

THE METHYLENE BRIDGE: A CHALLENGE TO SYNTHETIC, MECHANISTIC AND STRUCTURAL ORGANOMETALLIC CHEMISTRY

Wolfgang A. Herrmann

Institut für Anorganische Chemie der Universität Regensburg/Germany

In memory of Paolo Chini († Febr. 1, 1980)

Abstract - Within the past few years transition metal complexes containing bridging alkylidene functions (Fig. 1) have stimulated wide-spread interest in organometallic chemistry, due at least in part to the apparent significance of methylene intermediates in the metal-surface catalyzed reduction of carbon monoxide. Following the preparation of the first unsubstituted μ -methylene complex in 1974, we have continued our investigations into the synthesis, structures, and reactivity of dimetallacyclopropane-type compounds. An overview of these results will be presented. The most versatile synthetic method for the construction of μ -alkylidene systems is carbene transfer from easily accessible, highly reactive diazoalkane precursors to either mononuclear, coordinatively unsaturated substrates, or complexes with metal-metal multiple bonds. The structural features and the reactivity pattern of the resulting dimetallacyclopropanes are governed by both steric and electronic effects arising from the nature of the metals, the methylene bridges as well as the peripheral ligands. Emphasis will also be placed on the spectroscopic characteristics and the bonding situation of simple methylene bridges.

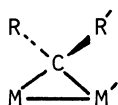


Figure 1

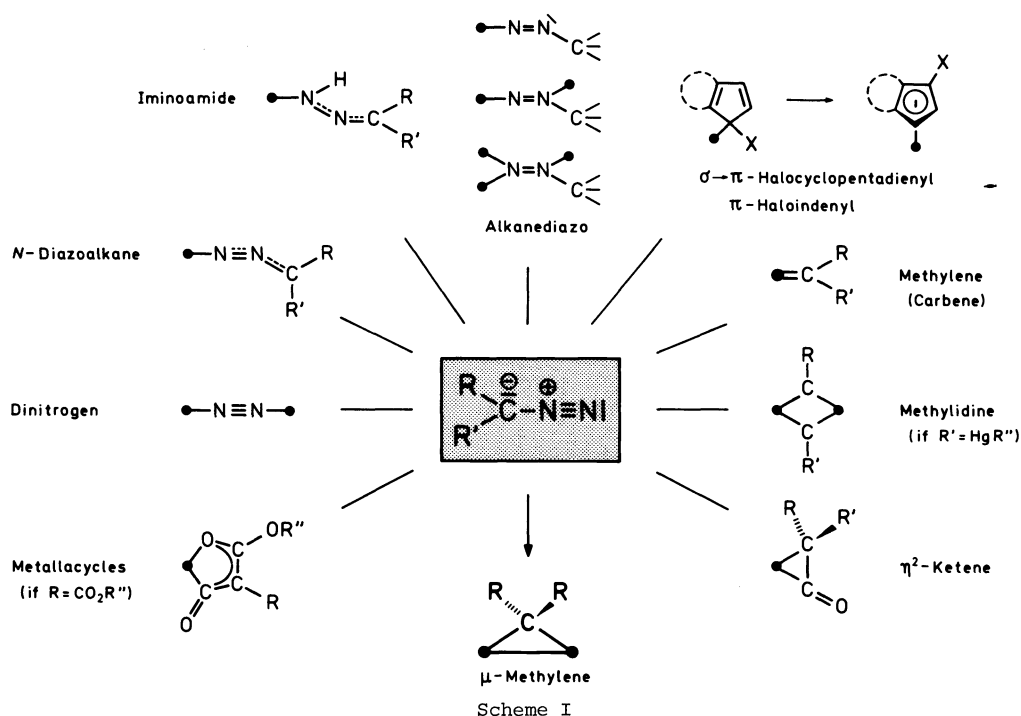
are governed by both steric and electronic effects arising from the nature of the metals, the methylene bridges as well as the peripheral ligands. Emphasis will also be placed on the spectroscopic characteristics and the bonding situation of simple methylene bridges.

Introduction

The pioneering work of Fischer and his group has produced an overwhelming number of transition metal carbene complexes, $L_x M=CRR'$, within a very short period of time. This work combined with subsequent results originating from other laboratories throughout the world has not only broadened our knowledge of structural and reactivity patterns of simple transition metal compounds, but has also catapulted the field of organometallic chemistry into new directions, for example the examination of carbon-metal multiply bonded species, e.g. carbenes or carbynes, as intermediates in metal catalysis. This is particularly true if we include those compounds containing bridging methylene groups, a relatively new field by comparison. The aim of this lecture is to outline some important principles with regard to the synthesis, spectroscopy, reactivity, structures, and bonding of methylene bridged compounds. Needless to say, only a few aspects of the widespread field of μ -methylene chemistry can be given here. A comprehensive review of the entire field is now available, which covers in detail the significant contributions of my colleagues Bergman, Knox, Levisalles, Rudler, Pettit, Puddephatt, Shapley, Stone, Tebbe, and Wilkinson to the rapidly developing field of μ -methylene chemistry [1].

The First Methylene Bridge

Early in our explorative work on the synthetic potential of diazoalkanes in organometallic chemistry (Scheme I) [2], we succeeded in preparing the first stable CH_2 -bridged transition metal complex. Low-temperature reactions of $(\eta^5-C_5H_5)Mn(CO)_2THF$ with diazomethane did not yield the mononuclear carbene derivative $(\eta^5-C_5H_5)Mn(CO)_2(=CH_2)$ which we had hoped for based upon our experience with the reactivity pattern of other diazoalkanes with the same



and similar substrates [1,2], but rather the dinuclear compound **1** characterized by its metal-to-metal bond bridging CH₂ unit (Fig. 2) [3-5]. The mononuclear species is certainly involved in the formation of **1**, since crossover experiments have demonstrated that subsequent treatment of $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2\text{THF}$ with first CH_2N_2 (1:1, low temperature) and then $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{Mn}(\text{CO})_2\text{THF}$ gives the mixed product $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Mn}-\text{CH}_2-\text{Mn}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)$. The thermal stability of

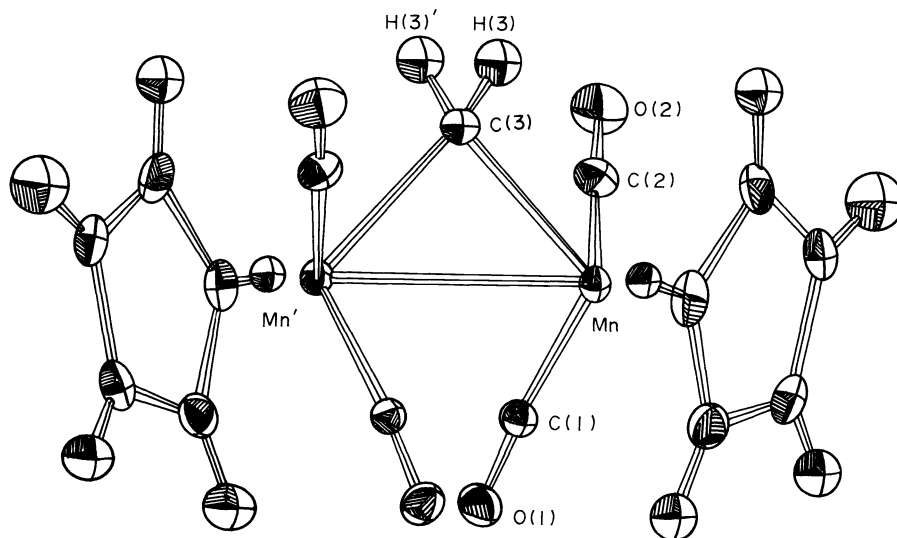


Figure 2

these prototypal compounds is quite high (e.g., mp. 135-136°C, for **1**) and parallels that of many other analogous derivatives prepared subsequently. Stable μ -methylene complexes are prevalent among the Fe, Co, and Ni sub-groups. They are also known for group VI and VII elements (W, Mn), but as yet no

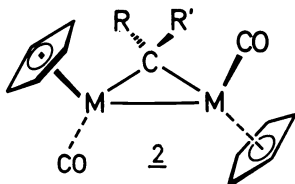
example has been encountered with the early transition metals. Therefore, the question arises whether titanium and vanadium methylene complexes and their heavy metal congeners might be catalytically relevant in CO reduction processes.

Syntheses of μ -Methylene Transition Metal Complexes

If we try to sort out what major routes have hitherto been used for the preparation of μ -methylene complexes, we figure that direct approaches can be employed complementary to indirect methods. The first possibility which was discovered in our laboratory comprises the use of reagents which have had a long history as outstanding carbene precursors in organic chemistry. Clearly, diazoalkanes represent the starting materials of choice: hundreds of well-characterized members of this class of compound are known and can easily be prepared, with all kinds of functional groups attached to the diazo-carbon center, ranging in nature from electron-withdrawing to electron-donating, from small to large, from open-chained to cyclic, from saturated to unsaturated. Moreover, different ways of activation are possible for inducing their reactions with organometallic substrates: photolysis, thermolysis, and catalysis. It now appears that one of the major advantages of diazoalkanes consists in their tendency to undergo metal-induced nitrogen elimination with concomitant carbene transfer to the metal substrate present. The methodological features of metal carbene (μ -methylene) syntheses from diazo precursors are (a) replacement of a less tightly bound two-electron-ligand with the carbene unit preformed in the diazoalkane or, (b) straight addition of the methylene building block to unsaturated metal-metal frames. In the first case, subsequent metal-metal bond formation is required in order to achieve di- or polynuclear μ -methylene derivatives, whereas the second route directly provides methylene-bridged compounds.

The formation of μ -methylene complexes from diazoalkane precursors generally occurs under very mild conditions, as exemplified by the low-temperature synthesis of compound 1. High yields are observed if the generation of reactive organometallic intermediates and nitrogen elimination from the diazo substrate occur at roughly the same rate and, in addition, if the mononuclear species thus formed have sufficient lifetime to allow metal-metal bond formation. Furthermore, the formation of the reactive organometal species has to occur under conditions which do not effect any uncontrolled decomposition or side reactions of the diazo molecules. It follows from this assessment that photolysis cannot be employed in case of diazoalkanes with pronounced photosensitivity (e.g., CH_2N_2) since light-induced decomposition of the organic precursor will successfully compete with the activation step (e.g., CO-elimination) of the organometallic reactant. It is well understandable that unsaturated metal-metal systems commonly give very high yields of methylene addition products: first, no activation of these species is necessary, since they react with diazoalkanes even at low temperatures and, secondly, the metal-metal bond is present from the very beginning. Diazoalkanes of higher thermal stability such as the diazomalonates tolerate more drastic reaction conditions in which cases the application of photochemical techniques can be avoided. For instance, thermal reaction of dicarbonyl(η^5 -cyclopentadienyl)cobalt with various diazoacetates and -malonates (boiling benzene!) gives the dinuclear μ -methylene derivatives 2 in good yields [6]. The rhodium complex of composition

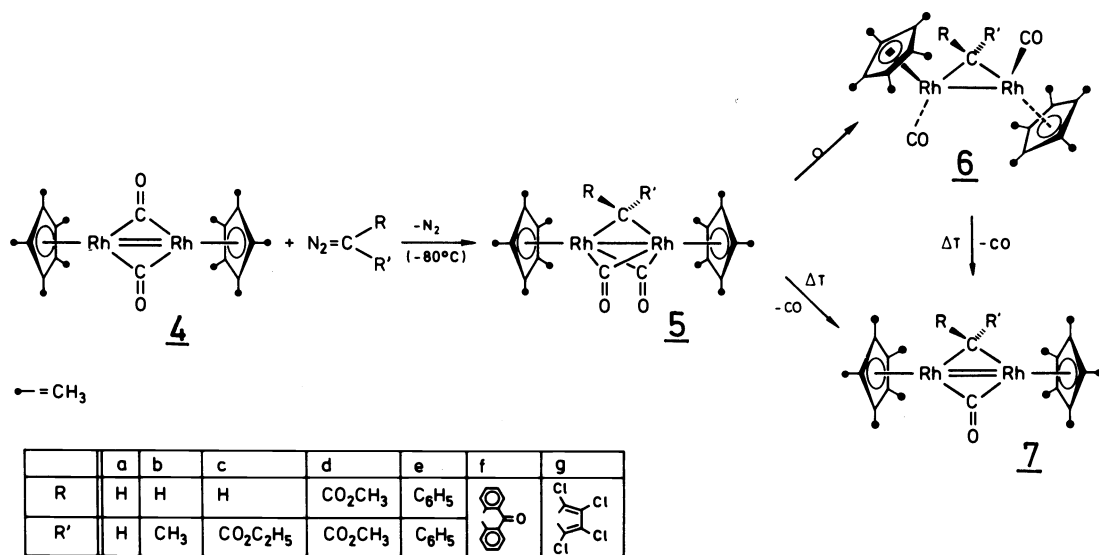
$[\mu\text{-C}(\text{CO}_2\text{C}_2\text{H}_5)][(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})]_2$ results from prolonged photolysis of the corresponding half-sandwich complex $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})_2$ in the presence of excess diazo diethylmalonate [7]. On the other hand, labile diazo precursors such as diazomethane suffer from extensive decomposition under comparable conditions; consequently, an alternate route to the stable parent methylene compound $(\mu\text{-CH}_2)[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})]_2$ has to be used [8,9].



The mechanistic details of the above-mentioned reactions still await elucidation. It now appears, however, that generation of coordinatively unsaturated dinuclear metal substrates prior to the actual reaction of the diazoalkanes represents the crucial prerequisite in methylene bridge formation. This assumption is beautifully substantiated by the following examples.

CARBENE ADDITION TO METAL-METAL "DOUBLE" BONDS

Cyclopropanation of alkenes by use of diazoalkanes constitutes a simple synthetic method of fairly general applicability [10]. If we think of $\text{M}=\text{M}$ -double bonds as being (at least formally!) analogues of $\text{C}=\text{C}$ -double bonds [11], then carbene addition should produce dimetallacyclopropanes. This overly simplified concept indeed provides the most powerful method of making μ -methylene complexes. The rhodium dimer **4** reacts according to Scheme II with a plethora of diazoalkanes to give the triply bridged carbene addition products **5** via nitrogen elimination [12]. These compounds are generally formed in quantitative yields and can be isolated in case of bulky methylene ligands such as tetrabromocyclopentadienylidene or anthrone(9)-ylidene(10) [12]. An X-Ray structure performed



Scheme II

with one of the key products has confirmed the triple bridged geometry predicted from spectroscopic data. Nitrogen elimination prior to formation of **5** is so fast, even at -80°C , that it could not be traced by means of low-temperature IR spectroscopy. The assumption that a five-membered dimetallacycle of type

$\overline{\text{Rh-N=N-CRR}'\text{-Rh}}$ is formed in the very first step [13] appears reasonable. The extreme reactivity of **4** is documented by the fact that even the most stable diazoalkanes (e.g., $\text{N}_2=\text{C}(\text{CO}_2\text{R})_2$) rapidly eliminate dinitrogen in the temperature range $-80\dots 0^\circ\text{C}$ when tetrahydrofuran is used as solvent. Further reactions branch out from the primary products **5**. First, carbonyl bridge-opening can occur, which isomerization process leads directly to the single bridged derivatives **6** commonly observed as the final products if (a), reaction temperatures around ambient are employed and (b), if sterically unpretentious carbenes are present [12-15]. By way of contrast, isomerization does not occur at all if we are dealing with bulky methylene bridges (e.g., C_5Br_4 , and other α -substituted cyclic carbenes; Figure 3) [12]. In the latter case, decarbonylation as an alternative pathway is observed. The rhodium-rhodium double bond present in the starting material **4** is restored in the resulting products **7**. This process is established to also start from type-**5** compounds (e.g., $\text{C}(\text{C}_6\text{H}_5)_2$). In this context, attention is drawn to a curious difference between the structurally identical compounds $(\mu\text{-CH}_2)[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})]_2$ and $(\mu\text{-CH}_2)[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})]_2$ (or their CRR' derivatives). The first molecule does not undergo carbonyl

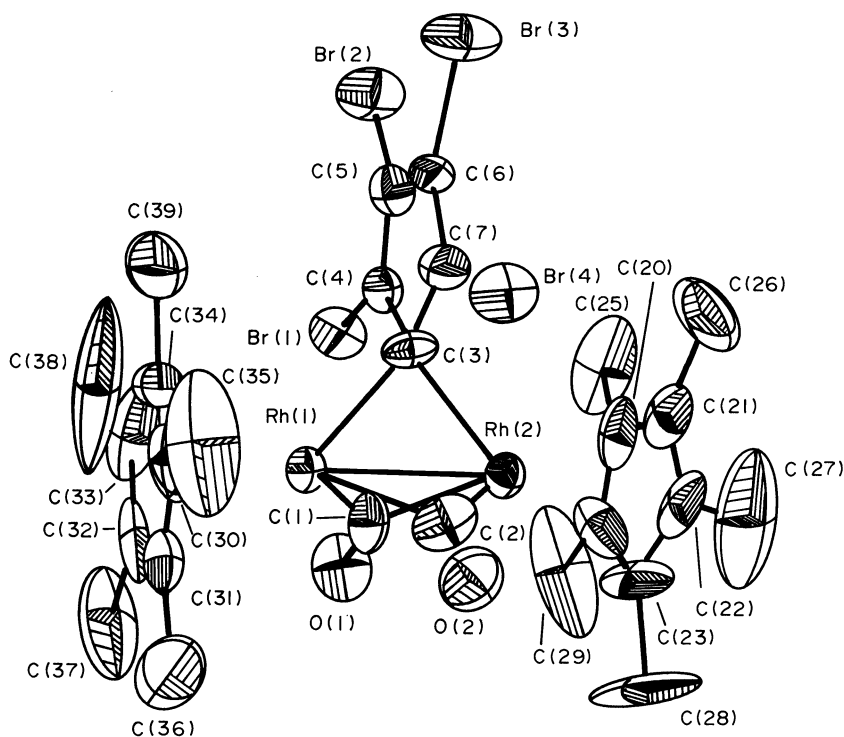


Figure 3

exchange up to at least 100°C , whereas the pentamethyl derivative exhibits dynamic behavior *via* pairwise CO scrambling commonly observed for complexes with carbonyl ligands disposed in *cis/trans* arrangements about the metal-metal bonds. This process is fast on the NMR time scale at room temperature and yields "enantiomerization" of the chiral (*S,S* or *R,R*, resp.) rhodium centers (Figure 4). ^{13}C NMR results show that in the unsymmetrically substituted CRR' -bridges (e.g., $\text{R} = \text{H/R}' = \text{CO}_2\text{Et}$ [13]; $\text{R} = \text{H/R}' = \text{CF}_3$ [16]) the two carbonyl ligands remain inequivalent while moving between rhodium atoms. Intramolecular

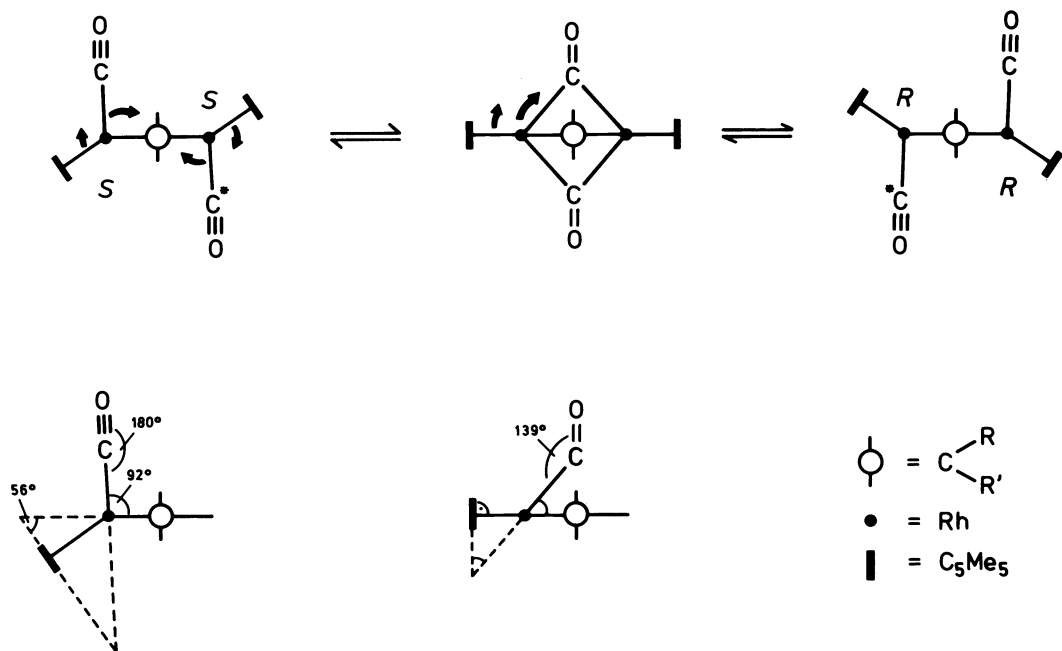


Figure 4

isomerization of the triple bridged primary products 5 to their single bridged counterparts 6 is largely controlled by steric factors. If bulky methylene ligands are present, this process is completely suppressed for a very simple reason: carbonyl bridge opening is accompanied by movement of the C_5Me_5 ligand from positions exactly perpendicular to the metal-metal vector (in 5) into positions above or below the Rh_2C plane (in 6). In the course of this ligand movement, the bulky C_5Me_5 rings further approach the methylene bridge. If we now have sterically demanding CRR' functions from the very beginning, the C_5Me_5/CRR' approach necessary for CO bridge opening is no longer possible.

Elimination of carbonmonoxide from the μ -methylene complexes 6 with concomitant formation of a rhodium-rhodium double bond does not involve significant concentrations of intermediates (Figure 5) and implies an interesting synthetic approach to multiply bridged dinuclear species having different methylene bridges. The only example of consecutive carbene addition known to date started from compound 4 [17]: diphenylmethylene transfer from the diazo compound gives 8 which undergoes decarbonylation in boiling tetrahydrofuran (95 %) to give 9; exposure of the latter compound to excess diazomethane finally produces the mixed $CH_2/C(C_6H_5)_2$ derivative 10, with the overall yield of this sequence amounting to as much as 91 %. Compound 10 constitutes the first known organometallic molecule containing structurally different methylene bridges; its stereochemistry is characterized by R,S - (or S,R -) configuration of the metal centers ("meso" form) (Scheme III). In a logical continuation of this work, carbene addition to an iron-iron double bond has also been exploited for the simple synthesis of the first μ -methylene complex in the nitrosyl series. The readily available μ -nitrosyl iron complex $[(\eta^5-C_5H_5)Fe(\mu-NO)]_2$ exhibits the same structural features as the rhodium dimer 4 and reacts with diazomethane

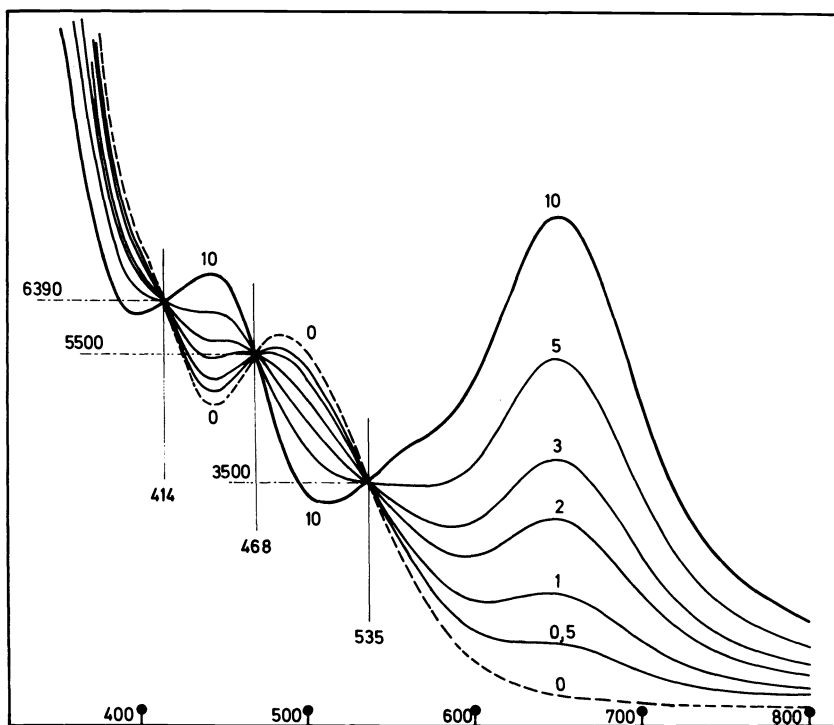
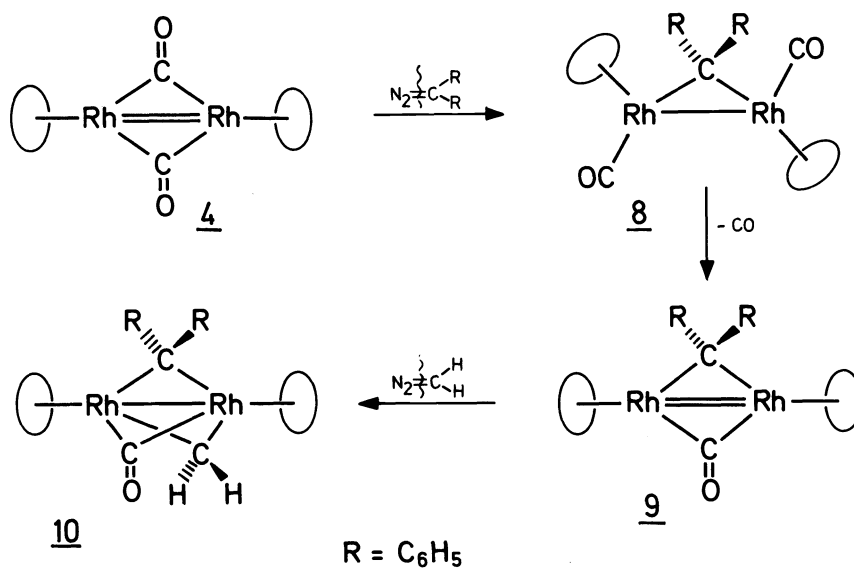
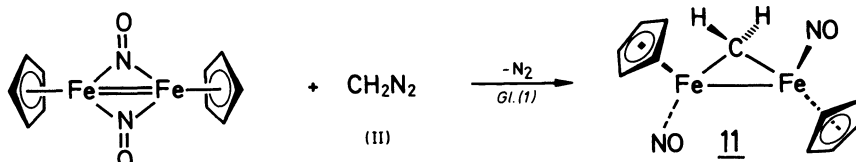


Fig. 5. Time-dependent UV/VIS spectra of the photodecarbonylation process $8 \rightarrow 9$ (tetrahydrofuran; room temp.). The dashed contour corresponds to cpd. 8 [16].

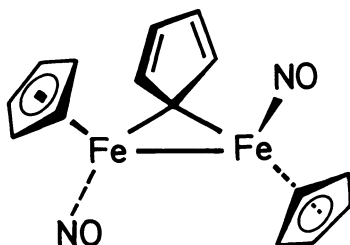


Scheme III

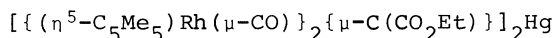
in the temperature range $-80 \dots +25^\circ C$ to give the expected μ -methylene derivative 11 (Scheme IV) [18]. Diazocyclopentadiene forms the μ, η^1 -cyclopentadienylidene complex of composition $(\mu-C_5H_4)[(\eta^5-C_5H_5)Fe(NO)]_2$ [19]. As expected, both molecules do not isomerize to nitrosyl-bridged species nor do they undergo clear thermolysis. Other iron and cobalt complexes of this type have been synthesized along similar lines [19,20]. The dependence of nitrosyl- and carbonyl-bridge



Scheme IV



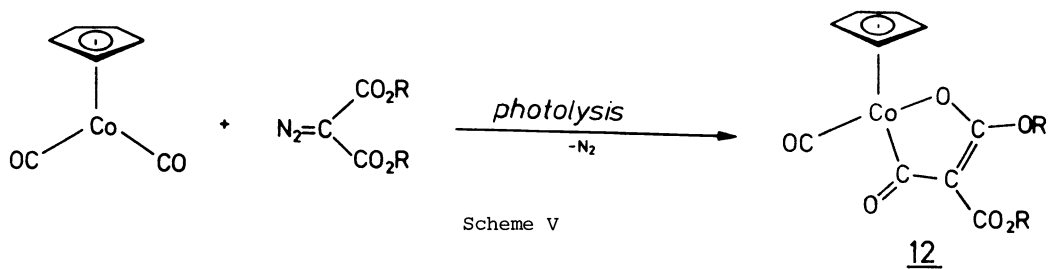
stability of μ -methylene complexes was found to increase with electron density provided by other peripheral ligands. Isoelectronic compounds in the Fe/NO- and Co/CO-series appear to adopt the same structures in terms of the coordination mode of NO and CO, respectively. μ -Methylene cobalt complexes having additional carbonyl bridges are more reluctant to CO bridge opening than their rhodium analogues [20]. The first example of heavy metal substituted dimetalla-cyclopropanes was achieved by reacting the α -mercuriodiazoalkane $\text{Hg}[\text{C}(=\text{N}_2)\text{CO}_2\text{-C}_2\text{H}_5]_2$ with the rhodium dimer 4 [21]. There is no doubt that the product,



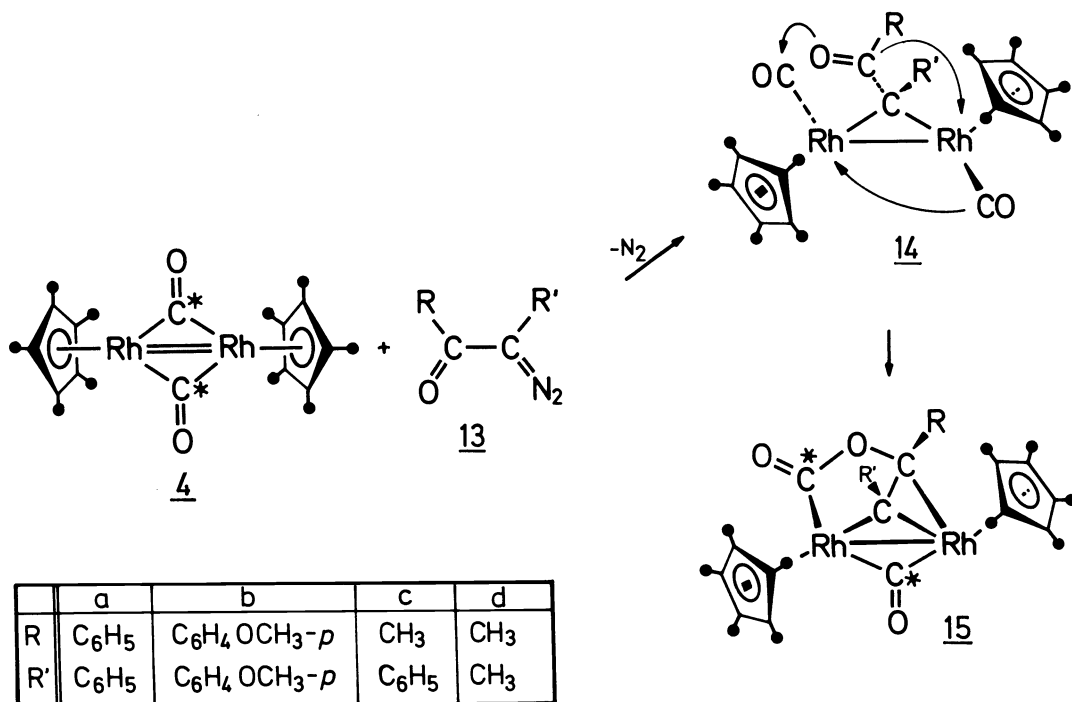
will serve as a useful substrate for μ -methylene bridge homologation.

CYCLOADDITIONS OF KETOCARBENES TO METALCARBONYLS

Open-chained α -ketodiazalkanes, $\text{R-C}(=\text{N}_2)\text{-C}(=\text{O})\text{R}'$, have long been known as useful starting materials for high-yield syntheses of the corresponding ketenes, $\text{RR}'\text{C}=\text{C}=\text{O}$ [22]. These ketenes arise from the facile *Wolff*-rearrangement of ketocarbenes derived from their diazo precursors by loss of N_2 , a process favored over other reactions such as 1.3-dipolar cycloadditions. In their reactions with some metalcarbonyls, however, α -ketodiazalkanes were found to cleanly form stable {2+3}-cycloaddition products under either photochemical or thermal conditions. Thus, photolysis of the cobalt half-sandwich complex 11 in the presence of diazomalonates gives the five-membered, strictly planar metallacycles 12, compounds which are not presently accessible by other means [23]. Whereas a new carbon-carbon bond is formed in this case (Scheme V), with concomitant complexation of a keto group, the opposite orientation of 1.3-cycloaddition occurs when the rhodium dimer 4 is allowed to react with α -diazoketones such as azibenzil (13a) (Scheme VI). Keeping in mind that carbene addition to the metal-metal "double bond" of 4 represents an exceptionally straight-forward synthetic method of constructing methylene bridges, we actually expected the formation of compounds 14 having carbonyl-flanked methylene groups. Nevertheless, nearly quantitative yields of the cyclic isomers 15 are formed,



Scheme V



Scheme VI

even under very mild reaction conditions. A typical structure of one of these molecules (Fig. 6) shows that nucleophilic attack of the peripheral keto function at a metalcarbonyl group has occurred subsequent to complexation of the ketocarbene unit to the metal-metal double bond. The C(1)—O(2) bond thus formed completes a five-membered non-planar metallacycle defined by Rh(1), C(1), O(2), C(3), and C(4). In addition, the ketocarbon atom C(3) coordinates to the second metal center Rh(2) while the remainder CO group C(5)—O(5) unsymmetrically bridges the dimetallic framework. ¹³C labelling experiments, as indicated in Scheme VI, have demonstrated that the keto functionalities of the diazo substrates 13 retain their identity [24]. However, the bridgehead carbon C(4) has lost its methylene character, one of the important results of cycloaddition reactions of this kind. Note that the dihedral angle between the "methylene" planes Rh(1),C(4),Rh(2) and C(3),C(4),C(41) (113.2°) no longer meets the "orthogonality criterion" of true μ -methylene complexes! Steric constraints resulting from both the five-membered metallacycle and the π -olefin type coordination through C(3) and C(4) are very likely responsible for the considerable deviation from tetrahedral geometry around C(4).

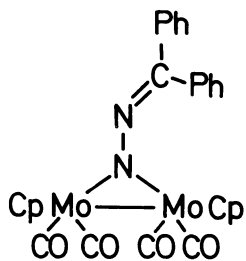
The following observations suggest the intermediate occurrence of the μ -methylene derivatives in the construction of the above-mentioned metallacycles:

- The terminal CO ligands of stable, structurally well characterized type-14 methylene compounds and the keto groups directly attached to the bridgehead carbon are in close proximity to each other. This is even true for the carbonyl bridged isomers of 14. μ -Bis(methoxycarbonyl)methylene- and μ -indanedion(1.3)-ylidene(2) derivatives may be quoted as striking examples to illustrate this effect.
- With the cobalt analogue $[(\eta^5\text{-C}_5\text{Me}_5)\text{Co}(\mu\text{-CO})]_2$ (16) (see Scheme VI), no metallacycle formation is observed; rather the μ -ketomethylene complexes 14 (Co in place of Rh) are the exclusive products (isolated yields > 90 %).

Again, nothing is known about possible diazoalkane complexation prior to loss of nitrogen. On the other hand, a simple rationale for the different product pattern from 16 and 4 - methylene bridge versus metallacycle - considers the fact that the carbon monoxide ligands in μ -methylene cobalt complexes appear less electrophilic (lower νCO frequencies!) than those of their rhodium congeners. Formation of metallacycles is not possible if the ketocarbene building block belongs to a rigid cyclic system, since in this case rotation around the C(3)-C(4)-bond, a prerequisite for cycloaddition, is not possible.

CARBENE ADDITION TO METAL—METAL "TRIPLE" BONDS

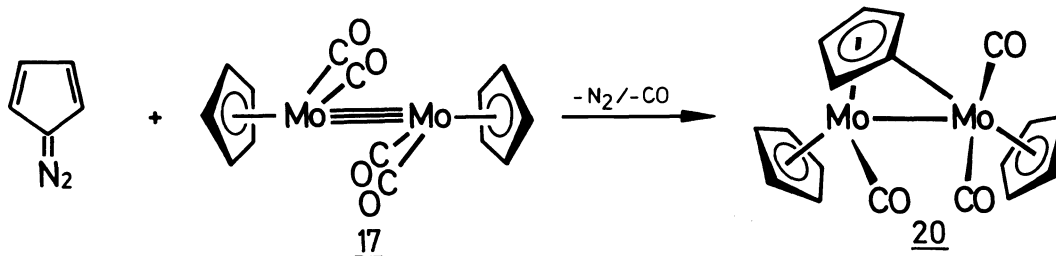
Let us now ask the question what happens if we react diazoalkanes with metal—metal "triple" bonds. Will *dimetallacyclopropenes* form? They should, provided both substrates bow to our simple formalism. The dimolybdenum compound $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2]_2$ (17) as one of the nicest examples of (electrophilic) metal—metal triple bonds amongst metallocarbonyls [25], generally displays high reactivity to diazo hydrocarbons. Diphenyldiazomethane promptly adds to the dimetal frame of 17 without loss of nitrogen. The diazoalkane complex 18 so obtained [26] structurally very much resembles other (di- and tri-nuclear) diazo bridged compounds [1]. However, the Mo=Mo double bond expected from formal reasons has not been retained, mainly due to the fact that the bridging nitrogen ligand acts as a four- rather than a commonly observed two-electron ligand *via* its terminal nitrogen atom. As judged on the basis of conventional electron-bookkeeping, nothing more than a Mo—Mo "single" bond has survived in the course of diazoalkane addition to the triple bond. This situation does not change when nitrogen departs at elevated temperatures,



Formula 18

leaving the diphenylmethylene complex $[\mu\text{-(C}_6\text{H}_5)_2\text{C}]\text{-Mo}_2\text{cp}_2(\text{CO})_4$ (19); the "methylene" ligand accomplishes a σ -alkyl/ π -allyl type four-electron system [26]. As a result, the dimetal frame once more escapes from maintaining a formal double bond.

Diazocyclopentadiene proceeds one step beyond simple carbene addition, in that one CO ligand is replaced with the C_5H_4 residue left from the organic substrate. Here, a compound of composition $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_3\text{-(C}_5\text{H}_4)$ (20) is formed in ca. 40 % yield (tetrahydrofuran, 25°) (equation below). An accurate X-Ray



structural determination revealed the "cyclopentadienylidene" ligand to act as a terminal-type σ -alkyl to the $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2$ fragment and, in addition, as aromatic η^5 -system bound to the remainder $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})$ unit (Figure 7). Exhausting its electronic capabilities, the unique cyclic ligand acts as a 6-electron ligand to the dimetal backbone. The latter has a metal-metal separation (309.8(0) pm) compatible with a Mo—Mo single bond [27]. The synthesis of dimetallacyclopropenes having M=M-double bonds thus remains a further challenge to the synthetic chemist.

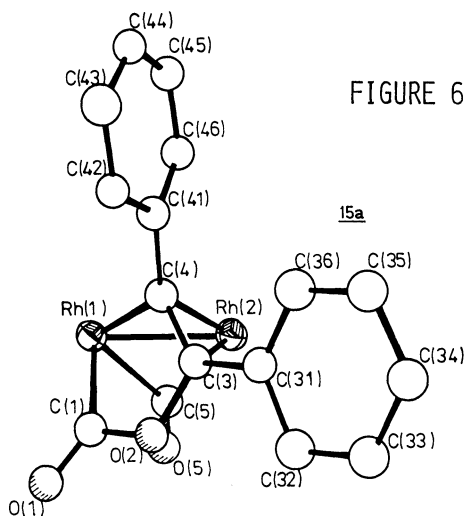


FIGURE 6

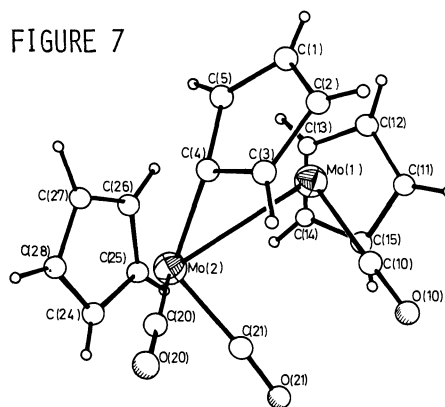


FIGURE 7

Figure 7. ORTEP representation of 20. Selected bond lengths [pm] and angles [deg]: Mo—Mo 309.8(0), Mo(2)—C(4) 211.1(4), Mo(1)—C(4) 222.4(4), Mo(1)—C(1) 230.4(4), Mo(1)—C(2) 231.5(4), Mo(1)—C(3) 225.0(4), Mo(1)—C(5) 226.4(4), Mo(1)—C(11–15) 228.3–232.5, Mo(2)—C(24–28) 233.2–239.1, C(1)—C(2) 139.7(6), C(2)—C(3) 142.4(6), C(3)—C(4) 144.2(6), C(4)—C(5) 145.1(6), C(5)—C(1) 141.7(6); Mo(1), C(4), Mo(2) 91.2(1), C(4), Mo(2), Mo(1) 45.9(2). For a brief discussion of the structure see Ref. [27].

Theory and Bonding of Dimetallacyclopropanes

Upon considering the structures of μ -methylene complexes, the important question arises as to whether the bridging CRR'-ligands are still carbenes, or alternatively: should they better be regarded as being derived from alkanes? From extended Hückel-type MO-calculations for the rhodium compound $(\mu\text{-CH}_2)[(\eta^5\text{-C}_5\text{H}_5)\text{-Rh}(\text{CO})]_2$ and comparison of this system with isolobal derivatives $(\text{Rh}(\text{CO})_2)^-$, CH^+ , $\text{cpRh}(\text{CO})$ in place of CH_2 , it appears that the methylene compound may best be viewed as to be composed of a CH_2 unit and the hypothetical $\text{cp}_2\text{Rh}_2(\text{CO})_2$

dimer having a Rh=Rh double bond, and the reader is reminded of the straightforward cyclopropanation reactions of metal-metal "double" bonds (see above). Apart from the σ -type bonding between the methylene group and the organometallic frame, the qualitative interaction scheme demonstrates the existence of a situation exactly corresponding to the *Walsh* description of cyclopropane, derived from an ethylene and a methylene structural unit [28,29]. Therefore, μ -methylene complexes very much resemble "dimetallacyclopropanes" which, in turn, are intermediate members of the series olefin complexes ("metallacyclopropanes"), μ -methylene complexes ("dimetallacyclopropanes"), and trinuclear metal clusters ("trimetallacyclopropanes"). Of importance to the bonding characteristics of the CH₂ unit is an electron transfer from the Rh—Rh σ -bond into an orbital containing a π_{xy}^* component and to the carbon atom. The formal metal—metal double bond thus becomes a "single bond"; in accord with NMR data [2], the carbon bridge exhibits far greater charge density than the carbene carbon of electrophilic *Fischer*-type carbene complexes $L_xM=CRR'$. The bonding scheme of the manganese compound $(\mu-CH_2)[(\eta^5-C_5H_4CH_3)Mn(CO)_2]_2$ again was constructed from the CH₂ orbitals and those of the hypothetical $cp_2Mn_2(CO)_4$ dimer [30]. In the first step of this analysis, the frontier orbitals of each $cpMn(CO)_2$ portion simply combine into the corresponding bonding and antibonding combinations. The strongest combination occurs between the d_{z^2} -type orbitals which are each directed towards the same region. As in the bonding of carbenes with metals, the methylene group has a filled orbital (a_1) that can act as a sigma donor to the metal. It also has an empty p_π orbital (b_1) that can accept π -electron density from the metals. The interaction of these orbitals with those of the dinuclear $cp_2Mn_2(CO)_4$ fragment are shown in Fig. 8. The bonding

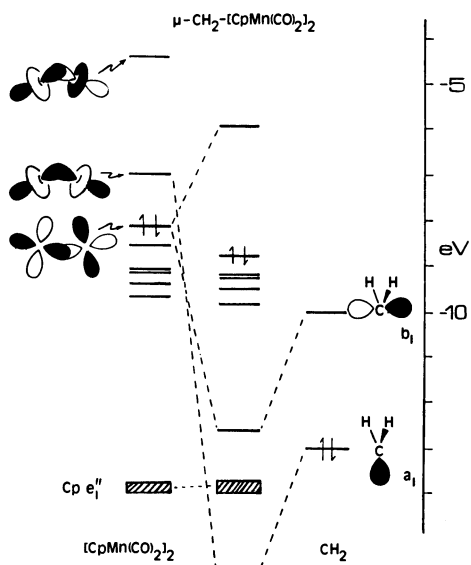


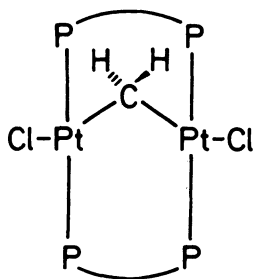
Figure 8

LUMO of the dinuclear fragment has the correct symmetry, is relatively low in energy, and has a nearly ideal spatial distribution for accepting electron density from the donor orbital of the CH₂ group. Similarly, the HOMO of the dinuclear framework is well-situated for donating electron density into the

empty p_{π} -orbital of the methylene group. The $\mu\text{-CH}_2$ ligand was shown to act as an overall better acceptor than donor in this system. Fenske-Hall calculations place the originally empty p_{π} -orbital of the CH_2 -group slightly below the filled metal levels. Because of this ordering the donation into this p_{π} -orbital should effectively be described as a charge transfer from the (antibonding) HOMO of the dinuclear fragment to the methylene group. This results in the high negative charge on the CH_2 carbon; the electron density value calculated amounts to $-0.526 e$ which is in reasonable agreement with the numerical result obtained from an experimental electron density determination [5]. Both electron donation from the methylene unit and its electron acceptor interaction tend to produce a net metal—metal bond. A comparative study of the unknown monomeric counterpart ($\eta^5\text{-C}_5\text{H}_5$) $\text{Mn}(\text{CO})_2(=\text{CH}_2)$ indicates that increased stability is gained by the additional metal bond formation which, in turn, seems to be the driving force of the formation of dimer favoured over the mononuclear system [30]. In agreement with the molecular orbital descriptions given for $(\mu\text{-CH}_2)[(\eta^5\text{-C}_5\text{H}_5)\text{-Rh}(\text{CO})_2]$ [28,29] and $(\mu\text{-CH}_2)[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2]$ [31], a 6-electron/3-center description similar to cyclopropane may be used to summarize the bonding situation of the Mn-C-Mn triangle. Hofmann has emphasized the close analogy between the bonding scheme of dimetallacyclopropanes and related molecules having other π -acceptor ligands in place of the CRR' -bridge (e.g., carbonmonoxide, vinylidenes, etc.) [28].

The Geometry of the Methylene Bridge

The occurrence of metal-metal interactions has been shown to enhance the stability of methylene bridges [30]. As a matter of fact, the entire set of μ -methylene transition metal complexes reveals quite short metal-metal separations, covering the range 245...320 pm, for $\text{M} = \text{Cr}, \text{Mo}, \text{W}, \text{Mn}, \text{Re}, \text{Fe}, \text{Ru}, \text{Os}, \text{Co}, \text{Rh},$ and Pt [1]. The single exception of this rule is Puddephatt's platinum CH_2 complex 21 [31], and we may learn from this example that a $\text{M-CH}_2\text{-M}$ linkage can possibly survive if chelating ligands span over both metals and, thus, prevent the bridging system to fall apart. Ligand bridging, possibly via semibridging CO's may also account for the exceedingly high stability of the radical cation $[(\mu\text{-CH}_2)\{(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2\}_2]^+$ cleanly obtained by electrochemical oxidation of its neutral precursor, in a fully reversible process. The Mn-Mn bond is not maintained upon oxidation, since the unpaired electron is localized at just one metal center [32]. A systematic survey of about 50 structures known to date permits the following general statements with regard to the common structural features of dimetallacyclopropane-type molecules:



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(a) *The symmetrical methylene (alkylidene) bridge* represents the prevalent geometry. However, asymmetric bridging has been encountered in a few heterodinuclear μ -methylene complexes. Also, carbonyl semibridging occasionally occurs along with asymmetric methylene bridging. It is generally observed that the metal—metal distances are slightly longer

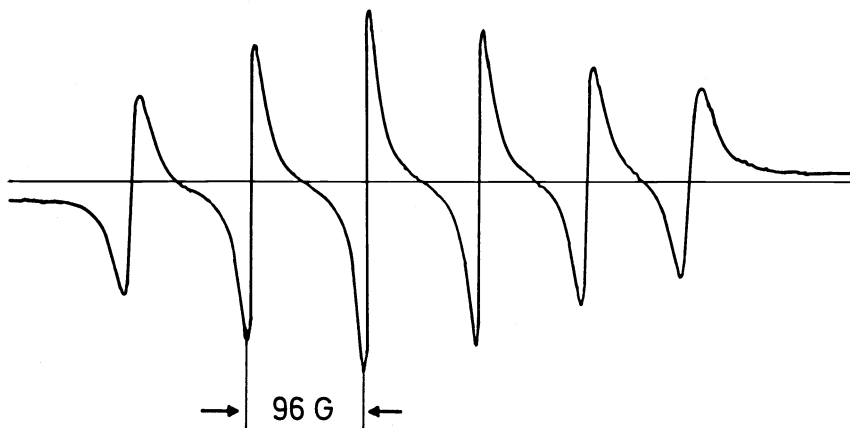
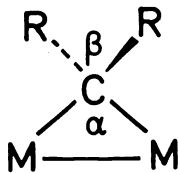


Fig. 9. ESR spectrum (in CH_3CN ; room temp.) of the radical cation $[(\mu\text{-CH}_2)\{(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2\}_2]^+$ (B.Geiger et al., unpublished results on the electrochemistry of μ -methylene complexes)

(av. ca. 15 pm) than the values calculated from the *Pauling* covalent radii for two "single bonded" metal atoms.

(b) The "internal" angle $\alpha[\angle(\text{M},\text{C},\text{M})]$ around the methylene carbon atom is principally very acute and shows little variation with the nature of metals and the carbene substituents. Typically, these angles fall in the range $76\text{--}81^\circ$, and no case is known in which the quantities are smaller or greater than $81\pm 7^\circ$. The bonding metal-metal interaction thus appears to be great enough to distort the angle to a significantly more acute one than expected for the tetrahedral result ($109^\circ 28'$). It is obvious that the metal-metal distance required for a bonding interaction determines the magnitude of α to a large extent.



(c) The "external" angle $\beta[\angle(\text{R},\text{C},\text{R}')]]$ defined by the bridgehead carbon and the non-metal atoms directly attached to it is far greater than α . The range $104\text{--}110^\circ$ is typical of dimetallacyclopropanes, but considerable variations within $105\pm 13^\circ$ are not unusual [1].

(d) Substitution of a methylene bridge by carbon monoxide does hardly effect the geometrical details of the three-membered framework.

Slight differences between these two systems are found to be consistent with the following general trends: (1) $\text{M},\text{CO},\text{M}$ angles are greater ($2\text{--}10^\circ\text{C}$) than $\text{M},\text{CRR}',\text{M}$ angles; (2) $\text{M}\text{--}\text{CO}$ distances are somewhat shorter ($2\text{--}12$ pm) than $\text{M}\text{--}\text{CRR}'$ distances; (3) metal-to-metal bonds are slightly longer (<10 pm) when bridged by CO rather than by a methylene function. This analogy still holds for apparently even more remote systems, e.g. $\mu\text{-SO}_2$ complexes. Thus, barely any structural difference is found along the isoelectronic series $(\mu\text{-X})[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})_2]$ ($\text{X} = \text{CH}_2, \text{CO}, \text{SO}_2$; [33]), with the small deviations observed for SO_2 being caused by the greater atomic radius of sulfur as compared with that of carbon. It is no longer surprising then, that μ -vinylidenes having an additional π^* -acceptor orbital orthogonal to the plane of the three-membered ring hardly depart from the typical methylene bridge geometry [1].

Spectroscopic Diagnosis of the Methylene Bridge

How can we discriminate terminal and bridging methylene groups if structural data are not available? Moreover, is spectroscopy a reliable tool to figure out whether a metal-to-metal bond is present in addition to methylene bridges? A survey of ^1H and ^{13}C NMR data has revealed a fairly safe NMR diagnosis [1,2] which often times allows unambiguous structural assignments:

(a) The metal-bound carbene- or alkylidene carbon atoms of the afore-mentioned classes of compounds resonate in ranges which are nicely separated from each other ($\delta^{13}\text{C}$; ppm):

$\text{M}=\text{CRR}'$ (A)	240...370
$\text{M}-\text{CRR}'-\text{M}$ (B)	100...210
$\text{M}-(\text{CRR}')_{\text{x}}-\text{M}$ (C)	0....10

The ^{13}C -NMR spectrum of a typical carbonyl μ -methylene complex is presented in Fig. 10. The alkane-diyl derivatives (type C) may even be distinguished from the closely related metal alkyls the chemical shifts of which latter compounds typically cover the δ -range -30...5. An average upfield shift of 100-200 pm is found for the carbene-carbon nuclei upon coordination of a mononuclear metalcarbene to another metal fragment. Note that the nucleophilic

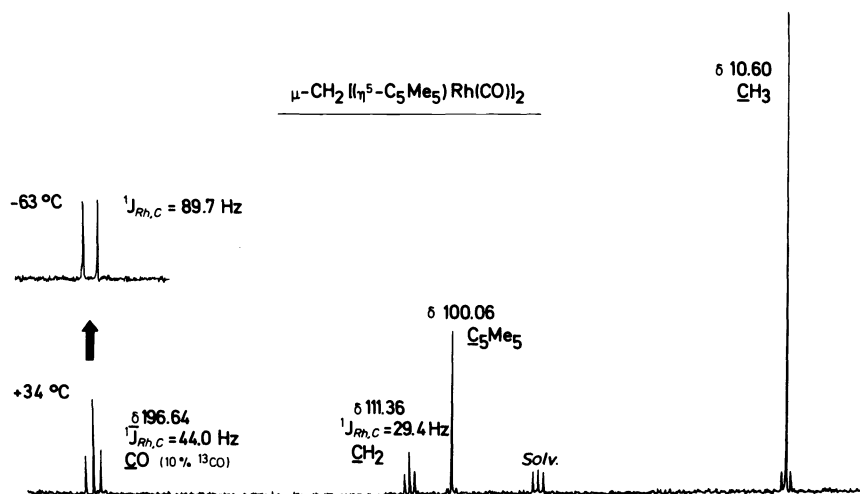


Figure 10. $\{^1\text{H}\}^{13}\text{C}$ -NMR spectrum of $(\mu\text{-CH}_2)[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})]_2$ (ca. 10 % ^{13}C -enriched sample; CD_2Cl_2 and CDCl_3) showing intramolecular CO-exchange at $+34^\circ\text{C}$ ($\Delta G^\ddagger = 13.0 \pm 1.5$ Kcal/mol (in $[\text{D}_8]\text{-THF}$) for CO scrambling [16]).

metal carbene $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ta}(\text{=CH}_3)(\text{CH}_3)$ (δ_{CH_2} 228; δ_{CH_2} -0.22) is one of the very few mononuclear metalcarbenes which are close to μ -methylene compounds in terms of their ^{13}C NMR chemical shifts.

(b) If the bridging methylene functions bear hydrogen(s), ^1H NMR spectroscopy at least enables us to tell whether an additional metal-metal bond is present or not: alkane-diyl compounds (type C) very much resemble metalalkyls with respect to their CH_x chemical shift range. Mononuclear metalcarbenes (A) and μ -methylene complexes (B), respectively, cannot be identified to a reliable degree on the basis of their ^1H NMR data, although methylene bridge hydrogens generally experience significant upfield shifts. The following δ_{CHR} -pattern (ppm)

should be considered along with the ^{13}C NMR data:

$\text{M}=\text{CHR}$ (A)	9...11
$\text{M}-\text{CHR}-\text{M}$ (B)	5...11
$\text{M}-(\text{CHR})_x-\text{M}$ (C)	1...3
$\text{M}-\text{CHRR}'$	1...-1

The fact that both the methylene carbon and the μ -alkylidene α -hydrogen resonances are shifted upfield from the corresponding metalcarbene resonances (type A) reflects, in a rough approximation, much higher electron-density in bridging carbene groups. Accordingly, additional upfield shifts of alkylidene α -hydrogen resonances are observed when electron-donating substituents are introduced into the peripheral ligands of dimetallacyclopropanes (e.g., substitution of C_5Me_5 for C_5H_5). The magnitude of hydrogen-hydrogen coupling [$^2\text{J}(\text{H},\text{H})$] in CH_2 -bridged compounds once again reminds us of cyclopropanes, but no trends are apparent from the hitherto limited set of data [1]. The same is true for carbon-hydrogen coupling [$^1\text{J}(\text{C},\text{H})$] which was found to amount to ≈ 145 Hz in some $\mu\text{-CH}_2$ rhodium and osmium complexes [1].

It is to be noted in this context that methylene bridges have never been observed to share fluxional behaviour of other peripheral ligands. Furthermore, methylene bridge-opening in the absence of other reagents (H_2 , ethylene etc.) is as yet an unknown process.

Reactivity of the Methylene Bridge

Stability against thermolysis and photolysis is one of the most striking features of dimetallacyclopropanes, especially of those pertaining to the carbonyl and cyclopentadienyl/carbonyl series. For example, the rhodium methylene complex $(\mu\text{-CH}_2)[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})]_2$ resists temperatures of 80°C over a two days' period (boiling benzene) or prolonged u.v. irradiation and is thus quite robust compared with the carbonyl analogue $(\mu\text{-CO})[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})]_2$. This and many other examples of this kind reflect our feeling that any μ -methylene complex should be accessible and stable if the corresponding μ -carbonyl is known. There is so far not a single exception from the rule that a μ -methylene complex is at least not less stable than its μ -carbonyl counterpart. Furthermore, methylene bridging is favored over carbonyl bridging the more electron-releasing peripheral ligands are present. Despite their thermodynamic stability, dimetallacyclopropanes proved to be quite reactive when treated with appropriate reagents, specifically unsaturated hydrocarbons and protic acids [2]. Of particular interest to catalysis-related questions (*Fischer-Tropsch* process) are reactions with hydrogen and olefins. Here, olefin insertion into the methylene bridge seems to be a facile process [34]. Protonation of an electron-rich metal-to-metal bond is greatly preferred over proton attack at the methylene bridge; μ_3 -methylidyne complexes are formed *via* both intra- and intermolecular pathways [35,36]. By way of contrast, protonation of the methylene carbon comes to the fore if an electron-rich metal-to-metal bond is either not present or else sterically not available, as is evident from comparison with results obtained by *Wilkinson* et al. [37]. A more thorough discussion of methylene bridge reactivity has been given in our recent review [1].

One of the major preparative challenges remaining in the relatively new field of dimetallacyclopropane chemistry undoubtedly involves the synthesis of heavy metal substituted methylene bridges that provide the starting point for both methylene bridge homologation and the preparation of carbyne and carbide clusters. In addition, bridge-opening processes induced by unsaturated organic substrates await further mechanistic elucidation, since these reactions seem to represent simple molecular models for surface reactions of methylene groups [38]. In this context, we consider reduction of metal-attached carbon monoxide to a methylene bridge [39] a new synthetic approach worthwhile of being studied in more detail and with other metalcarbonyls.

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