaction, as in the study by Mingos³⁹³ on the mechanisms of [$n+2$] cycloaddition reactions ($n = 2-6$) of cycloheptatriene complexes with olefins, but rather as a symmetry allowed [$(\pi 2_a + o 2_a) + \pi 2_s$] reaction, topologically identical to the [3+2] reactions. The dichotomy of [3+2] vs [4+2] addition modes, and the regio- and stereospecificity are discussed in detail on the basis of primary and secondary orbital interactions. It is concluded that in the present case the secondary orbital interactions strongly stabilize the endo transition state of the Diels–Alder reaction and are responsible for the exclusive formation of **379**.

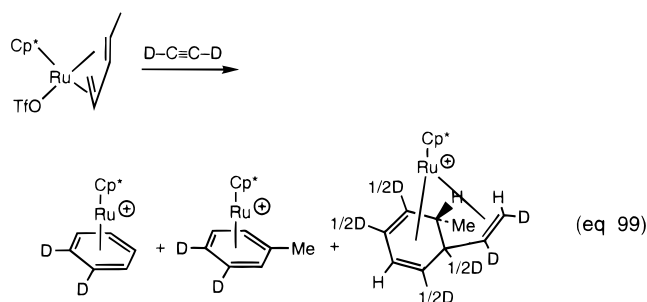


The thermally allowed, concerted Diels–Alder addition reaction seems impossible for 1,3-butadienes that are η^4 -coordinated to metal fragments as in **380**. Green et al.,^{606,607} however, have demonstrated the possibility of a stepwise reaction path (Scheme 54)

Scheme 54



from which compound **381** has been isolated in “moderate” yield.⁶⁰⁷ The low yield of **381** can be explained by the fact that its formation implies the partial decoordination of the diene to form the intermediate in square brackets with η^2 -diene and coordinated alkyne. The major photochemical event on ultraviolet irradiation of **380**, however, would not be the crucial η^4 to η^2 transition of the diene, but release of CO which does not lead to product. In refluxing hexane the carbon termini of the organic ligand in **381** are C–C connected and, under the reaction conditions, the resulting cyclohexa-1,4-diene in **382** immediately undergoes a 1,3-hydrogen shift to give the isolated cyclohexa-1,3-diene complex **383**.⁶⁰⁶ The authors suggest that the also photochemically induced [6+2] cycloaddition of (η^4 -cycloheptatriene)Fe(CO)₃ with dimethyl acetylenedicarboxylate⁶⁰⁸ (cf. section II.E), and the formation of 1,2-dimethylcyclohexa-1,4-diene from 2-butyne and butadiene, catalyzed by Fe(C₈H₈)₂⁶⁰⁹ may proceed by a similar stepwise reaction path. In this connection, i.e., because of the intermediacy of a σ, π -allyl intermediate analogous to **381** in a stepwise reaction, the “[4+2] cycloaddition” of 1,3-butadiene with ethyne and propyne, mediated by bare Fe⁺ in the gas phase, reported by Bakhtiar,⁶¹⁰ should also be mentioned here. Itoh et al.⁶¹¹ have studied the reaction of various [Cp^(*)Ru(η^4 -1,3-diene)]OTf complexes with acetylenes. From the product analyses and the deuterium distribution pattern when C₂D₂ was used (see, e.g., eq 99), the authors conclude that the first

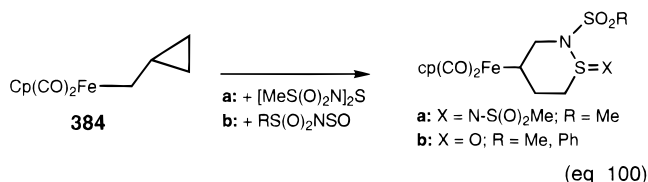


step in the reaction sequence is in each case a [4+2] cycloaddition between the acetylene and the η^4 -coordinated 1,3-diene ligand. The authors do not discuss a stepwise addition as in Scheme 54.

Hexafluorobutyne cycloadds to coordinated cycloocta-1,5-diene in [Rh(cod)Cl]₂ in a homo-[4+2] fashion.^{612,613} Mechanistically, a precoordination of the alkyne and a stepwise addition to the 1,4-

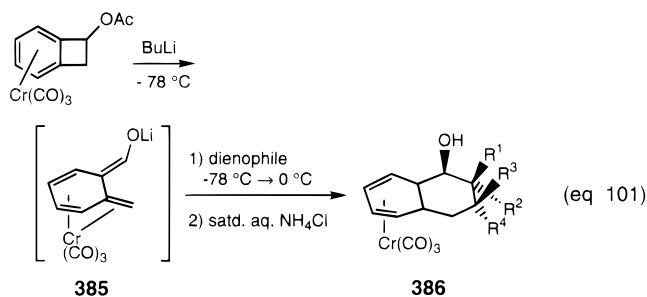
positions of COD is assumed. This is primarily based on the isolation of the iridium congeners of the respective intermediates.⁶¹⁴

Topologically, the reaction of sulfur bis(methanesulfonylimide), $[\text{MeS}(\text{O})_2\text{N}]_2\text{S}$, or *N*-sulfinyl sulfonamides $\text{RS}(\text{O})_2\text{N}=\text{S}=\text{O}$ ($\text{R} = \text{Me}, \text{Ph}$), with the Fp -cyclopropylmethyl complex **384** (eq 100) represents a [4+2] addition, with **384** reacting according to the 1,4-dipolar representation in eq 47. Strictly speaking, however, and according to the rules of Huisgen,² this is not a cycloaddition reaction because a σ -bond (of the cyclopropyl ring) is broken during the reaction.



Gladfelter and Hull⁶¹⁵ have investigated the effect of $\text{Cr}(\text{CO})_3$ coordination to octamethyl naphthalene (OMN) on the Diels–Alder/retro-Diels–Alder equilibrium constant with maleic anhydride as dienophile. Uncomplexed OMN has been known to undergo Diels–Alder reactions since its original synthesis.⁶¹⁶ It adopts a puckered conformation in which the methyl groups are pairwise displaced above and below the average ring plane. Coordination to $\text{Cr}(\text{CO})_3$ results in an increased distortion, pushing the peri-methyl groups further out of the plane. The reaction of maleic anhydride with $(\text{OMN})\text{Cr}(\text{CO})_3$ shows a greater than 2 orders of magnitude increase in the equilibrium constant in favor of the Diels–Alder adduct. An explanation for this 12–17 kJ/mol difference in energy for the complexed vs uncomplexed reaction is deduced from the molecular structures of starting materials and products, and is attributed to the weakened Cr–ring bond in the starting material, i.e., along the reaction coordinate the coordinated ring becomes planar and the increasing strength of the Cr–C(arene) interaction must be added to the overall energy change of the reaction.

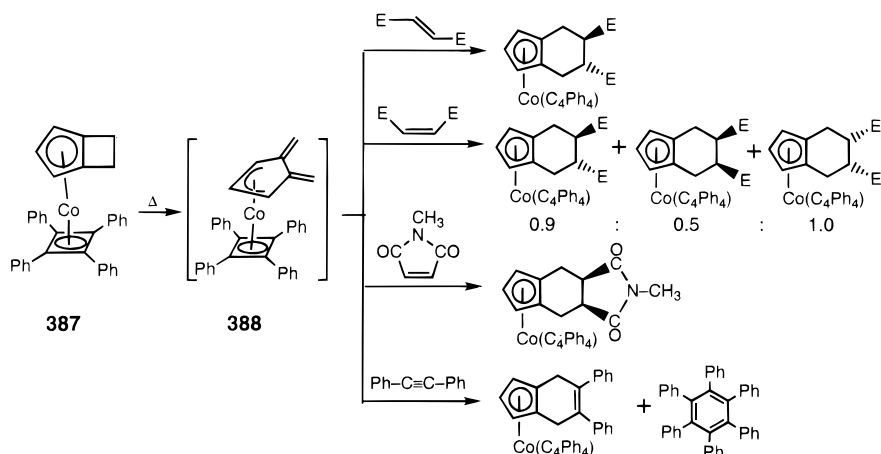
Kündig^{617–619} and Butenschön^{620,621} have, by slightly different routes, prepared a $(\eta^6\text{-}\alpha\text{-oxy-}o\text{-quinodimethane})\text{Cr}(\text{CO})_3$ intermediate (**385**) that was in situ reacted with various electron-deficient dienophiles (eq 101). The dienophiles attack highly stereoselec-



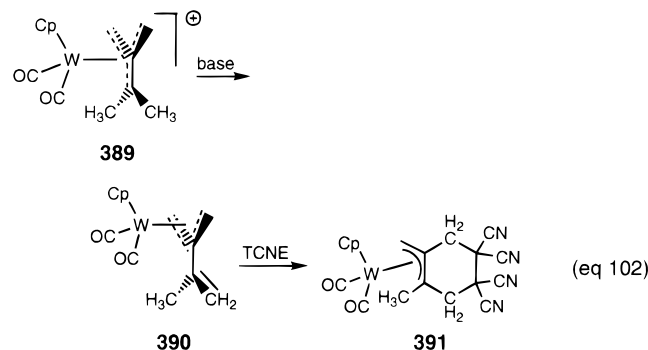
tively from the face opposite to the metal to give, after hydrolysis, $(\eta^6\text{-anti-1-hydroxytetrahydronaphthalene})\text{Cr}(\text{CO})_3$ complexes **386** from which the organic ligand is readily displaced by exposing an ethereal solution to air and sunlight. Yields are in the 70–80% range. With enantiomerically pure ($\alpha\text{-oxy-}o\text{-quinodimethane})\text{Cr}(\text{CO})_3$, ee's in the cycloadducts were $\geq 90\%$.⁶¹⁷ A comparable ring opening (Scheme 55), although at high temperature, has been found by differential scanning calorimetry in complex **387**.^{622,623} Above 200 °C a clean caloric effect was observed which the authors associated with a (reversible) ring opening of the annelated cyclobutene ring and η^5 to η^3 hapticity change of the Cp ring (ring slippage), giving the coordinatively unsaturated **388**. This assumption was verified by thermolysis of **387** at 200 °C in the presence of large excesses of dimethyl fumarate, maleate, *N*-methylmaleimide, and diphenylacetylene as dienophiles. The authors suggest that the product compositions are the result of some precomplexation of the dienophile at the metal prior to the cycloaddition, except for the poor ligand *N*-methylmaleimide which, by approach from the sterically less hindered side trans to the metal, exclusively gives the shown anti isomer in high yield. *o*-Quinodimethane has been generated⁶²⁴ by 1,4-dehalogenation of α,α' -dihalo-*o*-xylylene by highly reactive metallic nickel, and, in the presence of a variety of electron-deficient olefins gives Diels–Alder cycloadducts in moderate to good yields; however, it is not certain that the metal is present in the diene component at the moment of cycloaddition.

Deprotonation of the acidic methyl groups in the cationic $[(\eta^4\text{-1,1-dimethyltrimethylenemethane})\text{Cp}(\text{CO})_2\text{W}]^+$ complex **389** (eq 102)⁶²⁵ gives the stable $\eta^3\text{-}\beta\text{-isopropenylallyl}$ complex **390** which cycloadds TCNE in [4+2] fashion to yield **391**. Compare the different

Scheme 55

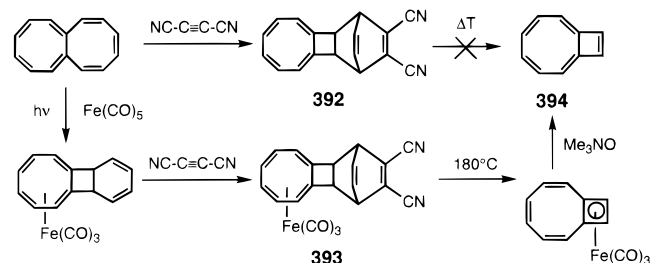


situation in the η^3 -trimethylenemethane complexes **130** and **131** which gives rise to a [3+2] addition of TCNE.



A few examples are known where metal-assisted retro-Diels–Alder reactions are used to generate otherwise inaccessible fragments. The intended synthesis of bicyclo[6.2.0]decapentaene **394** by Vogel et al.⁶²⁶ (Scheme 56) was not successful via thermolysis

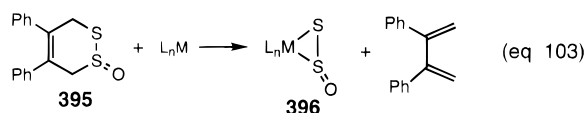
Scheme 56



of **392**. Heating the solid $\text{Fe}(\text{CO})_3$ complex **393**, however, obtained as 2:1 mixture of two stereoisomers, resulted in a clean fragmentation into phthalonitrile and the cyclobutadiene complex from which **394** was readily liberated by oxidative degradation with trimethylamine *N*-oxide.

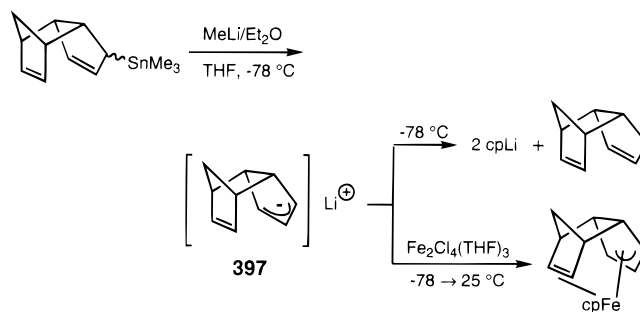
In their first communication⁶²⁷ mentioning in one last sentence what later became known as the Pauson–Khand reaction (cf. appendix II.F on [2+2+1] multicomponent cycloadditions), the authors report a retro-Diels–Alder reaction, i.e., scission of norbornadiene (NBD) to acetylene and cyclopentadiene, initiated by di- and trinuclear cobalt complexes $(\text{RC}\equiv\text{CH})\text{Co}_2(\text{CO})_6$ and $\text{PhCCo}_3(\text{CO})_7(\text{NBD})$, which are converted to $(\text{Cp})\text{Co}(\text{CO})_2$ and a trinuclear cyclopentadienylcobalt complex, respectively.

4,5-Diphenyl-3,6-dihydro-1,2-dithiine 1-oxide **395** has been prepared as a stable source of disulfur monoxide.⁶²⁸ Treatment of **395** with coordinatively unsaturated transition metal complexes (eq 103) such as $[(\text{dppe})_2\text{Ir}]^+$, or $\text{Cp}^{(*)}\text{Mn}(\text{CO})_2(\text{THF})$ results in the retro-Diels–Alder reaction with formation of diphenylbutadiene and the respective S_2O complexes **396** ($\text{L}_n\text{M} = [\text{Ir}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]^+$, $(\text{C}_5\text{H}_5)\text{Mn}(\text{CO})_2$, or $(\text{C}_5\text{Me}_5)\text{Mn}(\text{CO})_2$). Compound **395** has also been used as S_2O source to serve as dipolarophile in [3+2] cycloaddition reactions (cf., section II.C.1, Table 4, entry 18).



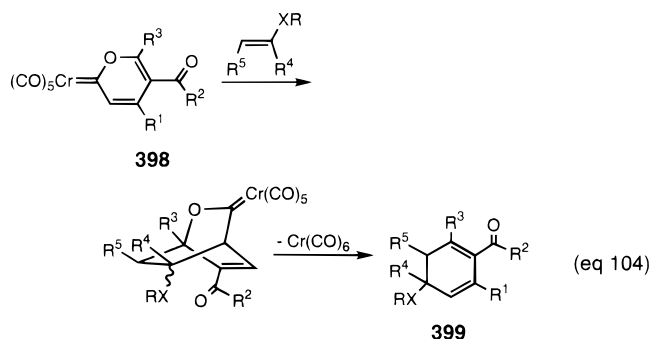
The opposite case has been reported by Köhler et al.,⁶²⁹ where the extremely reactive dicyclopentadienyl anion **397** (Scheme 57), which already under the

Scheme 57



conditions of its generation at dry ice temperature undergoes cycloreversion, has been stabilized and trapped by coordination.

Diels–Alder reactions with inverse electron-demand of pyranilidene complexes **398** (eq 104) with electron-rich olefins, such as alkoxy and silyl enol ethers, enamines and ketene acetals, have been described by Wulff et al.⁶³⁰ These reactions have the anticipated advantage of rate enhancements (cf. first paragraph of section II.D.1) compared to the reactions of α -pyrones and have the unexpected advantage that dihydrobenzenes **399** can be isolated from these reactions rather than the aromatized products normally obtained from the reactions of α -pyrones.



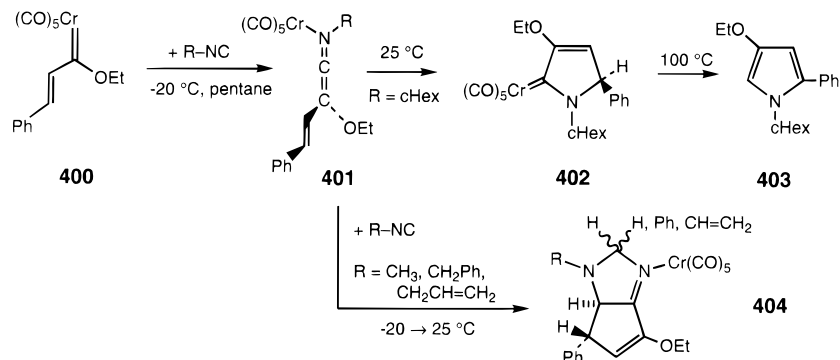
E. Metal-Assisted Cycloaddition Reactions of Higher Order

Rigby^{631,632} has reviewed metal-assisted [6+4] and [6+2] cycloaddition reactions, their mechanism, and applications in organic synthesis. Besides these typical higher-order topologies, some other, less common topologies have been included in this section in sequence of increasing ring size.

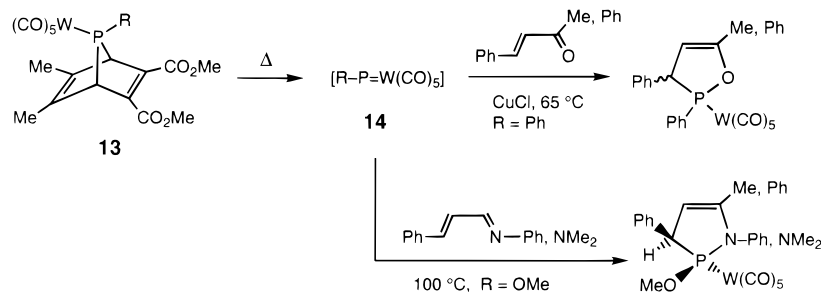
1. [4+1]

Vinylcarbene complex **400** (Scheme 58) reacts with cyclohexyl isocyanide⁵⁹⁷ to give the ketenimine complex **401** which at room temperature, via an intramolecular [4+1] cyclization, spontaneously forms **402** which readily decomposes at 100 °C with 1,3-hydrogen shift to give pyrrole **403**. When **400** is reacted with 2 equiv of a primary isocyanide⁶³³ (methyl, benzyl, or 3-propenyl), the corresponding ketenimine intermediates **401** readily add the second equivalent of isocyanide in [4+1] fashion to give the two diastereomeric bicyclic 3-imidazolines **404**.

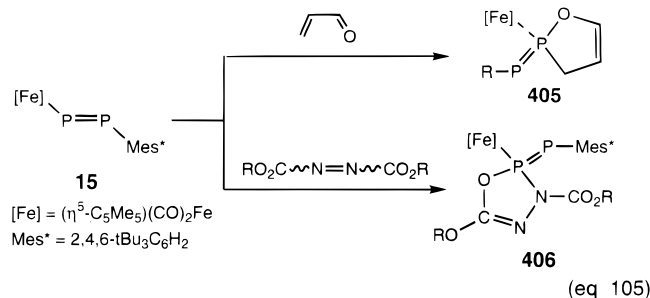
Scheme 58



Scheme 59



The carbene-like reactivity of phosphanediyl complexes **14**, including their [4+1] additions with heterodienes (Scheme 59), has been summarized by Mathey.⁷⁵ Likewise, when complex **13** (cf. eq 11 in section II.A) is heated in toluene at 150 °C in the presence of an excess of 2,3-dimethylbutadiene, the intermediate terminal phosphinidene complex **14**, suggestively from its singlet state, cleanly cycloadds in [4+1] fashion to the diene.⁷¹ An analogous reaction of the diphosphene complex **15** with acrolein, methacrolein, buten-3-one-2, and azodicarboxylic esters and amides (eq 105)^{85,92,634} has been reported to

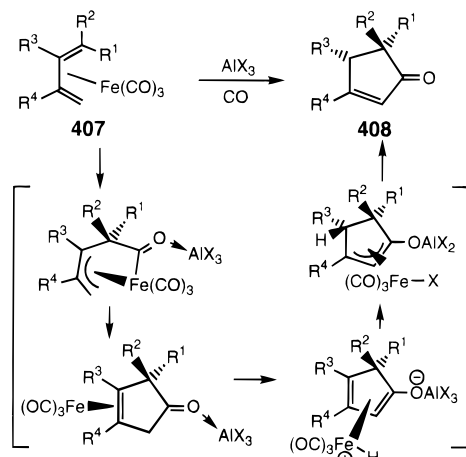


give dihydro-1,2-λ⁵-oxaphospholes **405** with exocyclic P=P bonds. The reaction is likely to proceed in a concerted fashion (with the α,β-unsaturated carbonyl in a cisoid conformation) and not via a [2+1] cycloaddition with consecutive ring expansion.⁸⁹ The reaction has been extended to azodicarboxylates,⁸⁸ which give metal-substituted oxadiazaphospholenes **406**. It is suggested that in these reactions the ring formation is initiated by attack of the lone pair of the metalated P atom (essentially the complex HOMO) at the LUMO of the electrophile.

A preparatively interesting, highly stereoselective [4+1] cyclocarbonylation of 1,1,3-tri- and 1,1,2,3-tetrasubstituted (1,3-diene)Fe(CO)₃ complexes **407** has been reported by Franck-Neumann.^{635,636} The

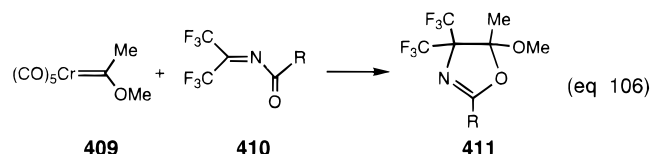
formation of cyclopentenones **408**, according to Scheme 60, induced by AlBr₃ or AlCl₃ as Lewis base, is

Scheme 60



presented as a valuable alternative to the intramolecular [2+2+1] Pauson-Khand reaction (see below). Other examples of stoichiometric cyclocarbonylation reactions for the preparation of γ-, but also δ-, and ε-lactones have been described.⁶³⁷⁻⁶⁴¹

Fischer-type carbene complexes **409** have been demonstrated to react with *N*-alkylideneamides **410** (eq 106) in a [4+1] fashion to form 4,5-dihydrooxazoles **411**.⁶⁴² A single case has been reported where

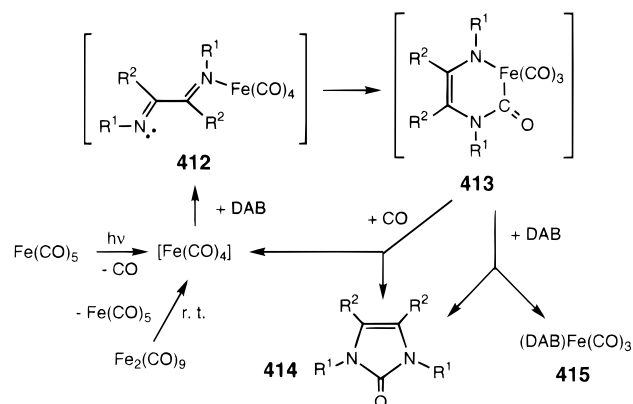


a Fischer carbene complex, (CO)₅Cr=C(H)NMe₂, undergoes a formal [4+1] cycloaddition to a diene,

methyl sorbate, to give 2-(carbomethoxy)-1-(dimethyl-amino)-5-methyl-3-cyclopentene.⁶⁴³ The reaction is proposed to proceed by an initial organometal [2+2] addition of Cr=C to the α -C=C bond of sorbate to an intermediate chromacyclobutane, insertion of the second double bond, and reductive elimination of the cyclopentene.

The formation of 2(3*H*)-imidazolones **414** has been observed⁶⁴⁴ in the reaction of sterically demanding 1,4-diaza-1,3-butadienes (DAB = R¹N=CR²CR²=NR¹; R¹, R² = *t*-Bu, H; 4-MeOPh, Me) with [Fe(CO)₄]. The stepwise mechanism of its formation^{645,646} is shown in Scheme 61. Due to steric congestion, the uncoor-

Scheme 61

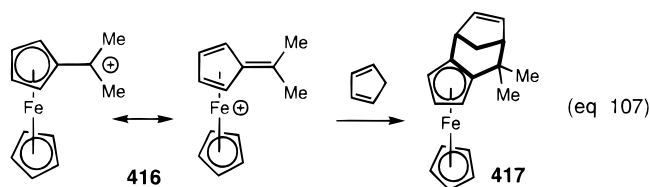
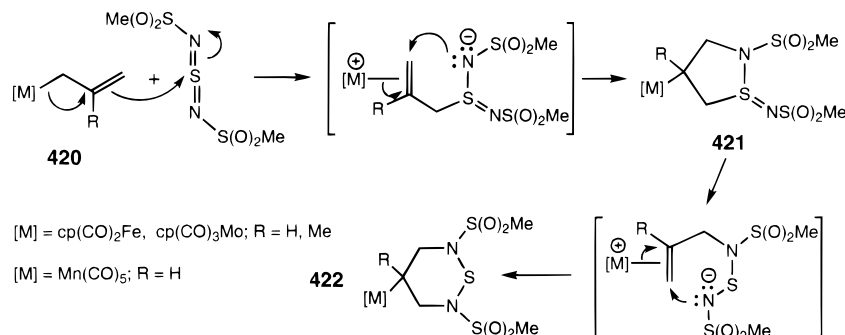


minated nitrogen in **412** cannot directly attack the iron, resulting in CO substitution and formation of **415**. Instead, the nitrogen nucleophilically attacks a carbonyl ligand, resulting in the coordinatively unsaturated **413** from which **414** is reductively eliminated when another DAB enters the coordination sphere. Vrieze et al.⁶⁴⁵ have shown that also CO can induce the reductive elimination of **414** from **413**, which results in a few catalytic cycles, i.e., in the presence of an atmosphere of CO, the product composition **414**:**415** exceeds the limiting value of 1:1 for the stoichiometric reaction.

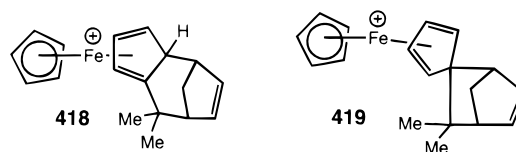
2. [3+3]

Obviously, there are no genuine [3+3] cycloaddition reactions. Cycloadducts, or rather (stepwise) cyclization reactions, relating to this topology are extremely scarce. An example where, superficially, a six-membered ring is produced in this fashion is shown in eq 107. When the complex cation **416**, which had been prepared by abstraction of the hydroxy group from the corresponding alcohol, was treated in situ

Scheme 62

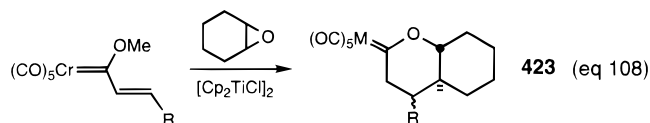


with an excess of cyclopentadiene, a 10% yield of complex **417** was isolated from oligomeric material by chromatography. The authors⁶⁴⁷ suggest two alternatives for the actual formation of the highlighted six-membered ring in **417**: either a [6 π +4 π] cycloaddition of the diene to the complexed fulvene followed by a rapid proton elimination from intermediate **418**, or the formation of a spiro intermediate **419** via a [4 π +2 π] cycloaddition of the diene to the exocyclic fulvene double bond, followed by a 1,5-sigmatropic rearrangement.



The formation of the six-membered ring in **422** (Scheme 62) from the reaction of η^1 -allyl complexes **420** with sulfur bis(methanesulfonylimide) has been reported by Wojcicki et al.^{336,648} Here, the reaction is assumed to occur by way of the normal [3+2] adduct **421** (cf. eq 44 and entry 15 in Table 4) which undergoes ring opening to a second metal- η^2 -alkene zwitterion which in turn collapses to **422**.

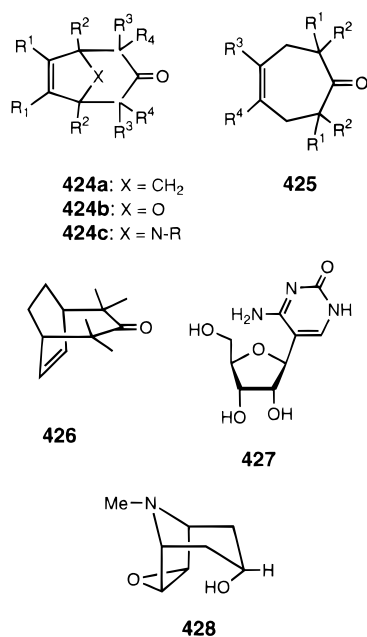
β -Alkoxy radicals, stoichiometrically generated from epoxides (cyclohexene oxide, cyclopentene oxide, styrene oxide, propene oxide, 2-butene oxide) by reaction with [Cp₂TiCl]₂, intermolecularly react with α,β -unsaturated chromium and tungsten Fischer carbene complexes in [3+3] fashion.^{649,650} With the cyclopentane and cyclohexane radicals, exclusively the trans-fused bicyclic products, e.g., **423** (eq 108), are formed. The modest diastereoselectivity with respect to R being axial or equatorial is dependent on the size of R.



3. [4+3]

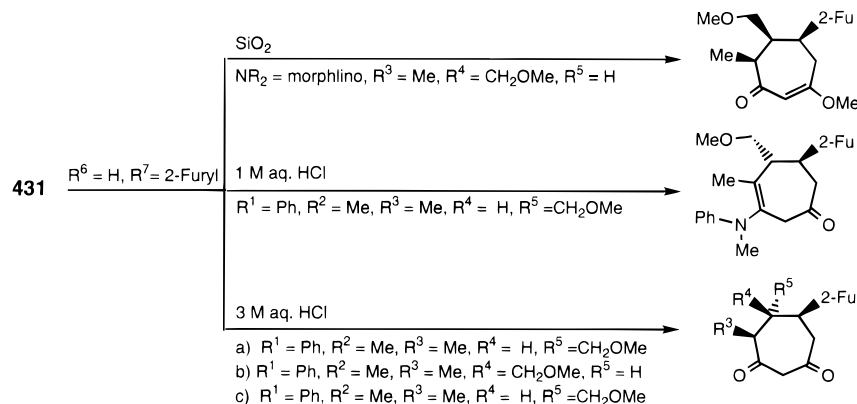
The reaction of α,α' -dibromo ketones in the presence of Fe₂(CO)₉ with olefins has already been

mentioned in section II.C.1 (cf. Schemes 24 and 25). The cycloaddition of 2-oxyallyl cations and 1,3-dienes, topologically a $[4+3]$ and electronically a symmetry-allowed, concerted $[2\pi+4\pi]$ process,^{416,651,652} has first been described by Hoffmann.^{652–656} Noyori et al.^{415,416,420,657–665} in particular have strongly contributed to the development of the methodology. The use of $\text{Fe}_2(\text{CO})_9$ to reductively dehalogenate the α, α' -dibromo ketones has the advantage that through coordination to iron, a great variety of oxyallyl cations **180** (cf. Scheme 24) are accessible, and the yields of cycloadducts are dramatically increased. As dienes, e.g., cyclopentadiene,^{661,666} cyclopentadienones,⁶⁵¹ furans,^{659,667} N-substituted pyrroles,^{660,662,667} butadienes,^{658,663,667} or cyclohexadiene⁶⁶⁸ have been used toward the synthesis of products such as **424–426**. Bicyclic ketone **424b** ($\text{R}_1\text{--R}_4 = \text{H}$) has served as starting material for the synthesis of various C-nucleosides,^{664,665} e.g., **427**, while tropane alkaloids, e.g., scopine **428**,⁶⁶² have been made from **424c**. Generation of **180** from α, α' -bis(sulfonyl) ketones⁴²⁴ in the presence of anthracene or furan gave the expected $[4+3]$ cycloadducts in good yields.

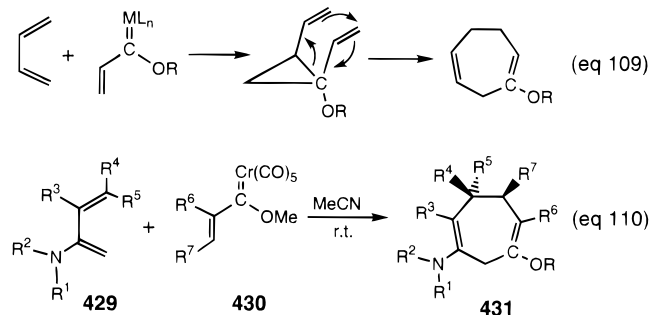


In the following examples, a net $[4+3]$ cycloaddition is achieved by the reaction sequence shown in eq 109. Transfer of a vinyl carbene ligand to one double bond

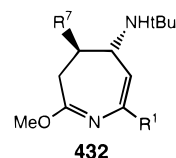
Scheme 63



of a 1,3-diene system, generating a *cis*-divinylcyclopropane, which instantly undergoes a $[3,3]$ -sigmatropic rearrangement to the seven-membered ring. This methodology has been applied and developed by Barluenga.^{489,669–672} A great variety of differently substituted 2-amino-1,3-butadienes **429** and vinylchromium Fischer carbene complexes **430** have been reacted to stereoselectively give the functionalized cycloheptadienes **431** (eq 110). Depending on the



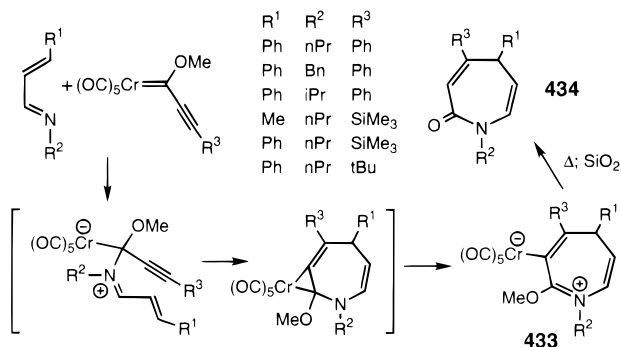
substituents, and the hydrolytic work-up conditions, the crude compounds **431** are selectively transformed to such cyclic seven-membered ketones as shown in Scheme 63. The synthesis of azepine derivatives **432**⁶⁷³ via the same reaction sequence was achieved



by reaction of **430** (R⁶ = H) with electron-rich 1-aza 1,3-dienes, $\text{HN}=\text{C}(\text{R}^1)\text{CH}=\text{CHNHt-Bu}$. Azepinones **434** (Scheme 64), from the reaction of 1,4-disubstituted 1-azadienes with alkynyl Fischer carbene complexes,⁶⁷⁴ are formed via a totally different mechanism. On the basis of the isolated zwitterionic intermediate **433** (R¹ = R³ = Ph, R² = *n*-Pr), the structure of which has been determined by X-ray crystal analysis, the authors suggest a formation by nucleophilic addition of the 1-azadiene imine nitrogen to the carbene carbon atom, followed by electrocyclic ring closure and 1,2-migration of the $\text{Cr}(\text{CO})_5$ group.

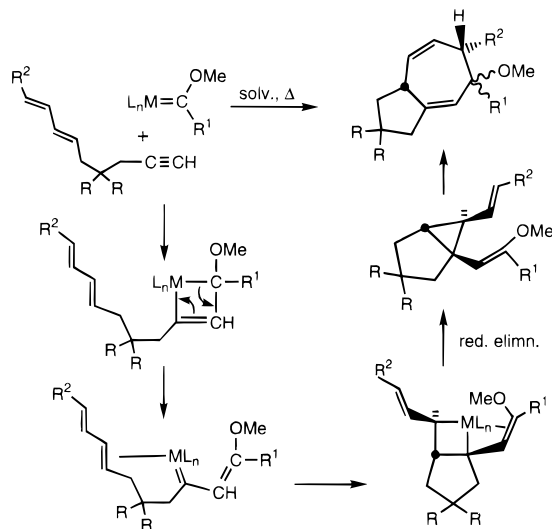
An access to fused cycloheptadiene systems has been elaborated by Harvey et al.^{675–677} The seven-membered ring is again formed by sigmatropic rearrangement of a *cis*-divinylcyclopropane, which, how-

Scheme 64



ever, is generated differently from eqs 109 and 110. Fischer carbene complexes react with dienes, either as substrates intermolecularly (Scheme 65),^{675,676}

Scheme 65



or, tethered via the terminal alkyne carbon to the carbene carbon atom, intramolecularly.⁶⁷⁷

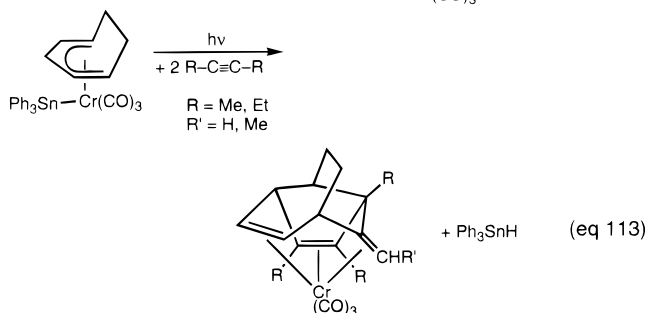
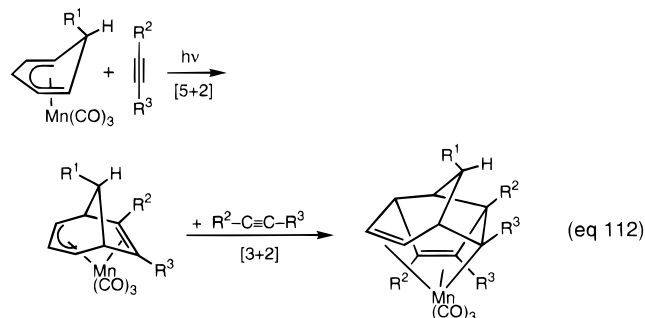
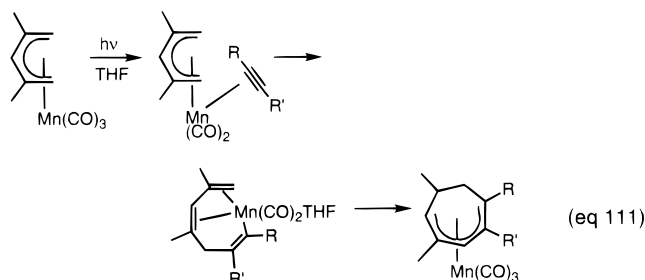
4. [5+2]

Photochemically induced formal [5+2]^{678–683} cycloadditions of alkynes to (η^5 -dienyl)Mn(CO)₃ complexes, sometimes followed by additional cycloaddition reactions, give access to (polycyclic) seven-membered ring compounds. Examples are shown in eq 111,⁶⁸⁰ and eqs 112⁶⁸¹ and 113,^{682,683} where one alkyne molecule adds to the dienyl ligand in [5+2] fashion and a second one consecutively by a [3+2] process.

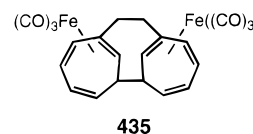
5. [4+4]

Several attempted syntheses of (heptafulvene)-tricarbonyliron have been reported^{684–686} to lead to a dimer, **435**, the molecular structure of which has been determined by deuterium labeling and NMR spectroscopy, and X-ray diffraction.⁶⁸⁷ No mechanistic details are known about the formation of this [4+4] adduct, which is formally the result of a [8 π +8 π] cycloaddition.

The reaction in Scheme 66^{688–691} is definitely not a cycloaddition reaction according to the rules of Huisgen,² but it is an elegant way to synthesize 1,4-disila-2,6-cyclooctadienes **439**, formally the result of a

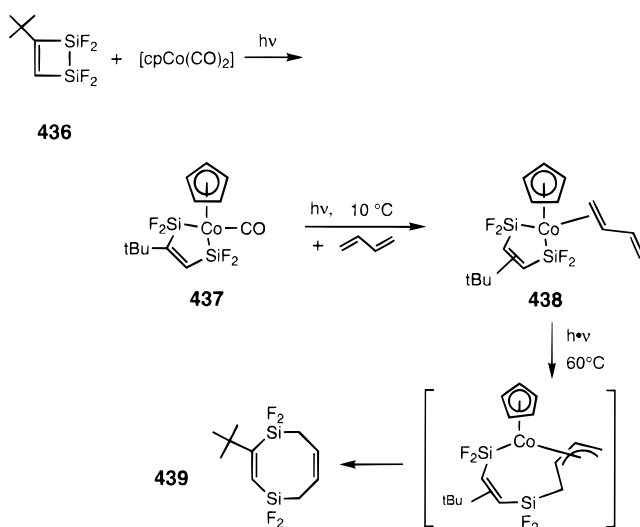


“forbidden” [4+4] addition of 1,3-butadienes and (nonexistent) 1,4-disila-1,3-butadienes. Differently



substituted disilacyclobutenes **436** have been reacted with metal carbonyls, e.g., PdCl₂L₂,^{688,689} Ni(CO)₄,⁶⁹⁰ CpCo(CO)₂,⁶⁹¹ CpMn(CO)₃,⁶⁹² or Ru₃(CO)₁₂.⁶⁹³ Depending on the metal, the reaction conditions are

Scheme 66

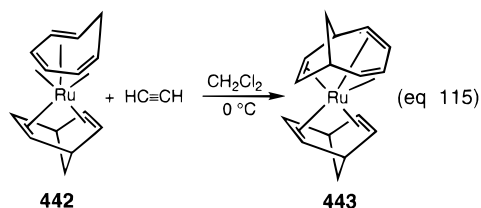
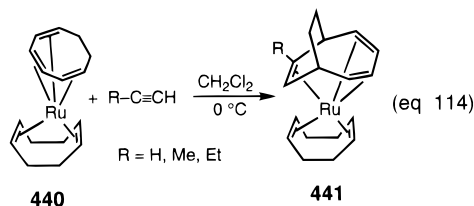


either thermal or photochemical. In Scheme 66, the reaction is shown for 3-*tert*-butyl-1,1,2,2-tetrafluoro-1,2-disilacyclobutene and $\text{CpCo}(\text{CO})_2$, because here, the intermediate complexes **437**^{694,695} and **438**⁶⁹¹ (ca. 1:1 mixture of the two isomers with different positions of the *tert*-butyl group relative to the η^2 -diene moiety) have been isolated and characterized. It should be mentioned that, depending on the metal and the substitution pattern of the butadiene, 1,1- and 1,2-addition of the two silicon atoms to the butadiene are also observed as main reaction paths.^{692,693,696–699}

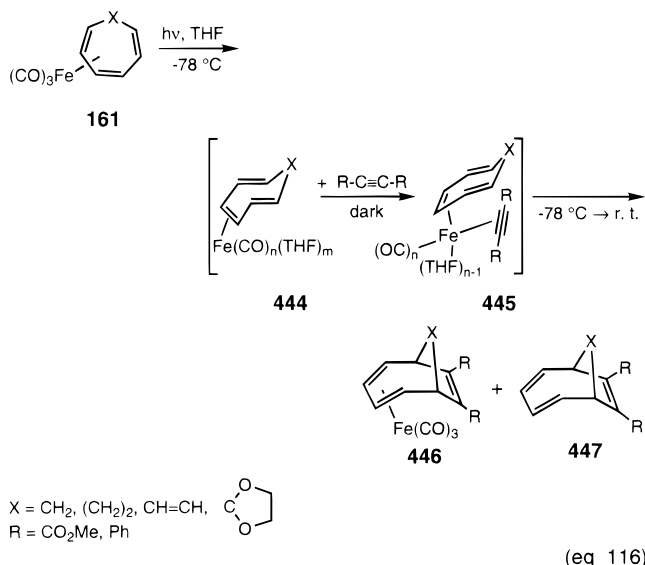
Nickel-catalyzed intramolecular [4+4] cycloadditions have been described by Wender.^{700–703} For a review on intermolecular nickel-catalyzed [4+4] cycloadditions, see ref 704. All these reactions, while formally [4+4] cycloadditions, proceed in a stepwise manner through metal-bonded intermediates and it appears that the electronically forbidden [4+4] process does not become allowed in the presence of a metal.

6. [6+2]

Several cyclohepta- or octa-1,3,5-trienes coordinated to iron⁶⁰⁸ or ruthenium^{705,706} fragments have been reported to undergo [6+2] cycloadditions with acetylenes to give the respective bicyclo[4.2.1] or -[4.2.2] compounds (cf. eqs 114–116). However, there is a significant difference in reactivity between the two metals. The ruthenium complexes **440**⁷⁰⁶ and **442**⁷⁰⁵ react under very mild thermal conditions with excellent yields of the cycloadduct complexes **441** and **443**. The (“diene”)tricarbonyliron complexes **161**, on

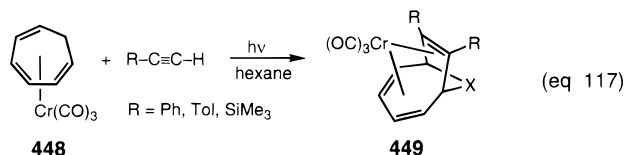


the other hand, show no activity as a di- or triene under purely thermal reaction conditions. They have to be photochemically activated by a η^4 to η^2 transition of the cyclic polyene (cf. also the comments accompanying Scheme 54). The further steps are purely thermal at or below room temperature. This has been shown, as indicated in eq 116, by experimentally separating the irradiation from the addition of the alkyne. The composition (*m* and *n*) of the initial photoproduct **444** depends on the type of cyclic polyene, i.e., the photochemical η^4 to η^2 transition is accompanied by various amounts of CO loss. This accounts for the varying product compositions with coordinated (**446**) and free (**447**) cycloadduct. Stable complexes **446** are only obtained when *n* = 3 and *m*

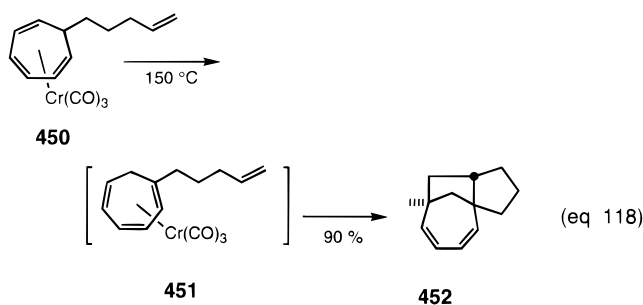


= 1 in the initial photoproduct **444**. The decent yields of 20–25% of combined **446** and **447** can be explained by the lower photochemical quantum yield for the η^4 to η^2 transition of the polyene as compared to the unproductive CO extrusion. There is no indication whatsoever for a stepwise cycloaddition mechanism as in the [4+2] addition in Scheme 54. The authors⁶⁰⁸ explicitly point to the extremely mild reaction conditions in the present case and the ideal disposition of the ligands in **445** for a concerted reaction to occur.

Photolysis of hexane solutions of (η^6 -cycloheptatriene) $\text{Cr}(\text{CO})_3$ (**448**) and 1 equiv of alkyne $\text{RC}\equiv\text{CR}$ (*R* = Ph, Tol, SiMe₃) produces (η^4 : η^2 -bicyclo[4.2.1]-nona-2,4,7-triene) $\text{Cr}(\text{CO})_3$ complexes (**449**) in high yield (eq 117),^{707–709} from which the organic ligands



can be readily exchanged for toluene by heating the complex (*T* > 80 °C) in toluene; for *R* = SiMe₃,⁷⁰⁷ decomplexation with Ce(IV) has been used. Irradiation of **448**, also with substituents in 1-, 3-, or 7-positions of the cycloheptatriene ring, with various electron-deficient alkenes gives, also intramolecularly, high yields of the metal-free bicyclo[4.2.1]-nonadiene adducts.^{710–712} The [6+2] addition of olefins has also been reported for (η^6 -1,3,5-cyclooctatriene) $\text{Cr}(\text{CO})_3$ and (η^6 -cyclooctatetraene) $\text{Cr}(\text{CO})_3$ complexes.⁷¹³ In each case, the only diastereomer formed results from an endo-approach. It has been found that certain metal-assisted cycloadditions of higher order can also be thermally induced.^{714,715} Thus, thermolysis of the readily available 7-exo-substituted cycloheptatriene complex **450** (eq 118) led in an intramolecular [6+2] addition, presumably after initial metal-facilitated hydrogen shift via **451**, directly in 90% yield to the metal-free tricyclic product **452**.^{716,717} Analogous results have been obtained with (η^{2-5} -tropone) $\text{Cr}(\text{CO})_3$ complexes with a (substituted) diene tether in 2-position.⁷¹⁷ Two



successive photochemically induced [6+2] cycloaddition reactions of cycloheptatriene complexes **453** (Scheme 67) with alkynes have been reported^{718,719} to give tetra- and pentacyclic products **454** and **456**. Heterocumulenes, such as alkyl- and aryl-substituted iso(thio)cyanates and ketenes⁷²⁰ have also been successfully used as 2π partners for **448**. Even the equivalency under photolytic conditions of Fischer carbene complexes with ketenes¹⁷⁷ has been tested. A mixture of three bicyclo[4.2.1]nonadienones was obtained in 30% yield on photolysis of **448** with $(\text{CO})_5\text{Cr}=\text{C}(\text{OCH}_3)\text{CH}_3$.⁷²¹ Catalytic reactions have also been reported.⁷¹¹ When cycloheptatriene, in the presence of **448**, and *N*-methoxycarbonyl azepine, in the presence of $(\eta^6\text{-naphthalene})\text{Cr}(\text{CO})_3$, were heated with ethyl acrylate in *n*-Bu₂O solution in a sealed tube, the corresponding bicyclo[4.2.1]nona-2,4-dienes were isolated in 90% and 77% yields, respectively.

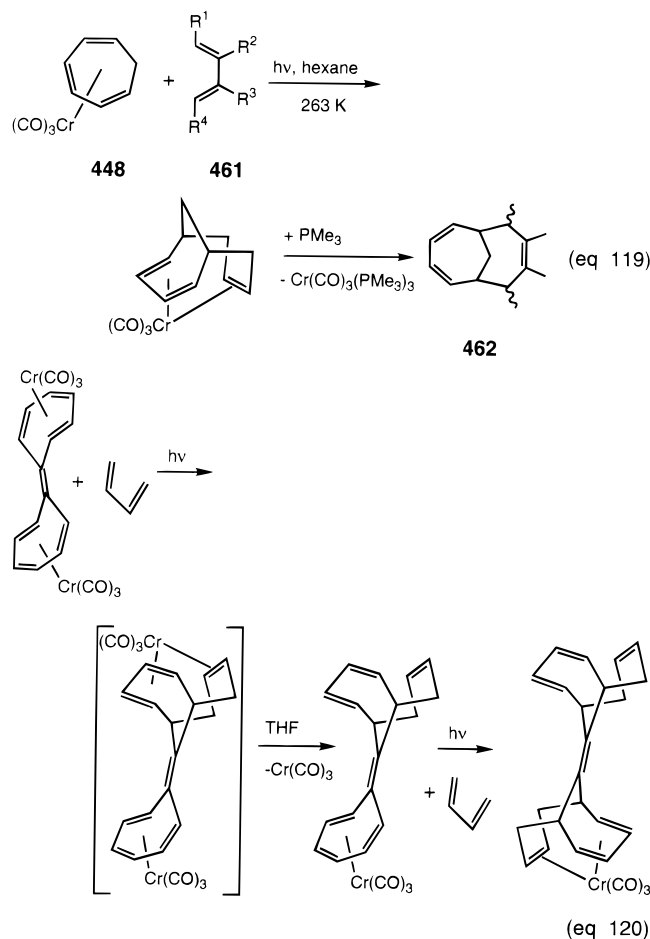
7. $[5+4]$

Kreiter et al.^{722–728} have reported the photochemical, formal [5+4] addition of (η^5 -2,4-dimethyl-2,4-pentadienyl)Mn(CO)₃ (**457**, Scheme 68) with 1,3-dienes **458**, but not with (*Z*)-1,3-pentadiene and 1,3-cyclohexadiene,⁷²⁵ to give the nine-membered ring complexes **459**. Besides these, 1:2 products such as **460a** (34%) are also formed. A stepwise mechanism

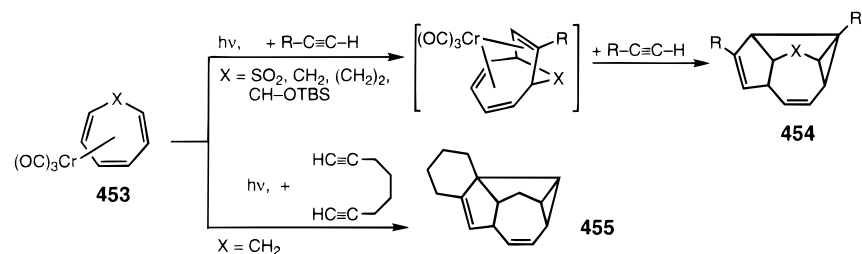
via intermediates as shown in square brackets is proposed.

8. $[6+4]$

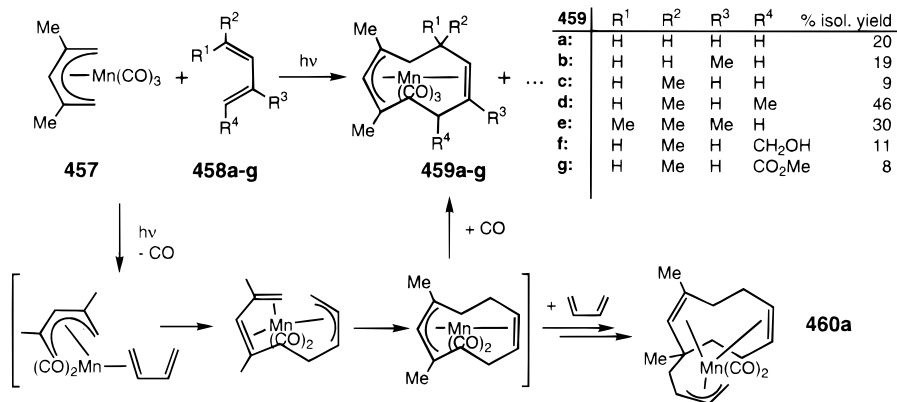
In a series of papers, Kreiter et al.^{729–735} have reported on the photochemically induced [6+4] cy-



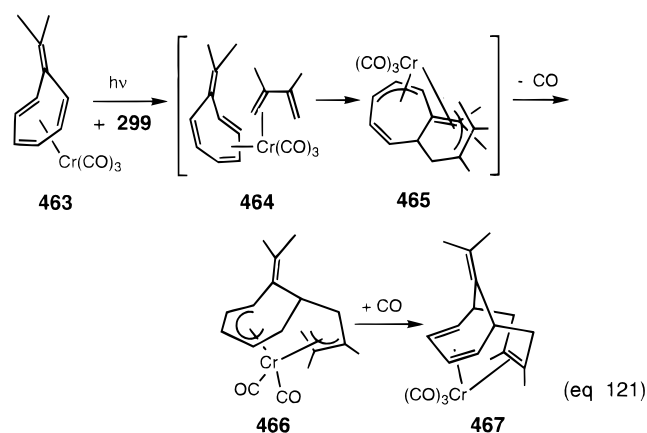
Scheme 67



Scheme 68



cloaddition of conjugated dienes **461** to (η^6 -cycloheptatriene)- (**448**), (η^6 -heptafulvene)- and (η^6 -heptafulvalene)tricarbonylchromium moieties. [An overview is given in ref 723.] Two examples are shown in eq 119^{729,731} and eq 120.^{734,735} The resulting bicyclic organic ligands, e.g. **462**, are readily displaced from the metal at room temperature by addition of PMe_3 ,⁷³¹ or if the reaction is run in a donor solvent (THF).⁷³⁴ The authors indicate⁷³¹ that the reaction cannot be extended to other η^6 -cyclopolyene complexes such as (η^6 -1,3,5-cyclooctatriene) $\text{Cr}(\text{CO})_3$ or (η^6 -1,3,5,7-cyclooctatetraene) $\text{Cr}(\text{CO})_3$ and that the molybdenum and tungsten homologues of **448** do not give comparable reactions. In the reactions (eq 121) of (η^6 -heptafulvene) $\text{Cr}(\text{CO})_3$ (**463**) with 1,3-dienes **461** [$\text{R}^2 = \text{Me}$; $\text{R}^2 = \text{R}^3 = \text{Me}$; $\text{R}^2 = \text{R}^4 = \text{Me}$; $\text{R}^2, \text{R}^3 = (\text{CH}_2)_2$], the intermediate thermolabile dicarbonyl complexes **466** have been isolated,⁷³³ which under normal conditions add CO to give the final product **467**. This



provides conclusive evidence that the connection of the seven-membered ring and the diene in the coordination sphere is not a concerted but rather a stepwise process. The plausible intermediates **464** and **465**, of which latter only one of several possible coordination isomers is shown, have not been observed. The reaction of **488** in eq 119 allows the highly stereoselective construction of substituted bicyclo[4.4.1]undecatriene systems.⁷³⁶ Several substituted (cycloheptatriene) $\text{Cr}(\text{CO})_3$ complexes **488** have enzymatically been resolved, and the resultant chiral, nonracemic complexes on photolysis with 1,3-dienes gave enantiomerically enriched [6+4] cycloadducts in high chemical yields.⁷³⁷ The diene part can also be tethered to the cycloheptatriene ring to give tricyclic products.⁷¹⁶ The reaction has been applied in natural product syntheses,⁷³⁸ e.g., as entry into the ingenane, tiglliane, and taxane ring systems,⁷³⁹ and has been extended to (*N*-carboalkoxyazepine) $\text{Cr}(\text{CO})_3$ and (η^6 -thiepine 1,1-dioxide) $\text{Cr}(\text{CO})_3$.⁷¹⁴ Stereochemical, regiochemical, and mechanistic aspects have been discussed, and it has been shown that the reaction can also be effected thermally in various ether solvents, giving cycloadducts identical to those produced in the photochemical reaction.^{714,740}

F. Appendix: Multicomponent Metal-Assisted Cycloaddition Reactions

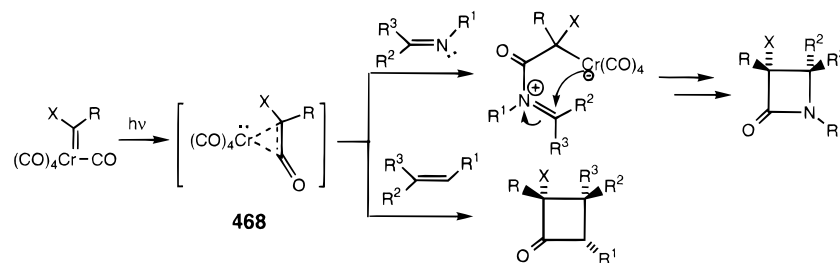
For several reasons it is debatable to which extent and according to which criteria the so called multi-

component cycloaddition reactions, be it stoichiometric or catalytic, should be included in this review. In many, if not most of the cases, they involve the formation of metal–carbon *and* consecutive cleavage of single bonds, e.g., in a reductive elimination step in which the final cyclic product is formed from a metallacycle or some kind of a σ, π -allyl intermediate. This means these are altogether *not* cycloaddition reactions according to rule 3 in the definitions of Huisgen.² However, such reactions have, for good reasons, also been included in the previous sections. Secondly, considering the involvement of intermediate metal–carbon σ -bonds, it is questionable if these reactions should be considered under the heading “metal-assisted” rather than “organometal”. On the other hand, there are reactions that most likely or definitely involve a genuine metal-assisted cycloaddition step. A prominent reason to include this section into the review is, that so many synthetically interesting (poly)cyclic organic compounds can and have been made this way and that, unfortunately, the term “cycloaddition reaction” for these multicomponent multistep cyclization processes has been extensively used in the literature. Further, very often, individual steps in these multicomponent multistep reactions have been addressed in the previous sections. In any case, the author has to premise a strong caveat with respect to the comprehensiveness of the literature coverage about these multicomponent reactions. There is most likely a considerable body of relevant references in which such reactions or individual steps of the reaction sequences are investigated and in which the term cycloaddition does not appear. It is a virtually impossible task to search for all metallacyclic or other organometallic compounds that are formed in a particular multistep process and from which eventually a cyclic organic product is cleaved. However, this appendix is certainly a useful overview with many leading references. Harvey⁷⁴¹ has recently reviewed “Carbene–Alkyne–Alkene Cyclization Reactions” which address multicomponent reactions from a substrate oriented point of view.

1. [2+1+1]

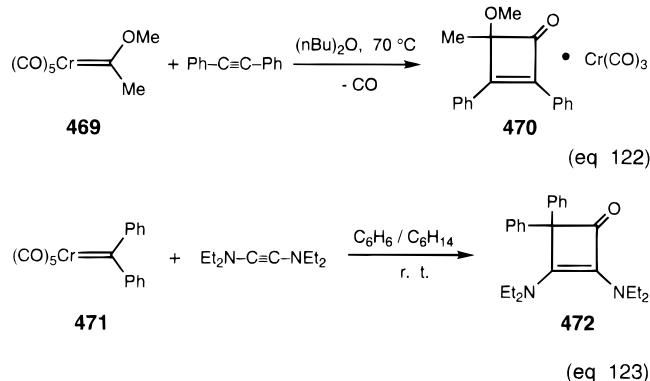
The efficient synthesis of β -lactams^{169–174,176,742–746} and cyclobutanones^{52,175,177,747} in high yields (cf. Scheme 69) from the photochemical reaction of Fischer carbene complexes and imines or olefins, respectively, according to the topological indicator [2+1+1] connects the imine $\text{C}=\text{N}$ or olefin $\text{C}=\text{C}$ two-atom fragments, the carbene carbon and one carbon monoxide. It has already been indicated in section II.A that this reaction, which has been developed by Hegedus et al., proceeds via an intermediate, photochemically generated η^2 -ketene complex (**468**) which then undergoes a [2+2] cycloaddition reaction with the $\text{C}=\text{N}$ and $\text{C}=\text{C}$ bonds. [Reference 224 gives an intramolecular example starting from ethoxycycloheptatriene-1-yl methyl]carbene $\text{Cr}(\text{CO})_5$. There, the initial tricyclic ketone resulting from the intramolecular [2_s+2_a] cycloaddition undergoes a 1,5-sigmatropic rearrangement to form 9-ethoxytricyclo[5.3.0.0^{2,9}]deca-3,5-dien-8-one which is isolated in 95% yield and which was further in 80% yield thermally rearranged in the presence of pyridine to 2-ethoxy-1,2,3,6-tetrahydro-

Scheme 69



azulen-1-one.] The reactivity of the photochemically generated **468** toward various imines and olefins has been compared with that of the respective free ketenes,^{176,177,748} and the products and stereoselectivities of both reactions were identical, although no evidence for the generation of free ketenes, such as consumption of ketene by cyclodimerization or formation of products containing one imine and *two* (or more) ketene fragments¹⁷⁶ was observed. Optically active β -lactams⁷⁴⁴ and cyclobutanones^{747,749} have been prepared with very high diastereoselectivities by the photochemical reaction of imines with optically active chromium carbene complexes⁷⁴⁵ and of chromium alkoxy carbene complexes with optically active ene carbamates. The cyclobutanones were readily transformed to optically active butenolides,^{749,750} and this route was applied in the synthesis of (+)-tetrahydrocerulenin and two other marine natural products.

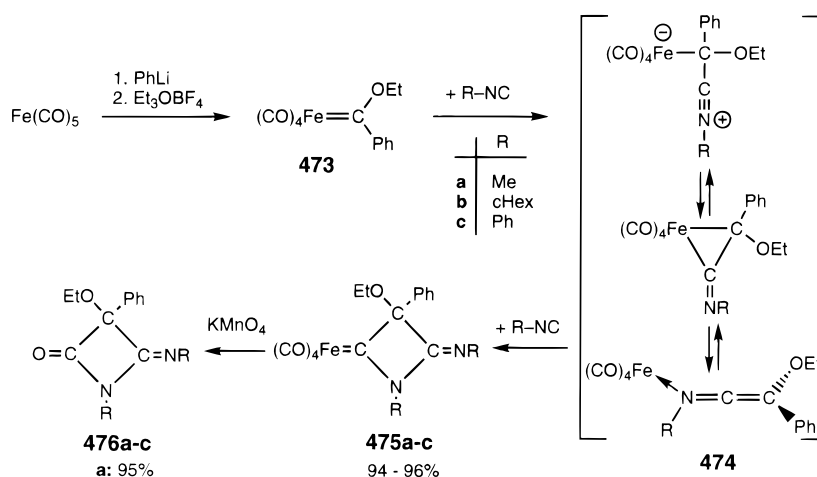
The reactions of chromium carbene complexes **469** and **471** in eqs 122 and 123 have demonstrated⁷⁵¹



that the annelation step in the [3+2+1] reactions of Dötz (vide infra), which results in two extra carbon atoms within the ring, does not necessarily take place in the reactions of chromium carbene complexes with alkynes. For **470** it has not been established, which of the two phenyl rings on the cyclobutenone is coordinated to the $\text{Cr}(\text{CO})_3$ fragment. For eq 123, it has been suggested that the uncoordinated cyclobutenone **472** may result from a [2+2] cycloaddition of the yneamine to diphenylketene, the latter initially being formed as carbonylation product of the carbene ligand in **471**. This is substantiated by the observation that **471** decomposes in solution at room temperature, i.e. under the reaction conditions, and that the solution shows an IR band at 2103 cm^{-1} , the region where ketene CO-stretching vibrations are found. Such a mechanism would also explain why with the phenyl substituted carbene ligand in **471** the usual annelation reaction is not observed—with the methyl substituent in **469**, annelation can obviously not occur.

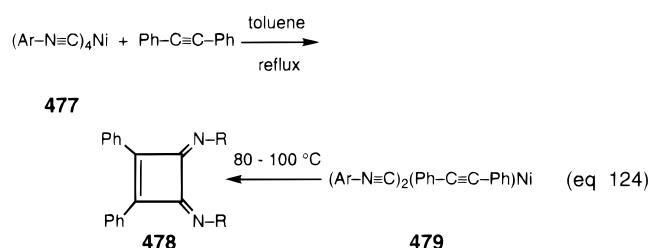
Starting from the (carbene)carbonyliron complex **473** (Scheme 70), the 3-iminoazetidinyldene complexes **475a–c** are formed with alkyl and aryl isocyanides in excellent yields via a [2+1+1] protocol.¹⁵⁸ These can be cleanly converted to the β -lactams **476a–c** by oxidative cleavage with KMnO_4 . The authors have shown by trapping experiments with ethanol, from which aminocarbene complexes are isolated, that the reaction proceeds via (ketenimine)- $\text{Fe}(\text{CO})_4$ complexes **474**. However, it is not clear from which bonding scheme the reaction proceeds further to **475** by addition of a second equivalent of RNC , since in solution differently bonded species may be in equilibrium. The position of these equilibria may be responsible that in the iron system exclusively the

Scheme 70



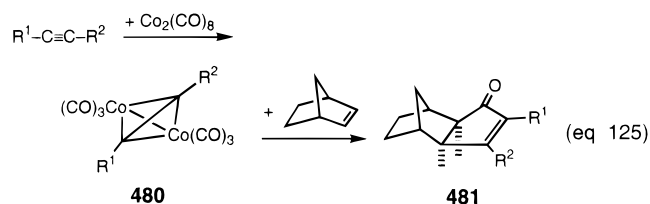
azetidinylidene complexes **475** are formed with alkyl and aryl isocyanides, while the analogous tungsten Fischer carbene complexes give this reaction only with alkenyl isocyanides and only as a side reaction.¹⁵⁹

Tetrakis(aryl isocyanide)nickel complexes **477** react with diphenylacetylene in refluxing toluene (eq 124) to give diiminocyclobutenes **478** in 22–90% yields.⁷⁵² With R being 2,6-Me₂-4-BrC₆H₂, the independently prepared mixed-ligand complex **479**, as a suggested intermediate, gives an identical yield of **478** as in the one-pot reaction. Therefore, a nickelacyclopentene is presumably a further intermediate along the reaction coordinate, which may or may not be formed in a concerted manner, and from which the final product is reductively eliminated.



2. [2+2+1]

Cyclopentenone derivatives, assembled from an alkyne, an alkene (or an enyne), and CO, are very conveniently accessible via the Pauson–Khand reaction.^{627,639,753–780} Several reviews have appeared.^{754,758,762,765,771,773} The recent review by Ojima et al.⁵ also contains a short paragraph. Normally, the tetrahedral (alkyne)Co₂(CO)₆ complex **480** (eq 125) is isolated and used in stoichiometric amounts.



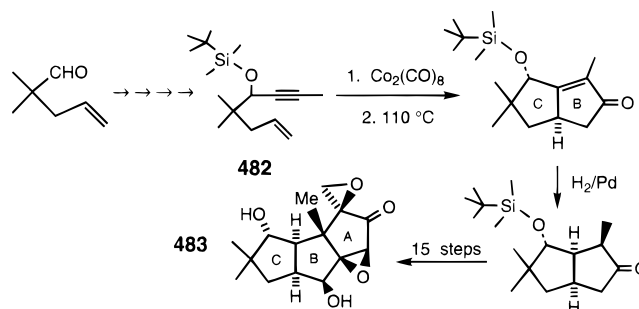
Besides strained cyclic alkenes, such as the initially used norbornadiene, most simple open-chain or cyclic alkenes can be used in the reaction with the exception of alkenes bearing strongly electron-withdrawing substituents, e.g., CN, CO₂R, SO₂R.⁷⁶² Early attempts to run the reaction according to eq 125 catalytically^{753,768,769} in the presence of CO met with limited success. Only more recently turnover numbers of several hundred have been achieved with modified cobalt catalysts under CO pressure.^{781–783}

The reaction is very regioselective with respect to the acetylene, and the CO group is normally found next to the bulkier R group of the alkyne (R¹ in eq 125), i.e., with terminal acetylenes, the substituted terminal is exclusively found at the C-2 position of the cyclopentenone.^{756,775} This infers that the olefin coordinates to cobalt from the less hindered side of complex **480**. The reaction is also very stereoselective^{756,769,784} in the case of cyclic olefins such as norbornene, and the exo product, e.g. **481**, is formed preferentially. Regioselectivity with respect to the

olefin however is rather limited.^{757,768,770} To enforce a particular preferred orientation of the olefin upon coordination to **480** and consecutively in the C–C bond-forming step and to enhance the reaction rates, Krafft et al.^{769,774–776,785} have tethered extra coordinating heteroatoms to the olefin, thus making it a bi- or even tridentate ligand. The ultimate solution to this regioselectivity problem is to make the reaction intramolecular,^{759,760,763,764,766,767,772,777,779} i.e., to use enynes as substrates where the alkyne and alkene moieties are a priori connected in the desired manner. Several attempts have been made to accelerate the rates of the reaction. Coordinating (co)-solvents, e.g., THF, acetone, DMSO, and MeCN, have been found to promote both inter- and intramolecular reactions and can lead to significant changes in regio- and stereoselectivity when compared to other reaction conditions.^{785,786} Addition of tertiary amine N-oxides^{768,785,787,788} very strongly accelerates the reaction by generating an open coordination site. Smit et al.⁷⁸⁹ have shown that the intramolecular Pauson–Khand reaction can be facilitated in a solvent-free system with the metal complex absorbed to silica gel or other absorbents. Even intermolecular reactions between alkyne complexes absorbed to various supports and neat methylenecyclopropane gave spiro[2.4]cycloheptenones^{790,791} in good yields.

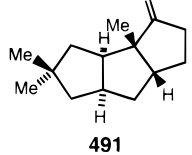
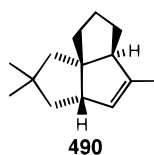
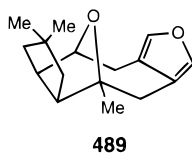
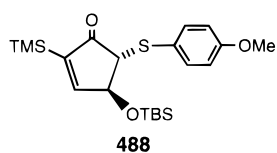
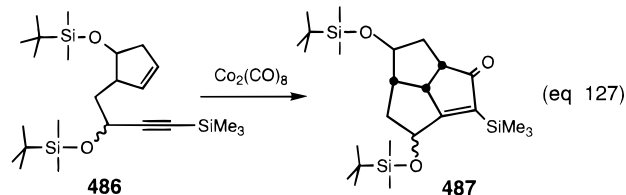
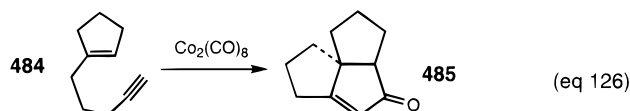
An elegant example of the intramolecular application of the Pauson–Khand reaction in the construction of the B/C rings of coriolin **483** by Magnus and Exon^{760,763} from the enyne **482** is shown in Scheme 71. The 15 steps completing the synthesis essentially

Scheme 71

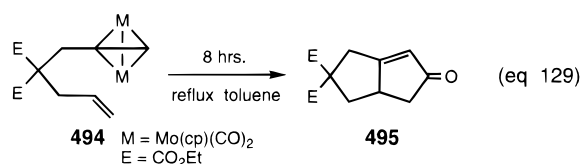
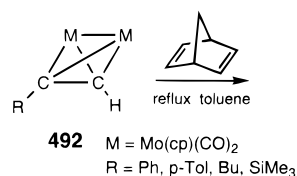


follow the route of Ikegami et al.^{792,793} Also in intramolecular Pauson–Khand reactions, the olefinic double bond of the starting enyne need not be terminal but can be contained in a ring as in **484** or **486** (eqs 126 and 127), giving rise to the angularly condensed tricyclic products **485**^{766,767} and **487**.⁷⁶⁴ Other examples where the Pauson–Khand reaction is applied in a crucial step in the total synthesis of natural products include the preparation of the *trans*-4,5-disubstituted 2-cyclopentenone (**488**),⁷⁹⁴ furanether B (**489**),^{795,796} (±)-pentalenene (**490**),⁷⁶⁷ or (+)-hirsutene (**491**).⁷⁹⁷

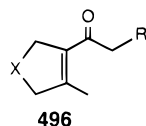
While it has been stated above that in the Pauson–Khand reaction with terminal alkynes, the substituted terminal is exclusively found at the C-2 position of the cyclopentenone, Hanaoka et al.⁷⁹⁸ have shown that also 3-substituted cyclopentenones, **493** and **495** can be obtained in inter- (eq 128) and intramolecular (eq 129) Pauson–Khand reactions using bis(cyclopentadienyl)tetracarbonyldimolybdenum–alkyne complexes **492** and **494**, respectively.



A deviation from the normal pattern of the Pauson–Khand reaction has been described by Krafft et



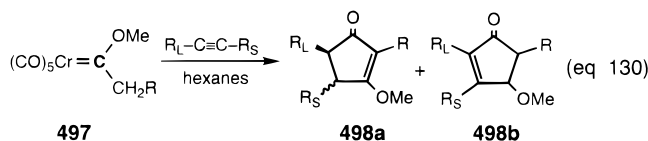
al.⁷⁹⁹ When dicobalt hexacarbonyl complexes of enynes with a three-atom-tether between the alkene and alkyne were warmed under an atmosphere of air (rather than inert gas), not the normal bicyclo[3.3.0]octenones, such as **495**, were formed, but enone products of type **496** into which oxygen had been



incorporated, but without carbon monoxide insertion, and without cyclization to form the second ring. The reaction has been termed the “interrupted Pauson–Khand reaction”, and is restricted to three-atom-tethers. The actual role of the molecular oxygen has not been elucidated.

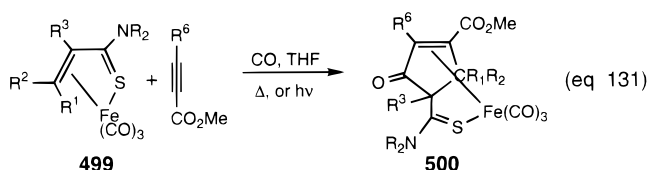
Formally related, but mechanistically distinct to the Pauson–Khand reaction, is the zirconium-catalyzed carbonylative cyclization of enynes to bicyclo[3.3.0]octenones which has been discovered by Negishi et al.⁸⁰⁰

(Alkyl)chromium carbene complexes **497** (eq 130) react with alkynes in [2+2+1] fashion in hexane to regioselectively give cyclopentenones **498**.⁸⁰¹ The



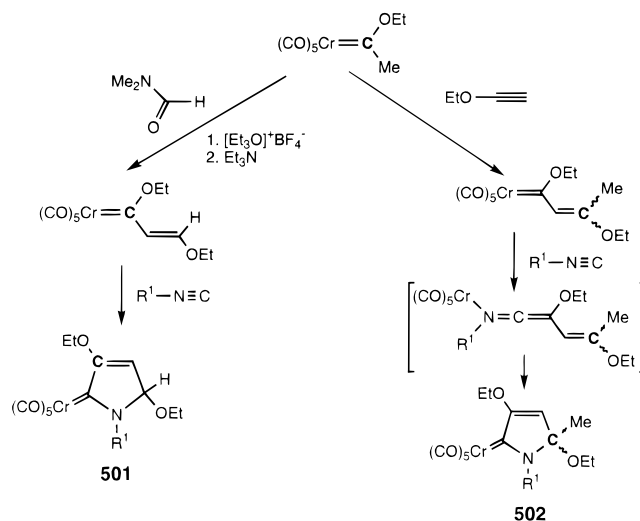
more bulky acetylene substituent R_L ends up in α-position to the carbonyl group. Mechanistically, the intermediacy of a free vinylketene has been excluded, and the reaction, which is unique to chromium, is proposed to involve metal hydride intermediates. Cyclopentenones have also been obtained from the reaction of [cyclopropyl(methoxy)methylene]Cr(CO)₅ with alkynes in aqueous dioxane or THF.^{802,803} The authors could show that the initial products are cyclopentadienones, which could be isolated when anhydrous THF and bulky alkynes were used, and which were easily reduced by water and the chromium(0) present in the reaction mixture.

Tricarbonyliron complexes of α,β-unsaturated thioamides (**499**) give cyclopentenone complexes **500** with activated alkynes (DMAD, methyl propynoate) and CO according to eq 131.⁸⁰⁴



2*H*-Pyrrole complexes of chromium (and tungsten), **501** and **502**, of different connectivity patterns have been prepared in a stepwise fashion (Scheme 72) via

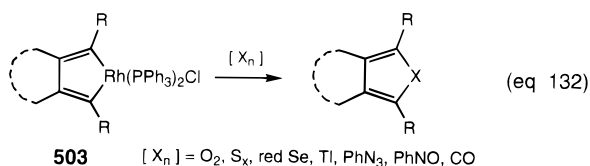
Scheme 72



a [2+1+2] and a [1+2+2] protocol respectively.⁸⁰⁵ The reactions proceed by successive insertion of alkyne and isonitrile into the M=C bond and consecutive

cyclization. The $L_nM=C$ bonds in **501** and **502** can be readily transformed in a variety of ways.³⁰ 2,3-Dihydro-5-hydroxypyrrol-2-ones were obtained in low yields from the reactions of chelate (formamidinio-carbene)Mo(CO)₄ or Cr(CO)₄ complexes with 3-hexyne.⁸⁰⁶

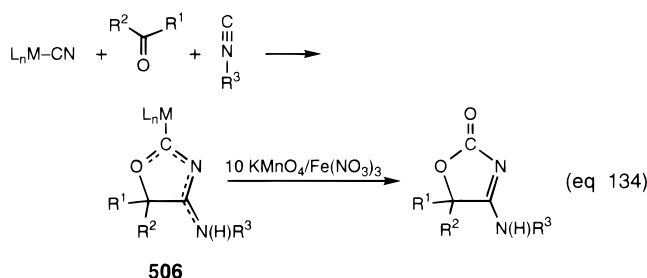
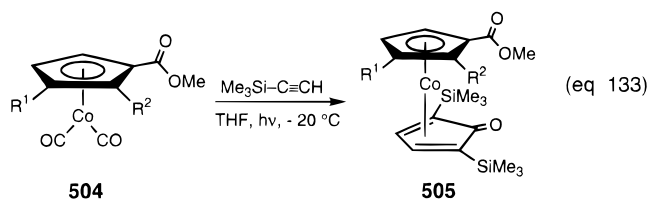
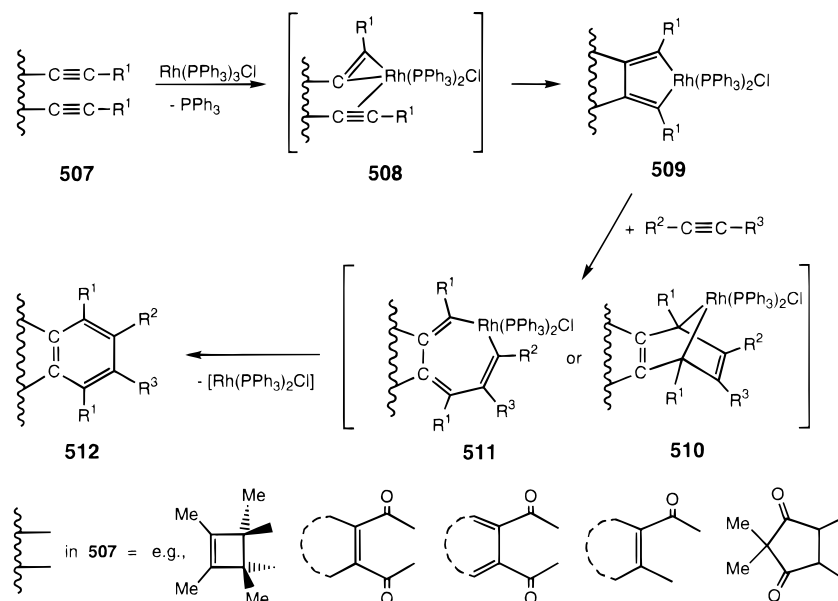
In the (Cp)cobaltacyclopentadiene complexes **347** (eq 92), the metal atom can be replaced by sulfur, selenium, or NR, thus completing a [2+2+1] protocol, and producing thiophenes, selenophenes, and pyrroles.⁵⁸³ The same type of reaction has been carried out with the rhodacyclopentadiene complexes **503** (eq 132) of Müller et al.^{807,808} The chalcogene atom is



introduced by reaction with oxygen gas or hydrogen peroxide, elemental sulfur, red selenium, and amorphous thallium, and the nitrogen by reaction with phenylazide or nitrosobenzene. The metal fragment can also be replaced by a carbonyl group on reaction with CO.⁸⁰⁹ Complexes of type **503** are further the isolated intermediates in the “diyne-reaction” which follows a [2+2+2] protocol producing (fused) aromatic systems (see below). When (Cp)Co(CO)₂ complexes,⁸¹⁰ e.g., **504** (R¹, R² = H, Me or Me, H),⁸¹¹ are irradiated in the presence of (trimethylsilyl)acetylene (eq 133), cyclopentadienone complexes **505** are formed in [2+2+1] fashion, probably analogous to the reaction sequence as in eq 92 with consecutive CO insertion and reductive elimination.

In a three-component [2+2+1] reaction (eq 134) of a range of cyano complexes $L_nM(CN)$ [L_nM = Cr(CO)₅, Mo(CO)₅, W(CO)₅, Mn₂(CO)₉, (Cp)(CO)Fe(CN), (Cp)(dppe)Fe] with a wide variety of different ketones and isocyanides, carbenoid oxazoline complexes **506** are formed, which by oxidative degradation give attractive yields of 4-amino- and 4-imino-oxazolidin-2-ones.^{812–814}

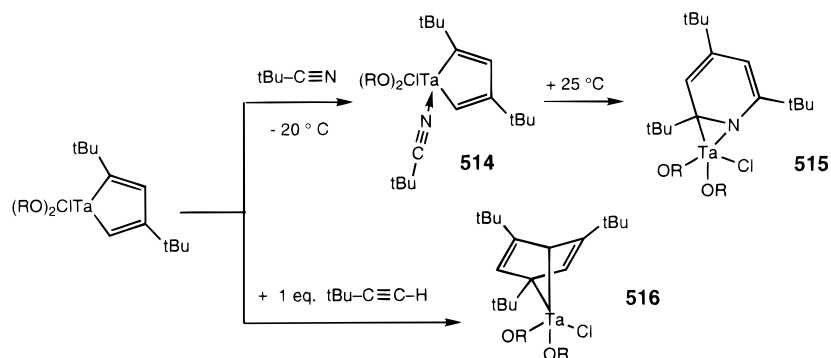
Scheme 73



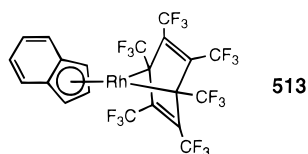
3. [2+2+2]

One of the oldest examples of stoichiometric, metal-assisted syntheses of (fused) benzene derivatives following a [2+2+2] protocol is the “diyne reaction” discovered by Müller. The results have been collected in a review in 1974⁸¹⁵ and a few later publications.^{586,807,816,817} According to Scheme 73, a diyne compound **507** is reacted with, in most cases, Rh-(PPh₃)₃Cl. It is suggested that as the first step toward the isolable rhodacyclopentadiene complexes **509** a rhodacyclopentadiene complex **508** is formed which is π -coordinated to the triple bond of the second alkyne. The nature of the bonds connecting the two triple bonds in **507** is of no relevance. The only important precondition is that the two “inner” sp carbon atoms in **507** are spatially not further apart than 3.4 Å. The last step in the reaction sequence is then the reaction of almost any alkyne R²C≡CR³ (cyclic, acyclic, terminal, internal, electron-poor, electron-rich) with **509**, either via a [4+2] addition (see also eq 94) with consecutive elimination of the metal fragment from **510** and aromatization, or via an insertion to a rhodacycloheptatriene **511** and consecutive reductive elimination, to give **512**.

Scheme 74

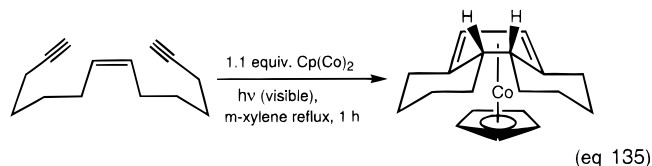


In the reactions of bis(ethylene)(η^5 -indenyl)rhodium⁸¹⁸ with 3,3-dimethylbut-1-yne or (η^4 -isoprene)(η^5 -indenyl)rhodium with hexafluorobut-2-yne both reaction pathways of the rhodacycle (analogous to **509**), i.e., [4+2] cycloaddition or insertion are discussed. 7-[(η^5 -Indenyl)rhoda]-1,2,3,4,5,6-hexakis(trifluoromethyl)norcaradiene (**513**) has been isolated, while



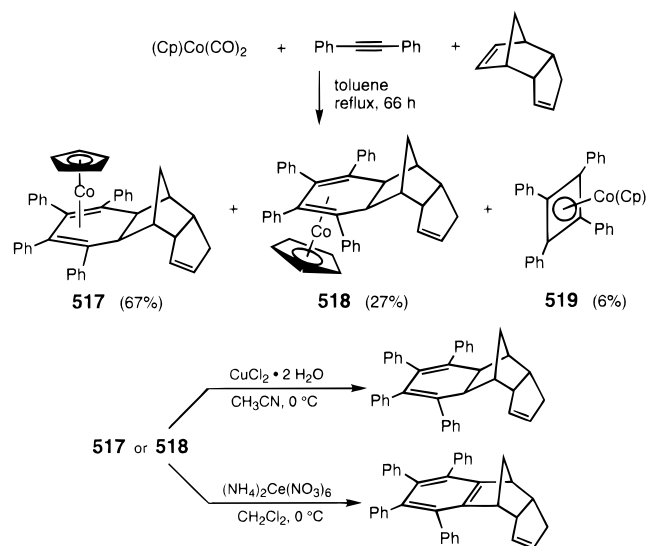
for the formation of di-*tert*-butylhexadienes and tri-*tert*-butylbenzenes an insertion/reductive elimination pathway via, respectively, rhodacycloheptadi- and trienes is suggested. A different mechanism is suggested for the formation of $[\eta^2(N,C)\text{-}2,4,6\text{-}(t\text{-Bu})_3\text{-NC}_5\text{H}_2]\text{Ta}[\text{O-}2,6\text{-}(i\text{-Pr})_2\text{C}_6\text{H}_3]\text{Cl}$ (**515**) from the tantalacyclopentadiene **514** in Scheme 74.^{819,820} The structure of the $2,4,6\text{-}(t\text{-Bu})_3\text{C}_6\text{H}_3$ complex **516** on the other hand, with a folding angle of $33.1 \pm 0.5^\circ$ between the two benzene halves is again very suggestive of a tantalonorcaradiene structure from a [4+2] addition.

Cyclopentadienylcobalt carbonyl complexes and many derivatives, e.g., substituted on the cyclopentadienyl ring, are well-known catalysts for the intramolecular cyclization of endiynes,^{821,822} for the intermolecular cyclotrimerization of alkynes to arenes and their [2+2+2] cocyclization with other unsaturated substrates.^{822–825} Besides with cobalt,⁸²⁶ such reactions of two alkynes and an alkene, giving free cyclohexadienes, are also known to be catalyzed by complexes of iron,⁸²⁷ nickel,⁸²⁸ rhodium,⁸²⁹ and palladium.^{830,831} However, there are also examples of $[(\text{Cp})\text{Co}(\text{CO})_2]$ -mediated stoichiometric [2+2+2] cocyclizations,⁸³² intramolecular with several stereoisomeric endiynes,⁸³³ (e.g., eq 135), and intermolecu-

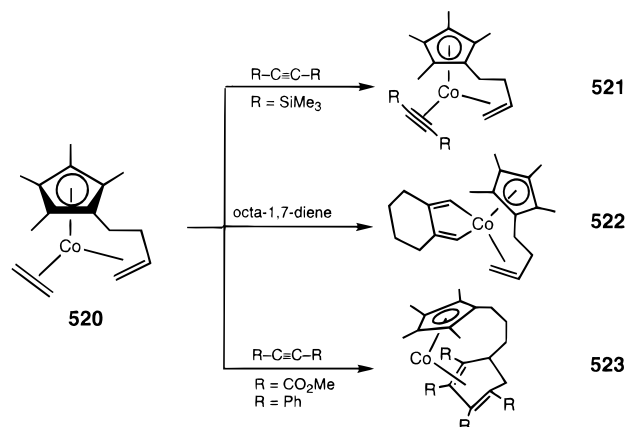


lar with two equivalents of alkyne (diphenylacetylene, dimethyl acetylenedicarboxylate) and 1 equiv of alkene (dicyclopentadiene, norbornene) (Scheme 75).⁸³⁴ In an elegant crossover experiment, using

Scheme 75

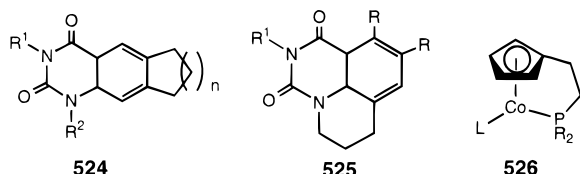


Scheme 76

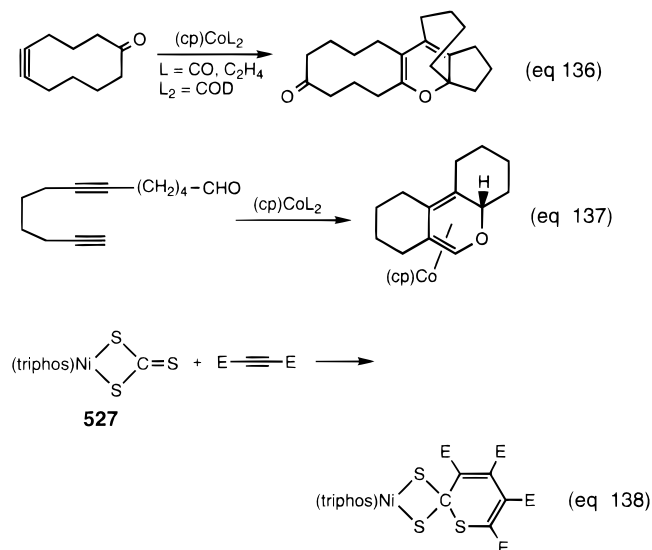


doubly labeled (at the Cp ring and the olefin) complexes, it has been shown by NMR that the endo isomer (e.g., **517**) cleanly thermally converts (154°C ; $>50\text{ h}$) to the exo isomer (e.g., **518**) in an intramolecular first order reaction. Surprisingly, with **517** or **518**, on oxidative decomplexation with $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ the cyclohexadiene ring is dehydrogenated, while with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ it is not. Using a Cp ring with a pendant alkene arm, as in **520** (Scheme 76), Okuda^{835,836} succeeded to isolate the reasonable intermediates **521**, **522**, and the final [2+2+2] product **523**, depending on what type of alkyne was used. (Cp)cobaltacyclopentadiene complexes such as **347** (eq 92) have been used by Wakatsuki et al.^{583,837–839}

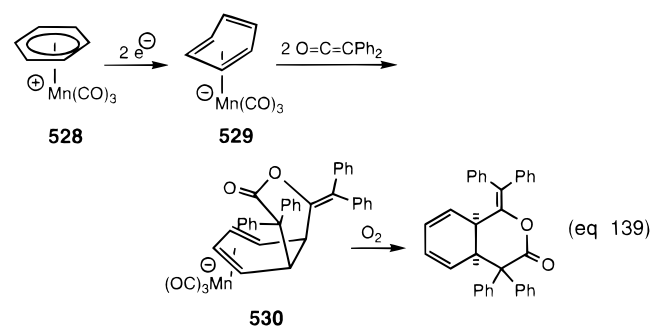
for the stepwise construction of $(\text{Cp})\text{Co}(\eta^4\text{-cyclohexa-1,3-diene})$ complexes. Vollhardt et al.⁸⁴⁰ have applied the CpCo -assisted $[2+2+2]$ cycloaddition for the synthesis of modified nucleosides. Using stoichiometric amounts of $[\text{CpCoL}_2]$ ($\text{L} = \text{CO}, \text{C}_2\text{H}_2$), the 5,6-double bond of uracil was used as olefin component and cocyclized with α,ω -diynes such as **524**, or **525**, with one external alkyne $\text{RC}\equiv\text{CR}$, and one terminal alkyne tethered to uracil-N(1). When a strongly coordinating phosphorus donor atom, as in **526** is tethered to



the Cp ring, the $[2+2+2]$ sequence is blocked,⁸⁴¹ and alkyne and vinylidene complexes are formed. Instead of an alkene double bond, also a $\text{C}=\text{O}$ double bond can be utilized, and $(\text{Cp})\text{Co}$ complexes of α -pyrans have been obtained by Gleiter et al.⁸⁴² (cf. eqs 136 and 137). Bianchini⁸⁴³ has reported the $[2+2+2]$ addition of 2 equiv of dimethyl acetylenedicarboxylate to the $\text{C}=\text{S}$ double bond of the η^2 -trithiocarbonate complex $[(\text{triphos})\text{Ni}(\text{S}_2\text{CS})]$ (**527**) in eq 138.

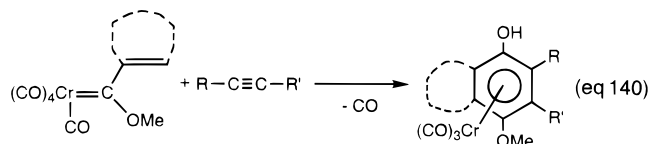


Two-electron reduction of $[\text{Mn}(\eta^6\text{-C}_6\text{H}_6)(\text{CO})_3]^+$ (**528**)⁸⁴⁴ with potassium naphthalenide gives the reactive anionic η^4 -benzene intermediate **529** which in situ reacts with 2 equiv of diphenylketene in $[2+2+2]$ fashion to give the dihydroisochroman-2-one complex **530** from which the organic ligand is released by simple oxidation (eq 139).⁸⁴⁵

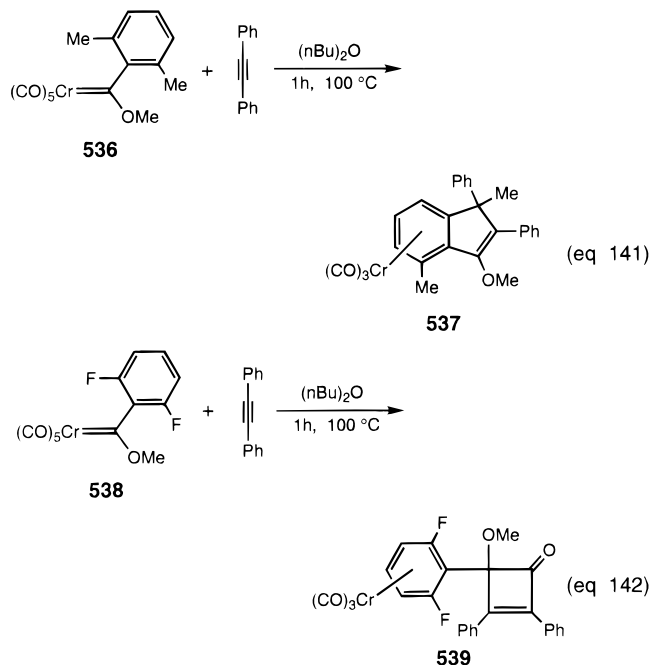


4. $[3+2+1]$

A formal $[3+2+1]$ cycloaddition reaction is represented by the benzannulation or Dötz reaction. It was first reported by Dötz in 1975.⁸⁴⁶ In the reaction, three carbon atoms of a vinyl- or aryl-Fischer-carbene complex, two alkyne carbon atoms, and a carbon monoxide are cyclized to a *p*-alkoxyphenol skeleton, η^6 -coordinated to the $\text{Cr}(\text{CO})_3$ fragment, cf. eq 140.

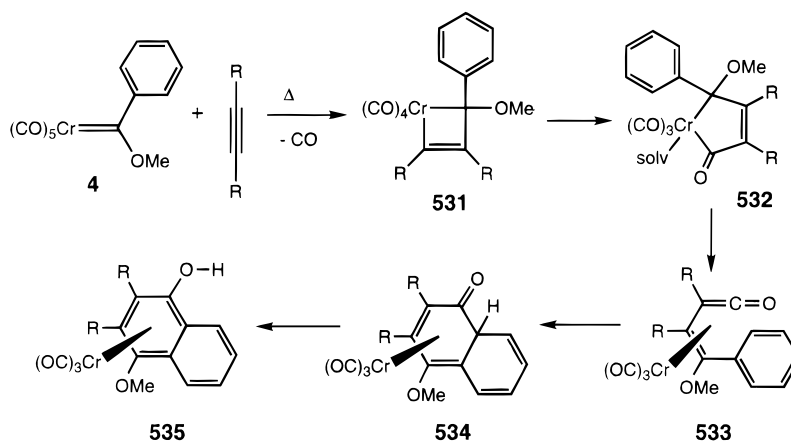


[By use of 2,2-dimethylpropylidynephosphane, i.e., a phosphaaalkyne as triple-bond component, the reaction has been extended to the synthesis of phospharenes and 1,3-oxaphospholes.^{847,848}] The *p*-alkoxyphenol ligand can be cleaved from the metal either by substitution by CO or by oxidation to the quinone. Several competent collecting and reviewing articles with many leading references have appeared.^{474,478,849–851} Scheme 77 shows some of the more important intermediates along the reaction coordinate toward the product **535**. The reaction is very complex, and depending on the reaction conditions and the substituents in the starting components, the product mixture may, besides hydroquinone derived complexes, e.g. **535**, contain varying amounts of cyclobutenone,⁷⁵¹ lactone,⁸⁵² indene,^{433,853–855} or furan^{855–857} products, they even may become the main products. A pertinent example has been described by Dötz.^{858,859} The *o,o'*-dimethyl-substituted aryl complex **536** (eq 141) does undergo annulation on reaction with diphenyl acetylene, though no CO insertion, to give the $[3+2]$ indene complex **537** as main product. The *o,o'*-difluoro-substituted complex **538** (eq 142) on the other hand does give CO inser-

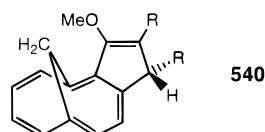


tion, but the carbene annulation step is blocked by the much more strongly bonded fluoro substituents,

Scheme 77

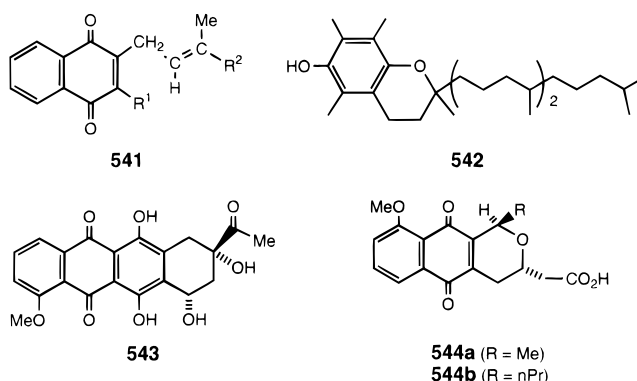


and the [2+1+1] cyclobutenone complex **539** is the main product, just as with complex **469** (eq 122) where the carbene carbon does not have an aryl substituent to be annealed. The choice of the metal also plays an important role, particularly if the reaction is not thermally induced, but photochemically.¹⁸⁷ Neidlein et al.^{860–862} have prepared 2-[1,6-methano[10]annuleny]-substituted Fischer carbene complexes. While the chromium complex underwent the normal benzannulation reaction with alkynes to give quinones and hydroquinones, depending on the work-up conditions,⁸⁶² the respective tungsten complex did not CO insert and gave **540**.⁸⁶¹ Intermedi-



ates **531–534** in Scheme 77 are branching points from which the reaction may depart to other products. Several mechanisms have been proposed, in particular by Dötz^{863,864} and Casey.⁸⁶⁵ A thorough discussion and extensive schemes giving an overview of the proposed intermediates and observed types of products have been given by Wulff.^{474,851,866} Vinyl carbene complexes for the [3+2+1] addition as indicated in eq 140 need not be stable and isolable, they can also be generated in situ.^{867,868} The Dötz reaction of aryl^{62,853,869–895} and alkenyl^{478,896–898} Fischer carbene complexes has found wide application as key step in the synthesis of natural products containing naphtho- and benzoquinone moieties. Some pertinent examples are the syntheses of vitamins K **541**,^{894,895} vitamin E (α -tocopherol) **542**,⁸⁹⁹ anthracyclines^{881,882,884,887,889,890,892,897,898} such as daunomycinone **543**, or naphthoquinone antibiotics^{891,893,900}

such as nanomycin A **544a** and deoxyfrenolicin **544b**.

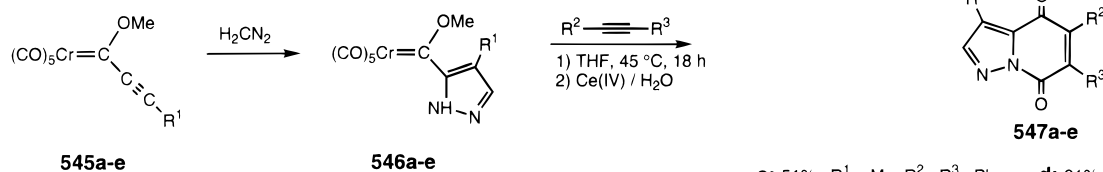


Benzannulation has also been applied as a key step in the synthesis of vaulted biaryls such as 3,3'-diphenyl-2,2'-binaphthalene-1,1'-diol,⁹⁰¹ the enantiomeric atropisomers of which are effective ligands in, e.g., Lewis acid catalyzed asymmetric Diels–Alder reactions.^{902,903}

As de Meijere et al. have shown, α,β -unsaturated Fischer carbenechromium complexes, bearing a donor substituent (NR_2 , OR) in the terminal vinylic position,^{904–906} react with alkynes to give a totally different range of products, e.g., highly substituted cyclopentadienes⁹⁰⁷ and fulvenes in a [3+2] cycloaddition,⁹⁰⁸ cyclopenta[*b*]pyrans⁹⁰⁹ in a [3+2+2+1] cycloaddition, or 5-methylene-2-cyclopentenones⁹¹⁰ in a [2+2+1] cycloaddition. See also the review by de Meijere⁴⁹⁰ on β -amino-substituted α,β -unsaturated Fischer carbene complexes as chemical multitolerants.

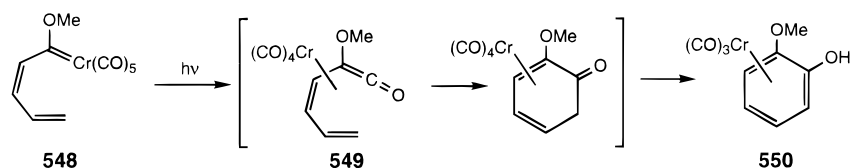
An interesting annulation reaction that produces pyrazolo[1,5-*a*]pyridine quinones **547** (Scheme 78) has been reported by Chan and Wulff.⁴⁵⁵ The [3+2] cycloaddition product **546** of alkynyl carbene com-

Scheme 78



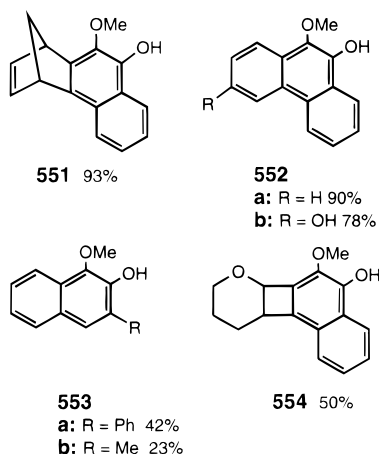
a: 51%; $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{R}^3 = \text{Ph}$ **d**: 31%; $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{nPr}$, $\text{R}^3 = \text{H}$
b: 22%; $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{Ph}$, $\text{R}^3 = \text{H}$ **e**: 41%; $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{Ph}$
c: 45%; $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{R}^3 = \text{Et}$

Scheme 79



plexes **545** and diazomethane (see also Scheme 32) is reacted with internal alkynes and **547** is obtained after oxidation with aqueous cerium(IV) ammonium nitrate. A double intramolecular two-alkyne annulation coupled to a Diels–Alder addition has been used by Wulff et al.⁹¹¹ for the construction of all four rings of the steroid ring system in one pot.

Whereas the normal Dötz reaction according to eq 140 and Scheme 77 always leads to *p*-alkoxyphenols, or, by oxidation of these, to *p*-quinones, Merlic et al.⁹¹² have devised an alternative route (Scheme 79) that leads to *o*-alkoxyphenols **550** or *o*-quinones. It starts off with dienylcarbene complexes **548**, and the pivotal intermediate ketene complex **549** is directly generated by photochemically induced CO insertion.^{176,177,913} By irradiating the appropriate chromium dienylcarbene complexes under an atmosphere of CO, the actual *o*-alkoxyphenols **551–554** have been prepared with the indicated yields, and the chromium has been recovered as Cr(CO)₆ in 40–70% yield.



The synthetic potential of these multistep multicomponent cyclization reactions has not yet been fully explored, and there are examples of other potentially useful sequences such as the topologies [2+2+1+1],⁹¹⁴ giving bicyclo[3.1.0]lactams from chromium aminocarbene complexes and alkynes, or the inter-^{850,868} or intramolecular⁹¹⁵ cyclization of two alkynes, a CO ligand and the carbene carbon of Fischer carbene complexes to give cyclohexadienones or phenols, [4+2+1]⁹¹⁶ giving seven-membered cyclic ketones from cyclopropylcarbene tungsten complexes and alkynes, [3+2+2],⁹¹⁷ coupling an η^3 -allyl ligand with two alkynes to yield an η^5 -cycloheptadienyl ring system, or the sequence [4+2+1–2]⁹¹⁸ giving cyclopentenones from the related cyclopropylcarbene chromium complexes and alkynes.

III. Concluding Remarks

The present review amply demonstrates the enormous amount of material that has been gathered, the

great utility of transition metal-assisted cycloaddition reactions in the synthesis of organometal and organic compounds, and the various roles that the metal fragment can play. The systematization with respect to topology should help to make the great diversity of reactions more easy to survey. I sincerely hope, for the sake of clarity, that the given definitions for metal-assisted and organometal cycloaddition reactions will be accepted by the chemical community and that these expressions will in the literature replace the various other terms that are and have been used. The term “metal-assisted” (as opposed to nonmetal-assisted) as it has been used by Merlic⁵⁷² is defined too narrowly and should not be applied in that sense.

IV. Acknowledgments

I thank my colleagues and co-workers for their putting up with my countless hours in the library or behind my computer. Thanks are also due to the Editors for their patience because of the prolonged time for the completion of this article. This was not only due to its unanticipated size, but also to several extended suspensions as the consequence of other duties and obligations.

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