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Synthesis and Reactivity of Ruthenium Allyl Carbene Complexes. C−H Activation/Dehydrogenation of a Cyclohexyl Substituent in PCy_3

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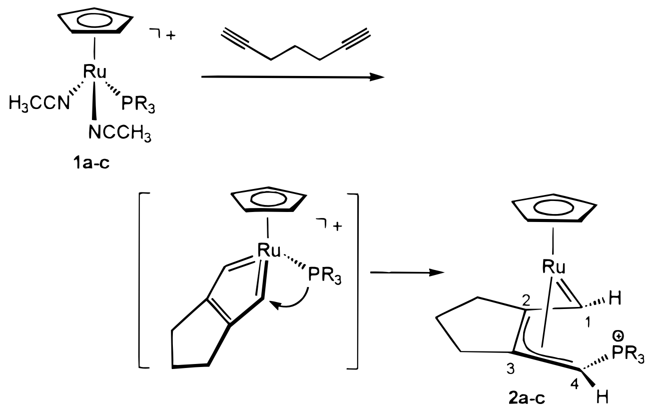
Summary: The complexes $[RuCp(PR_3)(CH_3CN)_2]PF_6$ (R = Me, Ph, Cy) react with 1,6-heptadiyne and HC≡CR′ (R′ = Ph, C_6H_9, n-Bu, H), most likely via a ruthenacyclopentatriene intermediate, to give the ruthenium allyl carbene complexes $[CpRu({=}CH\text{-}\eta^3\text{-}C(CH_2)_3CCHPR_3)]PF_6$ and $[CpRu({=}C(R')\text{-}\eta^3\text{-}CHC(R')CHPMe_3)]PF_6$, respectively. In the case of R = Cy, the allyl carbene complex rearranges to afford the complex $[CpRu(\eta^3\text{-}CH_2C(CH_2)_3\text{-}CCH_2PCy_2(\eta^2\text{-}C_6H_9)]PF_6$, featuring an η^2-coordinated cyclohexenyl ligand. This reaction involves dehydrogenation of one cyclohexyl substituent of the phosphine ligand.

Transition-metal complexes having a vacant coordination site or bearing weakly coordinating ligands are known to have a rich chemistry with alkynes to give, for instance, vinylidene complexes,[1] metallacyclopentadienes,[2] and in some cases metallacyclopentatrienes.[3] All these species are of considerable interest, because of being reactive intermediates in organic and organometallic synthesis as well as in catalytic processes, e.g., the polymerization and cyclization of alkynes. We have recently described the synthesis of the labile complexes $[RuCp(PR_3)(CH_3CN)_2]PF_6$ (R = Me (**1a**), Ph (**1b**), Cy (**1c**))[4] which serve as synthetic equivalents for the 14-electron fragment $[RuCp(PR_3)]^+$. In this communication we report that the reaction of **1a**−**c** with 1,6-heptadiyne and HC≡CR′ (R = Ph, C_6H_9, *n*-Bu, H) results in the formation of ruthenium allyl carbene complexes rather than ruthenacyclopentadiene or ruthenacyclopentatriene complexes. We further demonstrate that ruthenium allyl carbene complexes are acting as pseudo-16e species, reacting with both nucleophiles and electrophiles and being able to dehydrogenate alkyl groups of bulky phosphine ligands.

Scheme 1



Treatment of **1a**−**c** with 1 equiv of 1,6-heptadiyne results in the formation of the dark red allyl carbene complexes $[CpRu({=}CH\text{-}\eta^3\text{-}C(CH_2)_3CCHPR_3)]PF_6$ (**2a**−**c**) in essentially quantitative yields, as monitored by ^1H NMR spectroscopy (Scheme 1). Unfortunately, no intermediate could be detected. Preliminary stopped-flow studies revealed that the rate-determining step is the dissociation of the first acetonitrile ligand in **1**. The CH_3CN self-exchange in **1** has been recently studied by NMR spectroscopy.[4] The identity of **2a**−**c** was established by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy and, in the case of **2a** and **2b**, also by elemental analysis.[5] The ^1H NMR spectrum of **2a** exhibits a low-field resonance of the carbene hydrogen atom H^1 at 12.27 ppm and a signal for the allyl proton H^4 at 5.27 ppm (d, $^2J_{HP} = 8.4$ Hz). The most characteristic features in the $^{13}C\{^1H\}$ NMR spectrum are a low-field resonance

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(3) For metallacyclopentatriene complexes see: (a) Albers, M. O.; deWaal, P. J. A.; Liles, D. C.; Robinson, D. J.; Singleton, E.; Wiege, M. B. *J. Chem. Soc., Chem. Commun.* **1986**, 1680. (b) Gemel, C.; LaPansée, A.; Mauthner, K.; Mereiter, K.; Schmid, R.; Kirchner, K. *Monatsh. Chem.* **1997**, *128*, 1189. (c) Pu, L.; Hasegawa, T.; Parkin, S.; Taube, H. *J. Am. Chem. Soc.* **1992**, *114*, 2712. (d) Hirpo, W.; Curtis, M. D. *J. Am. Chem. Soc.* **1988**, *110*, 5218. (e) Kerschner, J. L.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1988**, *110*, 8235.

(4) Rüba, E.; Simanko, W.; Mauthner, K.; Soldouzi, K. M.; Slugovc, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1999**, *18*, 3843.

(5) Preparation and data for **2a**: A solution of **1a** (145 mg, 0.309 mmol) in acetone (5 mL) was treated with 1,6-heptadiyne (36 μL, 0.309 mmol) and was stirred for 45 min, whereupon the solution turned red. After the volume of the solution was reduced to about 1 mL, Et_2O (20 mL) was slowly added and a red microcrystalline precipitate was formed. The supernatant was decanted, and the solid was washed twice with Et_2O and dried under vacuum. Yield: 126 mg (85%). Anal. Calcd for $C_{15}H_{22}F_6P_2Ru$: C, 37.58; H, 4.63. Found: C, 37.34; H, 4.51. ^1H NMR (δ, CD_3NO_2, 20 °C): 12.27 (s, 1H, H^1), 5.27 (d, $J_{PH} = 8.4$ Hz, 1H, H^4), 5.19 (s, 5H), 2.90 (m, 2H, CH_2), 2.01 (m, 2H, CH_2) 1.43 (m, 2H, CH_2), 1.37 (d, $J_{PH} = 13.9$ Hz, 9H, Me). $^{13}C\{^1H\}$ NMR (δ, acetone-d_6, 20 °C): 236.5 (d, $J_{CP} = 6.2$ Hz, 1C, C^1), 115.2 (d, $J_{CP} = 3.5$ Hz, 1C, C^3), 83.1 (s, 5C, Cp), 70.4 (s, 1C, C^2), 36.5 (d, $J_{CP} = 4.9$ Hz, 1C, CH_2), 31.9 (d, $J_{CP} = 75.6$ Hz, 1C, C^4), 29.1 (s, 1C, CH_2), 25.1 (s, 1C, CH_2), 10.7 (d, $J_{CP} = 58.9$ Hz, 3C, Me). $^{31}P\{^1H\}$ NMR (δ, acetone-d_6, 20 °C): 31.7 (PMe_3), −142.7(PF_6). Complexes **2b**−**g** have been prepared analagously. However, **2c** is not stable and rearranges to give **5**.

10.1021/om9905409 CCC: $18.00

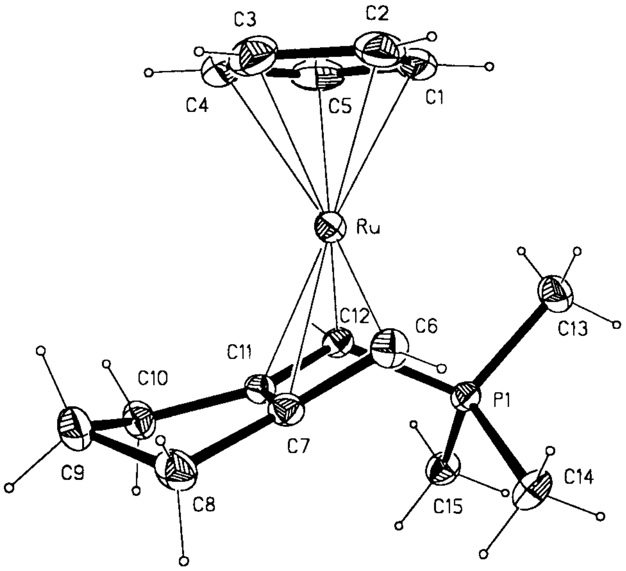


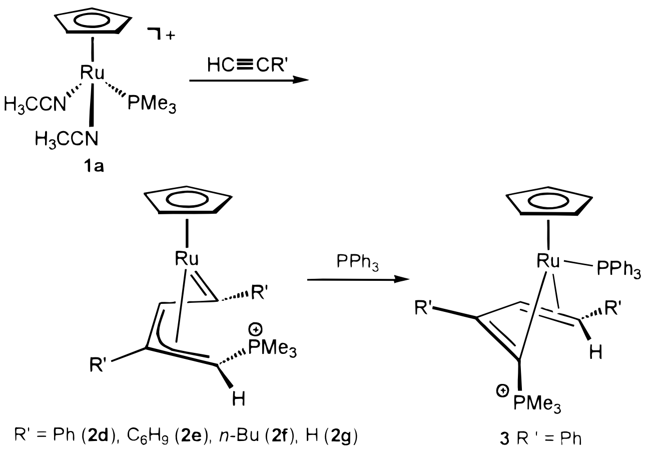
Figure 1. Structural view of **2a** showing 20% thermal ellipsoids (PF_6^- omitted for clarity). Selected bond lengths (Å) and angles (deg): Ru−C(1−5)$_{av}$ = 2.221(3), Ru−C(6) = 1.897(2), Ru−C(7) = 2.232(2), Ru−C(11) = 2.174(2), Ru−C(12) = 2.123(2), C(6)−C(7) = 1.403(3), C(7)−C(11) = 1.426(3), C(11)−C(12) = 1.432(3), C(7)−C(8) = 1.513(3), C(8)−C(9) = 1.542(4), C(9)−C(10) = 1.537(4), C(10)−C(11) = 1.514(3), C(12)−P(1) = 1.778(2); C(6)−C(7)−C(11) = 116.3(2), C(7)−C(11)−C(12) = 122.0(2), Ru−C(6)−C(7) = 83.7(1), C(6)−C(7)−C(11)−C(12) = 16.6(3).

at 236.5 ppm and a doublet resonance at 31.9 ppm (J_{CP} = 75.6 Hz) assignable to the carbene carbon atom C^1 and the terminal allyl carbon atom C^4 bearing the phosphine substituent. The NMR spectra of **2b** and **2c** are similar to those of **2a** and are not discussed here.

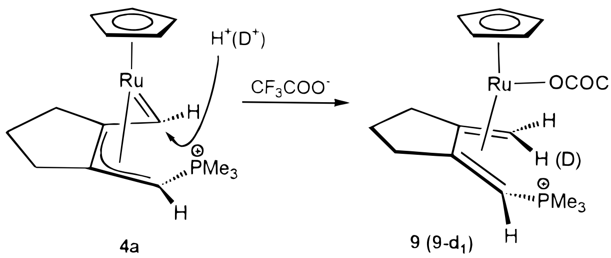
The structure of **2a** has been confirmed by X-ray crystallography (Figure 1).[6] Obviously C−C coupling had occurred between the internal sp carbons of the 1,6-heptadiyne ligand, forming an allyl carbene system with all four carbon atoms of the C4 chain bonded to the RuCp fragment. The C4 chain is nearly planar with a torsion angle C(6)−C(7)−C(11)−C(12) of 16.6(3)°. The Ru−C(6) bond is very short (1.897(2) Å), suggesting that C(6) is an alkylidene carbon doubly bonded to the ruthenium center. The remaining three carbons of the C4 chain have Ru−C(7), Ru−C(11), and Ru−C(12) distances of 2.232(2), 2.174(2), and 2.123(2) Å, respectively, in accordance with an η^3-allyl system. In view of the near-planarity of C(1−4), the π-system of the allyl unit is able to interact with the Ru=C π bond. In agreement with these observations the C−C distances within the allyl carbene moiety are 1.403(3), 1.426(3), and 1.432(3) Å, respectively. On the other hand, the unusual high-field shift of C^4 indicates a substantial sp^3 character of this atom, requiring a major contribution from a ruthenacyclopenta-1,3-diene resonance structure.[7]

In a similar fashion, **1a** reacts with HC≡CR′ (R′ = Ph, C_6H_9, *n*-Bu, H) to give the allyl carbene complexes [CpRu(=C(R′)-η^3-CHC(R′)CHPMe$_3$)]PF$_6$ (**2d**−**g**) in high yields with the substituents exclusively in the 1- and 3-positions (Scheme 2). A mechanism to account for the formation of **2** may involve a metallacyclopentatriene intermediate (Scheme 1). Subsequently, migration of the tertiary phosphine to one of the two electrophilic carbene carbon atoms leads to the formation of an allyl carbene complex. It has to be mentioned that analogous ruthenacyclopentatriene complexes are stable species if potential nucleophilic ligands are absent.[3]

Scheme 2



Scheme 3



Preliminary reactivity studies revealed that complexes **2** are capable of reacting with both nucleophiles and electrophiles. Thus, treatment of **2d** with 1 equiv of PPh$_3$ results in the formation of [CpRu(−CPMe$_3$=CPh-η^2-CH=CHPh)(PPh$_3$)]PF$_6$ (**3**) (Scheme 2). This reaction involves a 1,4-hydrogen shift. Furthermore, **2a** reacts with CF$_3$COOH to afford the η^4-diene complex [CpRu(η^4-CH$_2$=C(CH$_2$)$_3$C=CHPMe$_3$)(η^1(*O*)-CF$_3$COO)]-PF$_6$ (**4**) in 80% isolated yield (Scheme 3). When the protonation was carried out with CF$_3$COOD instead of CF$_3$COOH, the isotopomer **4-d$_1$** was formed. Comparison of the ^{1}H NMR spectra of **4** and **4-d$_1$** showed that deuterium had been incorporated exclusively into the *anti* position of the 1,3-diene moiety,[8] most likely involving delivery of the proton (deuterium) on the C_α via the inside face of the molecule. In this case the carbene carbon atom of **2** is nucleophilic.

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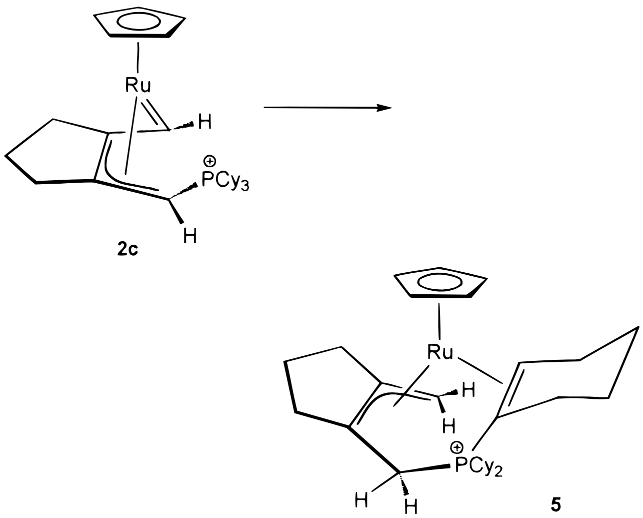
(6) Crystal data for **2a**: monoclinic space group $P2_1/n$ (No. 14), a = 8.456(2) Å, b = 10.942(2) Å, c = 19.917(4) Å, β = 92.63(1)°, V = 1840.9(7) Å^3, Z = 4, R1 = 0.037 (all data), wR2 = 0.081 (all data), 5343 reflections, 224 refined parameters.

(7) For related allyl carbene complexes see: (a) Crocker, M.; Green, M.; Orpen, A. G.; Neumann, H. P.; Schaverin, C. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1351. (b) Carlton, L.; Davidson, J. L.; Ewing, P.; Manjlovic-Muir, L.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1985**, 1474. (c) Morrow, J. R.; Tonker, T. L.; Templeton, J. *J. Am. Chem. Soc.* **1985**, *107*, 5004. (d) Morrow, J. R.; Tonker, T. L.; Templeton, J. *J. Am. Chem. Soc.* **1985**, *107*, 5004. (e) Crocker, M.; Froom, S. F. T.; Green, M.; Nagle, K. R.; Orpen, A. G.; Thomas, D. M. *J. Chem. Soc., Dalton Trans.* **1987**, 2803. (f) Crocker, M.; Green, M.; Nagle, K. R.; Orpen, A. G.; Neumann, H. P.; Morton, C. E.; Schaverin, C. J. *Organometallics* **1990**, *9*, 1422.

(8) Crocker, M.; Dunne, B. J.; Green, M.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1991**, 1589.

Scheme 4



In addition, these species are capable of activating C−H bonds of alkyl groups in tertiary phosphine ligands, provided they are sufficiently bulky. While **2a** and **2b** are stable even at elevated temperatures, **2c** reacts readily with one cyclohexyl substituent of the phosphine ligand to give **5**, featuring an η^2-coordinated cyclohexenyl ligand (Scheme 4). The formation of **5** involves hydrogen transfer from a cyclohexyl ring of PCy_3 to the C4 chain of the allyl carbene moiety. Notably, related reactions have been reported recently, requiring in some cases the presence of extra added olefin as an external hydrogen acceptor.[9] In addition to spectroscopic and analytical characterizations of **5** (see the Supporting Information), the solid-state structure of **5** in the form of $\mathbf{5}\cdot{}^1/_2Et_2O$ was determined by single-crystal X-ray diffraction.[10] An ORTEP diagram of $\mathbf{5}\cdot{}^1/_2Et_2O$ is shown in Figure 2 with selected bond distances and angles reported in the caption. Clearly, one cyclohexyl substituent of PCy_3 has been dehydrogenated and is bound in an η^2-fashion to the metal center. The allyl functionality is asymmetrically bonded to the metal with the Ru−C bond distance to the central allyl carbon atom C(7) (2.181(5) Å) distinctly shorter than the Ru−C bonds to the outer carbon atoms C(6) and C(11) (2.214(5) and 2.242(4) Å, respectively). The olefin moiety of the cyclohexenyl ligand is also asymmetrically bonded to the metal center, with the Ru−C bonds to the carbon atoms C(13) and C(14) being 2.221(4) and 2.195(4) Å, respectively. The C(13)−C(14) bond distance is 1.417(6) Å.

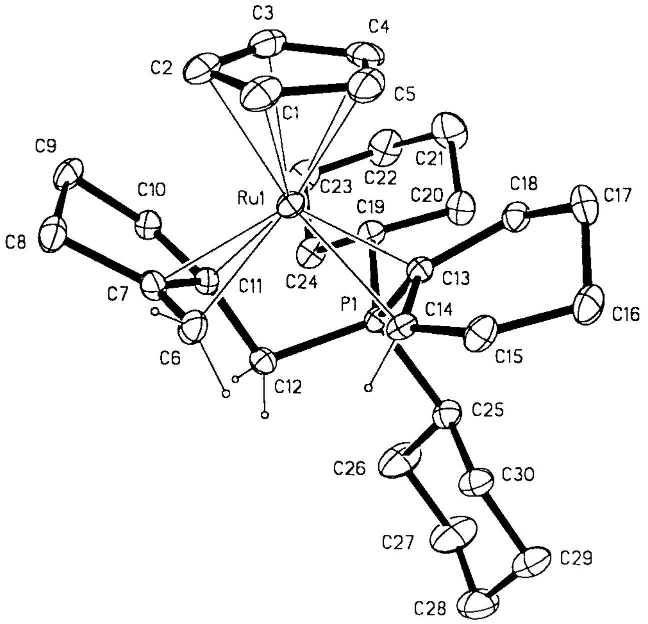


Figure 2. Structural view of $\mathbf{5}\cdot{}^1/_2Et_2O$ showing 20% thermal ellipsoids (most H atoms, PF_6^-, and Et_2O omitted for clarity). Only one of the two crystallographically independent complexes is shown. Selected bond lengths (Å) and angles (deg): Ru(1)−C(1−5)$_{av}$ = 2.234(5), Ru(1)−C(6) = 2.214(5), Ru(1)−C(7) = 2.181(5), Ru(1)−C(11) = 2.242(4), Ru(1)−C(13) = 2.221(4), Ru(1)−C(14) = 2.195(4), C(6)−C(7) = 1.409(7), C(7)−C(11) = 1.424(6), C(13)−C(14) = 1.417(6), C(12)−P(1) = 1.799(5), C(13)−P(1) = 1.802(5), C(19)−P(1) = 1.829(5), C(25)−P(1) = 1.840(5); C(6)−C(7)−C(11) = 123.5(4), C(11)−C(12)−P(1) = 108.7(3), P(1)−C(13)−C(14) = 116.2(3).

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Supporting Information Available: Text giving full experimental details and spectroscopic analytical data for complexes **2a**−**c** and **3**−**5** and tables of X-ray structural data, including data collection parameters, positional and thermal parameters, and bond distances and angles for complexes **2a** and $\mathbf{5}\cdot{}^1/_2Et_2O$. This material is available free of charge via the Internet at http://pubs.acs.org.

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[9] (a) Arliguie, T.; Chaudret, B.; Chung, G.; Dahan, F. *Organometallics* **1991**, *10*, 2973. (b) Christ, M. L.; Sabo-Etienne, S.; Chaudret, B. *Organometallics* **1995**, *14*, 1082. (c) Borowski, A. F.; Sabo-Etienne, S.; Christ, M. L.; Donnadieu, B.; Chaudret, B. *Organometallics* **1996**, *15*, 1427. (d) Hietkamp, S.; Hufkens, D. J.; Vrieze, K. *J. Organomet. Chem.* **1978**, *152*, 347. (e) Six, C.; Gabor, B.; Görls, H.; Mynott, R.; Philipps, P.; Leitner, W. *Organometallics* **1999**, *18*, 3316.

[10] Crystal data for $\mathbf{5}\cdot{}^1/_2Et_2O$: triclinic, space group $P\bar{1}$ (No. 2), a = 14.775(6) Å, b = 15.067(6) Å, c = 17.187(6) Å, α = 89.89(2)°, β = 75.75(2)°, γ = 63.07(2)°, V = 3280(2) Å^3, Z = 4, R1 = 0.078 (all data), wR2 = 0.13 (all data), 8985 reflections, 768 refined parameters.