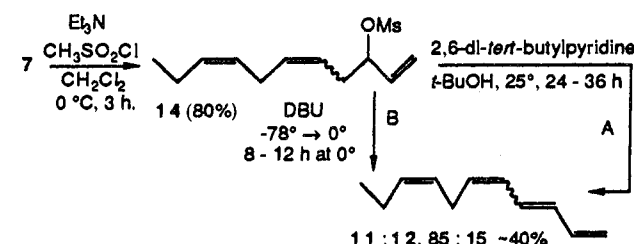J. Am. Chem. Soc. 1991, 113, 2314-2316

Scheme III

The exclusive formation of the cis,trans geometry of the conjugated diene in **10** suggests the following about the reaction mechanism: (1) The lack of change in the Z-olefin geometry ($C_{8,9}$) of **8** signified that either elimination in the anion **9** to form the cyclopropane **10** occurs faster than stereochemical equilibration of the pentadienyl anion or the cis,trans configuration of the pentadienyl anion is thermodynamically favored. On the basis of studies by Schlosser[15] of closely related systems, both of these possibilities seem likely. (2) The exclusive E geometry of the newly formed double bond in **10** may be attributed to steric interactions during deprotonation. Removal of that diallylic proton from **8** which results in a pentadienyl anion (indicated in bold type) most likely occurs in **8b** rather than **8a** in the case of the predominant cis isomer and in **8d** rather than **8c** in the case of the trans isomer since the resulting transition states would be less crowded in each case. **8b** and **8d** would afford dictyopterene B (**10**) while **8a** and **8c** would produce the cis,cis isomer of **10**.
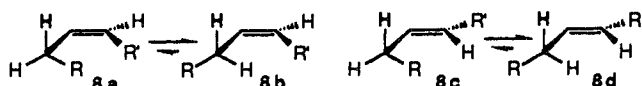
(±)-Dictyopterene B (**10**) was quantitatively converted to (±)-dictyopterene D (**13**)[16,17] through the known procedure of heating (±)-**10** in a sealed tube for several hours (eq 1).
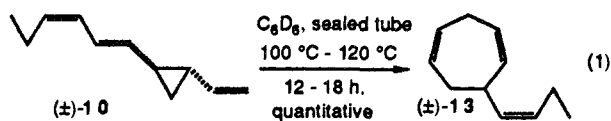
When the methanesulfonate ester **14** of **7** was solvolyzed (path A, Scheme III) or treated with excess 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) (path B[18]), a mixture of tetraene gamete attractants **11** and **12**[19] was produced in 40% yield and no dictyopterene B was detected. It is not surprising that **14** undergoes β-elimination under essentially neutral solvolytic conditions whereas **9**, in the presence of a strong base, undergoes deprotonation followed by an intramolecular S_N2 reaction. The solvolysis of **14**, bearing an excellent leaving group, presumably involves an E1 process in which the most acidic (β) proton of the carbocationic intermediate is removed.

The production of racemic dictyopterene B (**10**)[20] and dictyopterene D (**13**) in six and seven steps, respectively, in 16%

overall yield starting with commercial **1** is the most efficient synthesis to date.[21] It is also truly unique as all previous syntheses utilize a Wittig reaction to generate C–C unsaturation in a stereochemically controlled manner, usually in poor yield. More importantly, it has now been demonstrated for the first time that these gamete attractants can be prepared from their proposed[1] biogenetic precursor **7** in good yield. While the conditions used in the conversion of **7** to **10** do not resemble those in a biological system, our results render plausible a biosynthesis involving electrophilic enzymatic assistance to removal of a good leaving group such as a pyrophosphate with simultaneous enzymatic deprotonation of the developing cation.[22] The [1,2,(3),5]-elimination described here is apparently the only example of this rare type of ring closure in a noncyclic system[9] in which the entropy of activation should be less favorable than in the few known cases.

Acknowledgment. We thank the National Institutes of Health for financial support.

Supplementary Material Available: Sample procedures for the reactions described herein and spectral data and copies of the ^{1}H NMR spectra for the products (22 pages). Ordering information is given on any current masthead page.

(15) Schlosser, M.; Rauchschwalbe, G. *J. Am. Chem. Soc.* **1978**, *100*, 3258. Bosshardt, H.; Schlosser, M. *Helv. Chim. Acta* **1980**, *63*, 2393. Schlosser, M. *Proc. Jpn. Chem. Soc. (Tokyo)* **1984**, *3*, 1820. Schlosser, M. *Pure Appl. Chem.* **1988**, *60*, 1627.
(16) According to capillary GC and ^{1}H NMR (500 MHz), the isolated cycloheptadiene (±)-**13** was contaminated with ~5% of the same unknown and inseparable impurity that was in reactant **10**.
(17) The ^{1}H NMR, ^{13}C NMR, and mass fragmentation spectra of (±)-**13** were identical with those of the enantiomer of natural dictyopterene D.[10]
(18) Corey, E. J.; Su, W.; Mehrotra, M. *Tetrahedron Lett.* **1984**, *25*, 5123.
(19) According to both the 500-MHz ^{1}H NMR spectrum and the capillary GC analysis, the mixture of tetraenes **3** and **4**, isolated from procedure A, contained 10–15% of unidentifiable impurities along with a considerable amount of 2,6-di-*tert*-butylpyridine (~35%), while that from procedure B (DBU) contained 10–20% of unidentifiable impurities.
(20) It should be noted that even though the ova in most Pacific seaweeds secrete only (R,R)-(−)-**10**, the male gametes in some of the brown algae do not distinguish between R,R and S,S forms and thus are attracted to both enantiomers of **10**.[1]

Preparation, X-ray Molecular Structure, and Electronic Structure of the First 16-Electron Dihydrogen Complexes RuH(H₂)X(PCy₃)₂

Bruno Chaudret,*[†] Gwendolina Chung,[†] Odile Eisenstein,*[‡]
Sarah A. Jackson,[‡] Fernando J. Lahoz,*[§] and Jose A. Lopez[§]

*Laboratoire de Chimie de Coordination, CNRS
associé à l'Université Paul Sabatier et
l'Institut National Polytechnique de Toulouse
205, route de Narbonne, 31077 Toulouse Cedex, France
Laboratoire de Chimie Théorique, Bâtiment 490
Université de Paris-sud, 91405 Orsay, France
Departamento Quimica Inorganica
Instituto de Ciencia de Materiales de Aragon
Universidad de Zaragoza CSIC, 50009 Zaragoza, Spain*

Received August 13, 1990

Since the first demonstration by Kubas of the coordination of dihydrogen to a transition metal,[1] numerous examples of such compounds have appeared in the literature.[2] A large number of these resulted from the reinvestigation of complexes that had been previously assigned a polyhydride structure. This is the case for the polyhydrides FeH₄(PR₃)₃, RuH₄(PR₃)₃, and RuH₆(PCy₃)₂, which were shown to adopt a d^6 octahedral structure (FeH₂-(H₂)(PR₃)₃,[3,4] RuH₂(H₂)(PR₃)₃,[3,5] and RuH₂(H₂)₂(PCy₃)₂,[5] re-

†Laboratoire de Chimie de Coordination, CNRS, associé à l'Université Paul Sabatier et l'Institut National Polytechnique de Toulouse.
‡Laboratoire de Chimie Théorique, Bâtiment 490, Université de Paris-sud.
§Departamento Quimica Inorganica, Instituto de Ciencia de Materiales de Aragon, Universidad de Zaragoza CSIC.
(1) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120.
(2) (a) Crabtree, R. H. *Adv. Organomet. Chem.* **1988**, *28*, 295. (b) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95.
(3) Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126.

0002-7863/91/1513-2314$02.50/0   © 1991 American Chemical Society

spectively) considered as favored for H_2 complexes by several authors.[1,2]

The thermally stable bis(dihydrogen) complex $RuH_2(H_2)_2$-$(PCy_3)_2$[5] can be protonated by carboxylic acids to lead to novel hydrido dihydrogen derivatives containing anionic donor ligands which exhibit a dihydride dihydrogen equilibrium upon second protonation.[6] Its reactions with halocarbons were anticipated to lead to new unsaturated or polynuclear dihydrogen derivatives. They are described hereafter.

$RuH_2(H_2)_2(PCy_3)_2$ (1) reacts rapidly at room temperature with 1 equiv of PhI or CH_3I in hexane to give a brown solution (containing benzene if PhI is used) from which orange-brown crystals analyzing for $RuH(H_2)I(PCy_3)_2$ (2)[7a] are obtained after the solution is cooled, in 70% yield. A similar reaction between 1 and excess CH_2Cl_2 yields $RuH(H_2)Cl(PCy_3)_2$ (3)[7b] in 70% crystallized yield. 3 can also be obtained from the reaction of 1 with $AlCl_3$.

The high-field ^1H NMR spectrum of 2 consists of a broad peak at δ −16.3 ppm which remains broad down to −80 °C; a triplet pattern is visible at room temperature ($J_{P-H} \sim 11$ Hz). The intensity of this peak compared to that of the phosphine protons is less than 3:66 (ca. 2.5:66). The minimum observed T_1 value is ca. 30 ms at 243 K, a value identical with that observed for $RuH(H_2)(OCOR)(PCy_3)_2$.[6] 3 shows the same spectroscopic properties (high-field ^1H NMR and T_1) and thus adopts most probably the same structure. 2 does not react with N_2 but does react immediately with D_2 to exchange H_2 for D_2 (5 min at room temperature) and with pyridine to give a hydrido pyridine derivative not fully characterized.

In order to establish the nuclearity of 2 and confirm the presence of coordinated H_2, an X-ray diffraction study was undertaken at 100 K.[8] The complex is monomeric and contains two trans
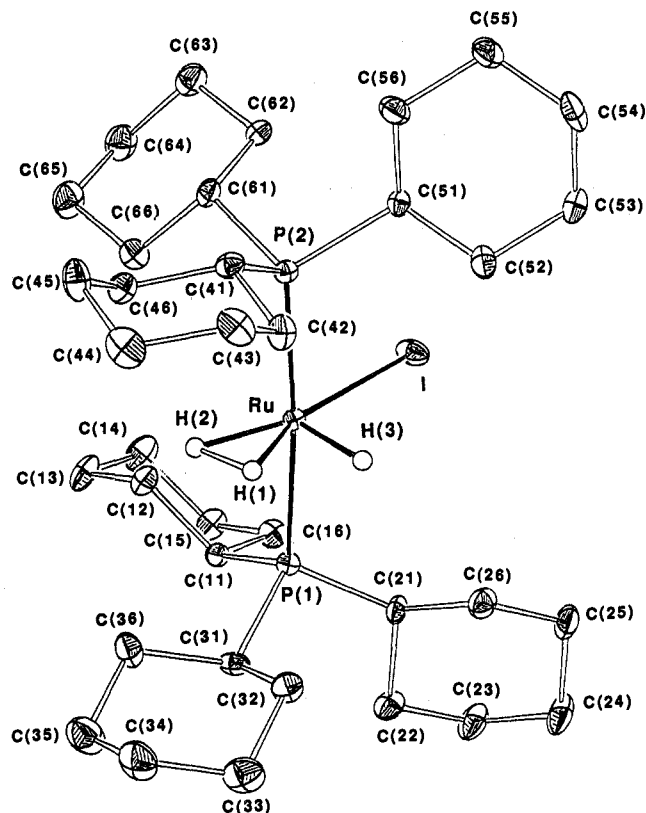
Figure 1. ORTEP plot for $[RuH(H_2)(PCy_3)_2]$. Selected bond lengths (Å) and angles (deg): Ru−P(1), 2.339 (1); Ru−P(2), 2.344 (1); Ru−I, 2.710 (1); Ru−H(1), 1.60 (5); Ru−H(2), 1.59 (4); Ru−H(3), 1.51 (5); H(1)−H(2), 1.03 (7); P(1)−Ru−P(2), 175.13 (6); P(1)−Ru−I, 90.80 (4); P-(2)−Ru−I, 91.82 (4); P(1)−Ru−H(1), 89 (2); P(1)−Ru−H(2), 88 (2); P(1)−Ru−H(3), 91 (2); P(2)−Ru−H(1), 90 (2); P(2)−Ru−H(2), 88 (2); P(2)−Ru−H(3), 93 (2); I−Ru−H(1), 163 (2); I−Ru−H(2), 159 (2); I−Ru−H(3), 99 (2).

phosphine groups with a cis iodine atom, at normal bonding distances. The high quality of the X-ray structure allows positioning of a hydride and a dihydrogen ligand, Figure 1.[10] The hydridic Ru−H(3) distance (1.51 (5) Å) is typical of a terminal ruthenium hydride bond,[11] and the Ru−H distances within the nonclassical moiety are similar (Ru−H(1) = 1.60 (5) Å and Ru−H(2) = 1.59 (4) Å). The ligand arrangement is that of a slightly distorted octahedral environment since the angles P−Ru−P and I−Ru−(H_2 midpoint) are close to 180°. The hydride is slightly tilted toward H_2 (I−Ru−H(3) = 99°), which makes the nonbonding distance H(1)−H(3) short (1.66 (6) Å) while that within the nonclassical H_2 ligand appears to be elongated (H(1)−H(2) = 1.03 (7) Å).

Extended Hückel calculations were carried out on this complex. The experimental structure appears to be a minimum.[12] This agrees with the fact that stable d^6 ML_5 complexes have a structure that can be alternatively viewed as a square pyramid or as a piece of an octahedron, depending on the distance between the basal plane and the metal.[13b] In these complexes the ligand trans to the empty site (apical ligand) is the strongest σ donor (H in 2).[13b] The structures with I or H_2 at the apical site are calculated to be 10 kcal/mol higher in energy.

(4) (a) Van Der Sluys, L. S.; Eckert, J.; Eisenstein, O.; Hall, J. H.; Huffman, J. C.; Jackson, S. A.; Koetzle, T. F.; Kubas, G. J.; Vergamini, P. J.; Caulton, K. G. *J. Am. Chem. Soc.* **1990**, *112*, 4831. (b) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *100*, 451. Kubas, G. J.; Ryan, R. R. *Polyhedron* **1986**, *5*, 473. Morris, R. H.; Sawyer, J. F.; Shiralian, M.; Zubkowski, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5581. Ricci, J. S.; Koetzle, T. F.; Bautista, M. T.; Hofstede, T. M.; Morris, R. H.; Sawyer, J. F. *J. Am. Chem. Soc.* **1989**, *111*, 8823.

(5) Arliguie, T.; Chaudret, B.; Morris, R. H.; Sella, A. *Inorg. Chem.* **1988**, *27*, 599.

(6) Arliguie, T.; Chaudret, B. *J. Chem. Soc., Chem. Commun.* **1989**, 155.

(7) (a) $RuH(H_2)[(PCy_3)_2]$. Satisfactory microanalyses were obtained. Selected spectroscopic data: IR (KBr) ν(Ru−H) 2109 cm^{-1} (br); ^1H NMR (200 MHz) −16.3 (br t, 3 H, $^2J_{P-H}$, 11 Hz), 1−2 ppm (m, 66 H); ^{31}P NMR 56.00 ppm (s). T_1 values for the high-field signal: 296 K, 59 ms; 273 K, 46 ms; 248 K, 32 ms; 243 K, 30 ms; 228 K, 30 ms; 213 K, 42 ms; 198 K, 65 ms; 193 K, 72 ms. (b) $RuH(H_2)Cl(PCy_3)_2$. Satisfactory microanalyses were obtained. Selected spectroscopic data: IR (KBr) ν(Ru−H) 2059 cm^{-1} (br); ^1H NMR (200 MHz) −16.3 (br t, 3 H), 1−2 ppm (m, 66 H); ^{31}P NMR 54.00 ppm (s). T_1 values for the high-field signal: 296 K, 61 ms; 273 K, 46 ms; 243 K, 30 ms; 193 K, 75 ms.

(8) A prismatic brown-black block (0.21 × 0.17 × 0.13 mm), grown by a slow diffusion of hexane into a toluene solution of 2, was used for data collection. Crystal data: orthorhombic, space group *Pbca*, $a = 14.745$ (4) Å, $b = 22.574$ (9) Å, $c = 26.316$ (5) Å, $V = 8759$ (5) Å^3 [from 2θ values of 20 reflections measured at ±ω ($2\theta = 20-30°$), $\lambda = 0.71069$], $M = 884.00$, $Z = 8$, $\rho_{calcd} = 1.341$ g cm^{-3}, μ(Mo Kα) = 1.146 mm^{-1}. Intensity data were collected at 100 K using an Enraf-Nonius CAD4 diffractometer equipped with a commercial Oxford Cryosystems device (temperature fluctuations ≤0.2 K). A total of 9316 reflections were measured to $2\theta_{max} = 45°$ with 5708 unique, of which 4496 with $F > 6\sigma(F)$ were used in all calculations. Data reduction was carried out with the DREAM package.[9] The structure was solved by Patterson and conventional Fourier methods. All non-hydrogen atoms (except solvent) were refined first isotropically and then with anisotropic thermal parameters. All the hydrogen atoms were located in difference Fourier maps and included in the last cycles of refinement riding at their carbon atoms and with a common thermal parameter. Hydrogens directly bonded to the metal were treated as normal isotropic atoms and refined with free positional and thermal parameters. A crystallization toluene molecule disordered between two positions was clearly found from a different Fourier map. A model of solvent disorder was built up from toluene molecules which were refined as rigid groups with occupancy factors 0.70 (1) and 0.30 (1). Final $R = 0.027$ and $R_w = 0.029$, weighting scheme $w = 1.0/[\sigma^2(F)]$. Further details of the crystal structure investigation are available on request from the Cambridge Crystallographic Data Center, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, G.B. Any request should be accompanied by a full literature citation for this communication.

(9) Blessing, R. H. *Crystallogr. Rev.* **1987**, *1*, 3.

(10) It is noteworthy that these results are in excellent agreement with a potential energy calculation (Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1980**, 2509) which only shows two minima of energy in the proximity of the metal at the exact places where the hydride and dihydrogen ligands are found by X-ray.

(11) Hampton, C.; Cullen, W. R.; James, B. R.; Charland, J. *J. Am. Chem. Soc.* **1988**, *110*, 6198.

(12) The structure cannot be an octahedral trihydride since this would be unstable for a d^4 electron count. Ab initio calculations are currently underway to understand the structure of 2 in more depth: Riehl, J. F.; Eisenstein, O.; Pélissier, M., private communication.

H_2 remains preferentially in the same plane as the Ru–H(3) bond with a small rotational barrier of 3 kcal/mol. Remarkably the interaction between the metal d orbitals and σ^*_{HH} is similar for the in-plane and out-of-plane orientation of H_2. The preference for a coplanar arrangement can be traced to a cis interaction between the Ru–H σ bond and the σ^*_{HH} orbital (4). This interaction is also responsible for the fact that the Ru–H is bent toward the H_2 ligand. As has been previously shown in an Fe(II)–H/H_2 complex,[4a] this interaction creates a nascent bond between the hydride and the closest H center of H_2. This nascent bond should facilitate the exchange process between the hydrogens.

4
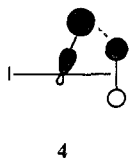
A possible path for exchanging the H centers is shown in 5 (perpendicular phosphine ligands removed for clarity). The transition structure between two equivalent square pyramids (5a) is a distorted trigonal bipyramid with an acute angle between H_2 and H and the I ligand trans to it (5b). Such a structure, which is calculated to be very close in energy to the minimum and which has even been observed as a stable structure in the case of an Ru(II) and two Ir(III) complexes (with R and H at the acute angle),[13,14] should facilitate the exchange process by favoring the proximity between H and H_2.

5
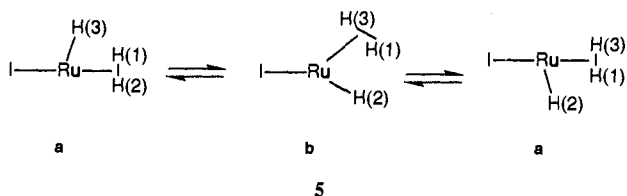
Compound 2 is unusual for several reasons. Firstly, it is the first well-characterized 16-electron dihydrogen derivative, which demonstrates that electron saturation is not a necessary condition for the stabilization of coordinated H_2; there is no evidence for an agostic interaction between the cyclohexyl group and the metal. Secondly, the molecule adopts an octahedral type structure with a vacant coordination site. The dihydrogen molecule lies in the I–Ru–H(3) plane and not along the P(1)–Ru–P(2) axis, which is shown to be a manifestation of the cis interaction. Finally the H(1)–H(2) distance (1.03 (7) Å) is one of the longest reported so far in nonclassical H_2 complexes,[15] whereas the H(1)–H(3) distance (1.66 (6) Å) is short, a structure that should facilitate hydride/dihydrogen exchange.

Supplementary Material Available: Experimental data of the X-ray diffraction study of compound 2 including full experimental details and tables of atomic coordinates and thermal parameters (8 pages); table of observed and calculated structure factors for 2 (27 pages). Ordering information is given on any current masthead page.

(13) (a) Jean, Y.; Eisenstein, O. *Polyhedron* **1988**, 7, 405. (b) See references in the following: Rachidi, I. E.-I.; Eisenstein, O.; Jean, Y. *Nouv. J. Chim.* **1990**, 14, 671.

(14) Werner, H.; Hohn, A.; Dziallas, M. *Angew. Chem., Int. Ed. Engl.* **1986**, 25, 1090. Fryzuk, M. D.; MacNeil, P. A.; Ball, R. G. *J. Am. Chem. Soc.* **1986**, 108, 6414. Mezzetti, A.; Del Zotto, A.; Rigo, P.; Bresciani Pahor, N. *J. Chem. Soc., Dalton Trans.* **1989**, 1045.

(15) Kim, Y.; Deng, H.; Meek, D. W.; Wojcicki, A. *J. Am. Chem. Soc.* **1990**, 112, 2798.

Synthesis and Structure of [{Ru(CO)₂(Cp)}₂(μ-C≡C)]: An Ethynediyl Complex Formed during Tungsten-Catalyzed Alkyne Metathesis

George A. Koutsantonis and John P. Selegue*

Department of Chemistry, University of Kentucky Lexington, Kentucky 40506-0055

Metal complexes with all-carbon ligands provide interesting models for the carbide fragments formed as reactive intermediates during carbon monoxide and acetylene conversion reactions on heterogeneous catalyst surfaces.[1] There are several bicarbide clusters which fall into two classes, those with encapsulated C_2 ligands[2] and those with two separate C_1 ligands.[3] Generally, the carbide ligands tend to be unreactive because they are "buried" in the clusters. Complexes with C_2 ligands bonded to only two or three metals are quite rare.[4,5] We are interested in using metal ethynediyls ($L_nMC\equiv CML_n$) as an approach to reactive metal bicarbide complexes.

We previously reported that the stoichiometric reaction of [Ru(C≡CMe)(CO)₂(Cp)] with [W(≡CEt)(OCMe₃)₃] leads to the μ-carbide complex [(Cp)(CO)₂RuC≡W(OCMe₃)₃] by alkyne metathesis, with elimination of MeC≡CEt.[6] While optimizing this procedure, we realized that the direct reaction of [Ru(C≡CMe)(CO)₂(Cp)] with [W₂(OCMe₃)₆] should be equally capable of forming the carbide complex, since the initial reaction of these complexes should give equimolar amounts of [(Cp)(CO)₂RuC≡W(OCMe₃)₃] and [W(≡CMe)(OCMe₃)₃], ultimately leading to only [(Cp)(CO)₂RuC≡W(OCMe₃)₃] by loss of volatile MeC≡CMe (Scheme I). Although this is the case in toluene solvent, carrying out the reaction in isooctane solution leads to the formation of a yellow precipitate of [{Ru(CO)₂(Cp)}₂(μ-C≡C)] (1) in 52% yield.[7] The compounds remaining in solution (NMR) are [(Cp)(CO)₂RuC≡W(OCMe₃)₃], [W(≡CMe)(OCMe₃)₃],

(1) (a) Somorjai, G. A. *Chemistry in Two Dimensions: Surfaces*; Cornell University Press: Ithaca, NY, 1981; pp 494-499. (b) Anderson, R. B. *The Fischer-Tropsch Synthesis*; Academic Press: New York, 1984. (c) van der Lee, G.; Ponec, V. *Catal. Rev.—Sci. Eng.* **1987**, 29, 183-218.

(2) (a) Examples of μ_7-C_2: Arrigoni, A.; Ceriotti, A.; Pergola, R. D.; Longoni, G.; Manassero, M.; Sansoni, M. *J. Organomet. Chem.* **1985**, 296, 243. (b) Example of μ_4-C_2: Bruce, M. I.; Snow, M. R.; Tiekink, E. R. T.; Williams, M. L. *J. Chem. Soc., Chem. Commun.* **1986**, 701-702.

(3) Example of $(\mu_6$-$C)_2$: Hayward, C.-M. T.; Shapley, J. R.; Churchill, M. R.; Bueno, C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1982**, 104, 7347-7349.

(4) (a) Neithamer, D. R.; LaPointe, R. E.; Wheeler, R. A.; Richeson, D. S.; Van Duyne, G. D.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1989**, 111, 9056-9072. (b) Listemann, M. L.; Schrock, R. R. *Organometallics* **1985**, 4, 74-83. (c) Blau, R. J.; Chisholm, M. H.; Folting, K.; Wang, R. J. *J. Am. Chem. Soc.* **1987**, 109, 4552-4560.

(5) μ_2-Ethynediyls. (a) W–Ru, W–Fe: Frank, K. G.; Selegue, J. P. *J. Am. Chem. Soc.* **1990**, 112, 6414-6416. (b) Fe: Akita, M.; Terada, M.; Oyama, S.; Moro-oka, Y. *Organometallics* **1990**, 9, 816-825. (c) Re: Appel, M.; Heidrich, J.; Beck, W. *Chem. Ber.* **1987**, 120, 1087-1089. (d) Re: Beck, W.; Niemer, B.; Breimair, J.; Heidrich, L. *J. Organomet. Chem.* **1989**, 372, 79-83. (e) Re: Heidrich, J.; Steimann, M.; Appel, M.; Beck, W.; Phillips, J. R.; Trogler, W. C. *Organometallics* **1990**, 9, 1296. (f) W: Ustynyuk, N. A.; Vinogradova, V. N.; Kravtsov, D. N.; Oprunenko, Y. F.; Piven, V. A. *Metalloorg. Khim.* **1988**, 1, 884-888; *Chem. Abstr.* **1989**, 111, 233074c. (g) Cr, W: Ustynyuk, N. A.; Vinogradova, V. N.; Kravtsov, D. N. *Metalloorg. Khim.* **1988**, 1, 85-88; *Chem. Abstr.* **1989**, 110, 231804w. (h) V: Kreisel, G.; Scholz, P.; Seidel, W. *Z. Anorg. Allg. Chem.* **1980**, 460, 51-55. (i) Pt, Pd: Ogawa, H.; Onitsuka, K.; Joh, T.; Takahashi, S.; Yamamoto, Y.; Yamazaki, H. *Organometallics* **1988**, 7, 2257-2260. (j) Au: Nast, R.; Schneller, P.; Hengefeld, A. *J. Organomet. Chem.* **1981**, 214, 273-276. (k) Au: Cross, R. J.; Davidson, M. F.; McLennan, A. J. *J. Organomet. Chem.* **1984**, 265, C37-C39.

(6) Latesky, S. L.; Selegue, J. P. *J. Am. Chem. Soc.* **1987**, 109, 4731-4733.

(7) A mixture of [Ru(C≡CMe)(CO)₂(Cp)] (187 mg, 0.716 mmol) and [W₂(OCMe₃)₆] (20 mg, 0.025 mmol) in isooctane (30 mL) was stirred at ambient temperature for 2 h. The pale yellow precipitate was collected on a glass frit to give 1 (90 mg). The filtrate was further stirred for 12 h to give a second crop of 1 (20 mg, total yield 66%). A stoichiometric reaction of [Ru(C≡CMe)(CO)₂(Cp)] (450 mg, 1.72 mmol) and [W₂(OCMe₃)₆] (693 mg, 0.86 mmol) in isooctane (50 mL) gave a precipitate of 1 (211 mg, 52%) in addition to [(Cp)(CO)₂RuC≡W(OCMe₃)₃] (365 mg, 33%) which was recovered from the solution.