Carbido Complexes

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Carbon–Carbon Bond Formation at a Neutral Terminal Carbido Ligand: Generation of Cyclopropenylidene and Vinylidene Complexes**

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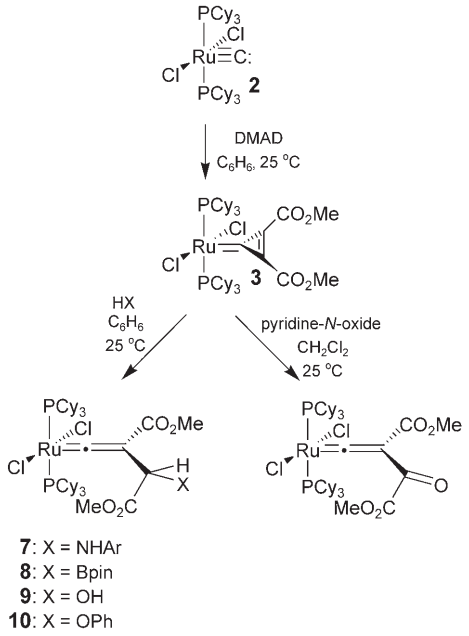
Olefin metathesis is an important tool for organic and polymer synthesis.[1] However, some key functional groups are not tolerated even by Ru-based catalysts.[2] We recently showed that vinyl esters can deactivate [Ru(CHPh)-$(PCy_3)_2Cl_2$] (**1**)[3] by quantitative formation of [Ru(C)-$(PCy_3)_2Cl_2$] (**2**)[4,5] A rare neutral terminal carbido complex,[4–7] **2** is surprisingly stable and has few reported reactions.[5–7] However, protonation of **2** by strong acid yields catalysts that rapidly initiate olefin metathesis.[7] Thus, **2** is both a precursor to and a decomposition product of olefin metathesis catalysts. We see **2** as a potential source of a C_1 fragment. Accordingly, we describe herein the first C–C bond-forming reaction of this unusual compound.

The terminal carbido ligand in **2** is a poor nucleophile, as shown by its failure to react with MeI, MeCOCl, and $PhCH_2Br$. Although **2** does not react with a variety of alkenes and alkynes (see the Supporting Information), it reacts cleanly with $MeO_2CC{\equiv}CCO_2Me$ (dimethyl acetylenedicarboxylate, DMAD) over 4 h in C_6H_6. A new blue-purple complex, **3**, is formed as the carbido signal for **2** (^{13}C NMR: $\delta = 471.8$ ppm) is replaced by a new signal at $\delta = 195.7$ ppm. The ^1H NMR spectrum evinces formation of a 1:1 adduct of **2** with DMAD. Formation of the cyclopropenylidene complex [Ru{=$CC_2(CO_2Me)_2$}$(PCy_3)_2Cl_2$] (Scheme 1) accounts for these observations. Several cyclopropenylidene complexes exist. Unlike **3**, however, the cyclopropenylidene units in these complexes are substituted by phenyl or electron-donating groups.[8–23] [Ru(C)(H_2IMes)$(PCy_3)Cl_2$] (**4**; H_2IMes = 4,5-dihydro-1,3-bis(mesityl)imidazol-2-ylidene) reacts similarly with DMAD, but the reaction is not clean since the product reacts further with DMAD before all of **4** has been consumed. However, **4** reacts more cleanly with $HC{\equiv}CCO_2Me$ (see the Supporting Information).



Scheme 1. Formation of **3** and ring-opening reactions. HBpin = pinacolborane, Ar = 3,5-$Me_2C_6H_3$.

Single-crystal X-ray diffraction confirmed the structure of **3**.[24] Figure 1 depicts a thermal ellipsoid plot of one of the two chemically equivalent but crystallographically independent molecules of **3** in the crystal. The data establish the expected connectivity in **3**, but the large uncertainty associated with the Ru=C bond length of 1.846(10) Å precludes comparison with those in related alkylidene complexes. The cyclopropenylidene ring lies in the Cl-Ru-Cl plane. The structure shows significant bond localization in the cyclopropenylidene fragment. These distances closely resemble those observed in free

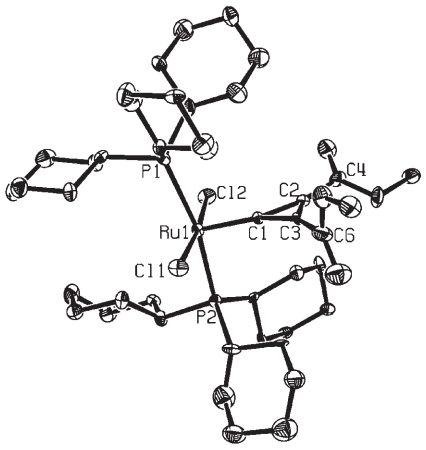


Figure 1. X-ray crystal structure of **3** (50% thermal ellipsoids). Selected bond lengths [Å] and angles [°]: Ru1-C1 1.846(10), Ru1-Cl1 2.389(3), Ru1-Cl2 2.402(3), Ru1-P1 2.407(3), Ru1-P2 2.390(3), C1-C2 1.410(13), C1-C3 1.425(14), C2-C3 1.300(14); C1-Ru1-Cl1 91.6(3); C1-Ru1-Cl2, 95.3(3), C1-Ru1-P1 97.0(3), C1-Ru1-P2 95.8(3), C2-C1-C3 54.6(7), C1-C2-C3 63.3(7), C1-C3-C2 62.1(7).

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Supporting information for this article (including complete experimental details for new reactions) is available on the WWW under http://www.angewandte.org or from the author.

$C_3(NiPr_2)_2$ (**5**)[25] and in other cyclopropenylidene complexes.[9,14–23]

The formation of **3** from **2** is interesting because the cyclopropylidene complex $[Ru\{=CC_2H_2(CO_2Me)_2\}(PCy_3)_2Cl_2]$ (**6**) is not observed as an intermediate when **2** is formed from **1** by reaction with Feist's ester.[4] Addition of 2 equivalents or less of PCy_3 to $[Ru\{=CC_2H_2(CO_2Me)_2\}(PPh_3)_2Cl_2]$ similarly yields **2**. In this case, too, **6** is not seen.[6]

The ^{13}C NMR shifts of the ring atoms in **3**, 195.7 and 162.2 ppm, closely resemble those observed for **5**[25] but less so other cyclopropenylidene complexes, for which some cyclopropenium character is often invoked.[14–23] Unlike **1**, **3** does not react appreciably with common olefins or alkynes, although under some conditions small amounts of **2** are formed, suggesting reversibility of the **2**→**3** transformation (see the Supporting Information). However, several reagents effect 1,1-addition of HX to the ring to form vinylidene complexes **7**–**10**; reaction with pyridine-*N*-oxide similarly yields **11** (Scheme 1). Cyclopropenium character could account for the observed reactivity, as all the reagents shown can act first as nucleophiles; however, there may be other explanations.

The structure of one vinylidene complex, $[Ru\{=C=C(CO_2Me)CH(NHAr)CO_2Me\}(PCy_3)_2Cl_2]$ (**7**, Ar = 3,5-$Me_2C_6H_3$), was determined by single-crystal X-ray diffraction.[26] The vinylidene unit is apical in square-pyramidal **7** (Figure 2).

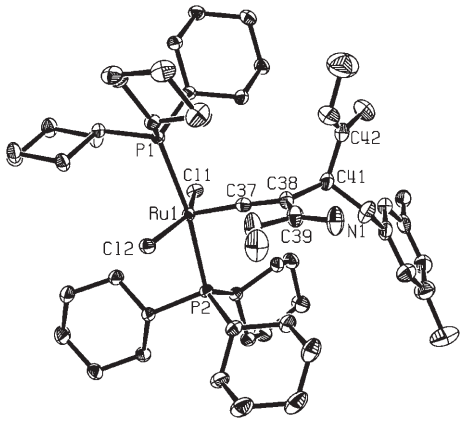

Figure 2. X-ray crystal structure of **7** (50% thermal ellipsoids). Selected bond lengths [Å] and angles [°]: Ru1-C37 1.7458(17), Ru1-Cl1 2.3441(4), Ru1-Cl2 2.3454(4), Ru1-P1 2.4405(4), Ru1-P2 2.4098(4), C37-C38 1.344(2); C37-Ru1-Cl1 105.16(5), C37-Ru1-Cl2 100.68(5), C37-Ru1-P1 95.78(5), C37-Ru1-P2 93.39(5), Ru1-C37-C38 176.16(14), C37-C38-C39 118.76(16), C37-C38-C41 121.94(16), C39-C38-C41 119.23(15).

Ruthenium vinylidenes are useful as catalysts and catalyst precursors for olefin metathesis, alkyne dimerization, and other reactions.[27,28] Like the "parent" vinylidene complex $[Ru(=C=CH_2)(PCy_3)_2Cl_2]$,[3] **7**–**11** do not catalyze the ring-closing metathesis of diethyl diallylmalonate, but they do polymerize norbornene.

In summary, terminal carbido complex **2** undergoes [2+1] addition with DMAD to yield the cyclopropenylidene complex **3**. Complex **4** reacts similarly with $HC{\equiv}CCO_2Me$ in the first C–C bond-forming reactions reported for neutral terminal carbido complexes. Protic reagents HX (X = OH, OPh, $NH(3,5\text{-}Me_2)C_6H_3$) as well as pinacolborane add in a 1,1 manner to one of the distal ring C atoms in **3**, forming vinylidene complexes **7**–**11** in high yield. We are currently exploring the reactivity of **7**–**11** as well as seeking a means of regenerating a metathesis-active alkylidene complex or the carbide complexes **2** and **4**.

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[24] Crystal data for **3**·1.5 CH_2Cl_2: $C_{44.50}H_{75}Cl_5O_4P_2Ru$, monoclinic, $P2_1/c$, $a = 11.926(2)$, $b = 18.555(3)$, $c = 45.638(8)$ Å, $\beta = 96.800(3)°$, $V = 10028(3)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.344$ g cm^{-3}, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $T = 123(2)$ K, 43778 measured reflec-

tions, 8524 unique ($R_{int} = 0.1875$), 4942 reflections with $I_{net} > 2.0(I_{net})$, $\mu = 0.681\ mm^{-1}$, min/max transmission = 0.8758 and 0.9412, $R1$ ($I > 2\sigma$) = 0.0775, $wR2 = 0.1954$, GoF = 1.066, no. of parameters = 1056, final difference map within 1.008 and $-1.258\ e\ Å^{-3}$. CCDC-604841 (**3**·1.5 CH_2Cl_2) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[26] Crystal data for **7**: $C_{51}H_{83}Cl_2NO_4P_2Ru$, monoclinic, $P2_1/c$, $a = 15.5355(8)$, $b = 18.9133(10)$, $c = 17.5169(9)$ Å, $\beta = 97.403(1)°$, $V = 5104.0(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.312\ g\,cm^{-3}$, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $T = 123(2)$ K, 101 108 measured reflections, 12 702 unique ($R_{int} = 0.0321$), 11 419 reflections with $I_{net} > 2.0(I_{net})$, $\mu = 0.518\ mm^{-1}$, min/max transmission = 0.8197 and 0.8602, $R1$ ($I > 2\sigma$) = 0.0295, $wR2 = 0.0740$, GoF = 1.059, no. of parameters = 554, final difference map within 0.885 and $-0.727\ e\ Å^{-3}$. CCDC-604842 (**7**) contains the supplementary crystallographic data for this paper. Data can be obtained as in Reference [24].

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