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Alkyne Scission on a Trimetallic Framework: Experimental Evidence and Theoretical Analysis

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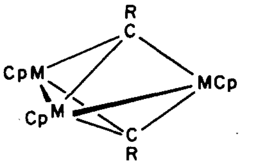
The conversion of an alkyne complex, $Cp_3M_3(CO)(C_2R_2)$, into a dialkylidyne complex, $Cp_3M_3(CR)_2$, has been examined theoretically (M = Co; R = H) and experimentally (M = Rh, Ir; C_2R_2 = C_2Ph_2, C_2PhTol). The alkyne complexes have been synthesized in useful amounts via photolysis of $Cp_3M_3(CO)_3$ in the presence of excess alkyne. Flash vacuum pyrolysis of the alkyne complexes cleanly provides the corresponding dialkylidyne complexes. The reaction proceeds without fragmentation of the trimetallic framework and without exchange of the CR moieties. No evidence was obtained for an unsaturated alkyne complex $Cp_3M_3(C_2R_2)$ as an intermediate. The theoretical analysis shows that such an intermediate leads to a much higher energy pathway for alkyne scission than a pathway in which the carbonyl ligand remains coordinated until the alkyne is cleaved.

Introduction

The scission of alkyne C≡C bonds (bond energy ca. 200 kcal/mol) upon interaction with metal centers is one class of metal-induced cleavage reactions of small molecules with multiple bonds (e.g., C≡O, N≡O, N≡N, etc.). Alkyne scission at one and two metal centers has been analyzed theoretically;[1] the involvement of two metal centers experimentally is suggested by the isolation of binuclear dialkylidyne complexes.[2] Recently, scission of an alkyne coordinated to a tetranuclear complex has been reported.[3] The most extensive evidence for alkyne scission, however, involves trimetallic frameworks, which are the focus of this paper.

The results of several groups lead to the conclusion that heating mononuclear cyclopentadienyl cobalt triad complexes with alkynes generates a class of trinuclear dialkylidyne cluster compounds (eq 1).[2a,4–6a] Structural features of this class have been defined by several X-ray studies.[4a,5,9] Since the starting material contains no metal–metal bonding, a natural question is how (why and when) does the metal triangle assemble? Apparently, generation of CpM(CO) (M = Co,[10] Rh,[11] Ir[12]) allows formation of the trimer $Cp_3M_3(CO)_3$. It therefore seems reasonable that under the conditions necessary for the reaction shown in (1), metal trimers may preassemble in solution and serve as templates for the dismantling of an alkyne.

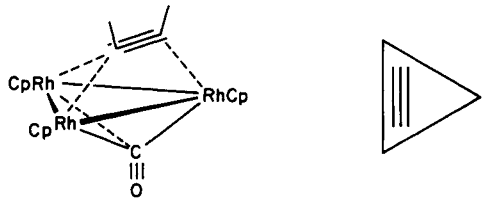
CpM(CO)L + RC$_2$R′ $\xrightarrow{\Delta}$  (1)

L = CO, PPh$_3$

M = Co, Rh, Ir

I

In a trinuclear alkyne complex there are two established modes of alkyne coordination.[13] Configuration II, exemplified by $Cp_3Rh_3(CO)(C_2Ph_2)$,[14] has the alkyne parallel to a metal–metal edge. Configuration III, with the alkyne perpendicular to a metal–metal edge, is shown by $Fe_3(CO)_9(C_2Ph_2)$,[7] which has two valence electrons fewer.



II

The framework in question in this paper and the earlier ones is Cp_3M_3, M = Co, Rh, Ir, in which case the alkyne

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[1] (a) Hoffmann, R.; Wilker, C. N.; Eisenstein, O. *J. Am. Chem. Soc.* **1982,** *104,* 632–634. (b) Wilker, C. N.; Hoffmann, R., Eisenstein, O. *Nouv. J. Chim.* **1983,** *7,* 535–544. (c) Hoffmann, R.; Wilker, C. N.; Lippard, S. J.; Templeton, J. L.; Brower, D. C. *J. Am. Chem. Soc.* **1983,** *105,* 146–147.

[2] (a) King, R. B.; Harmon, C. A. *Inorg. Chem.* **1976,** *15,* 879–885. See especially ref 26. (b) Pettersen, R. C.; Cash, G. C. *Acta Crystallogr., Sect. B* **1977,** *B33,* 2331–2334. (c) The fluxionality of $(COD)_2Pt_2(C_2RR)$ suggests a dialkylidyne intermediate. See: Boag, N. M.; Green, M.; Howard, J. A. K.; Stone, F. G. A.; Wadepohl, H. *J. Chem. Soc., Dalton Trans.* **1981,** 862–872.

[3] Park, J. T.; Shapley, J. R.; Churchill, M. R.; Bueno, C. *J. Am. Chem. Soc.* **1983,** *105,* 6182–6184.

[4] (a) Fritch, J. R.; Vollhardt, K. P. C.; Thompson, M. R.; Day, V. W. *J. Am. Chem. Soc.* **1979,** *101,* 2768–2770. (b) Fritch, J. R.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1980,** *19,* 559–561.

[5] Yamazaki, H.; Wakatsuki, Y.; Aoki, K. *Chem. Lett.* **1979,** 1041–1044.

[6] (a) Gardner, S. A.; Andrews, P. S.; Rausch, M. D. *Inorg. Chem.* **1973,** *12,* 2396–2402. (b) Todd, L. J.; Wilkinson, J. R.; Rausch, M. D.; Gardner, S. A.; Dickson, R. S. *J. Organomet. Chem.* **1975,** *101,* 133–138. These workers formulated $Cp_3Rh_3(C_2Ph_2)$ as an alkyne complex analogous to $Fe_3(CO)_9(C_2Ph_2)$.[7] However, ^{13}C NMR data reported for $Cp_3Rh_3(C_2Ph_2)$[6b] and subsequently for $Cp_3Rh_3(CNEt_2)_2$[2a] led Deeming[8] to reformulate the former compound as $Cp_3Rh_3(CPh)_2$, i.e., a dialkylidyne complex. Presumably, the compound similarly formulated by Rausch and co-workers as $Cp_3Ir_3[C_2(C_6F_5)_2]$[6a] also is a dialkylidyne compound.

[7] Blount, J. F.; Dahl, L. F.; Hoogzand, C.; Hübel, W. *J. Am. Chem. Soc.* **1966,** *88,* 292–301.

[8] Deeming, A. J. *J. Organomet. Chem.* **1978,** *150,* 123–128.

[9] Although not prepared according to eq 1, two closely related compounds have been characterized recently. (a) de Miguel, A. V.; Isobe, K.; Bailey, P. M.; Meanwell, N. J.; Maiths, P. M. *Organometallics* **1982,** *1,* 1604–1607. (b) Pardy, R. B. A.; Smith, G. W.; Vickers, M. E. *J. Organomet. Chem.* **1983,** *252,* 341–346.

[10] Vollhardt, K. P. C.; Bercaw, J. E.; Bergman, R. G. *J. Organomet. Chem.* **1975,** *97,* 283–297.

[11] (a) Lawson, R. J.; Shapley, J. R. *J. Am. Chem. Soc.* **1976,** *98,* 7433–7435. (b) Lawson, R. J.; Shapley, J. R. *Inorg. Chem.* **1978,** *17,* 773–774.

[12] Shapley, J. R.; Adair, P. C.; Lawson, R. J.; Pierpont, C. G. *Inorg. Chem.* **1982,** *21,* 1701–1702.

[13] Schilling, B. E. R.; Hoffmann, R. *Acta Chem. Scand., Ser. B* **1979,** *B33,* 231–232.

[14] Toan, T.; Broach, R. W.; Gardner, S. A.; Rausch, M. D.; Dahl, L. F. *Inorg. Chem.* **1977,** *16,* 279–289.

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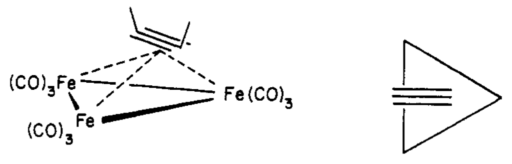

III

should be perpendicular, type III. Theoretically, we have probed the relationships among these forms for M = Co. Experimentally, our attention was attracted to the fact that both $Cp_3Rh_3(CO)(C_2Ph_2)$ and $Cp_3Rh_3(CPh)_2$ were isolated from the reaction of $CpRh(CO)_2$ with diphenylacetylene (yields 4.3% and 0.6%, respectively).[6a] This suggested the possibility of examining whether the former could be converted into the latter, keeping the metal triangle intact. After developing a new synthesis to provide useful quantities of $Cp_3Rh_3(CO)(C_2Ph_2)$ and related compounds, we have found that flash vacuum pyrolysis[15] (FVP) of these alkyne complexes results in decarbonylation and intramolecular alkyne scission to yield the corresponding bisalkylidyne compounds (eq 2).

$$Cp_3M_3(CO)(C_2RR') \xrightarrow[-CO]{FVP} Cp_3M_3(CR)(CR') \qquad (2)$$

$$M = Rh, Ir$$

Experimental Section

General Comments. Solvents were reagent grade and were distilled under nitrogen from appropriate drying agents prior to use. Diphenylacetylene and 4-methylbenzophenone were purchased from Aldrich. Phenyl-*p*-tolylacetylene (C_2PhTol) was synthesized by the reaction of 4-methylbenzophenone with (diazomethyl)trimethylsilane promoted by *n*-butyllithium as described by Colvin.[16] C_{3v}-$Cp_3Rh_3(CO)_3$ was synthesized by reaction of $CpRh(CO)_2$ with Me_3NO as previously described.[11] $Cp_3Ir_3(CO)_3$ was prepared similarly or by thermal decomposition of $CpIr(CO)H_2$.[12]

Infrared spectra were obtained on a Perkin-Elmer Model 281-B spectrophotometer. Proton NMR spectra were obtained on Varian EM-390 (90 MHz) instruments. Electron impact mass spectra were measured in the University of Illinois, School of Chemical Sciences, Mass Spectrometry Center with a Varian-MAT CH-5 spectrometer.

Synthesis of $Cp_3Rh_3(CO)(C_2Ph_2)$. Diphenylacetylene (303 mg, 1.70 mmol) and $Cp_3Rh_3(CO)_3$ (156 mg, 0.266 mmol) were combined in a 200-mL three-neck cylindrical quartz photolysis vessel equipped with a magnetic stir bar. Benzene (ca. 150 mL) was added and the vessel was fitted with a nitrogen inlet tube extending into the solution. After rapid stirring of the solution with nitrogen bubbling through for several minutes, the dark green solution was photolyzed for 13 h, resulting in a color change to dark blue. The benzene was removed in vacuo followed by column chromatography over neutral alumina. Elution with benzene produced first a greenish yellow band containing diphenylacetylene mixed with a small amount of unreacted $Cp_3Rh_3(CO)_3$, followed by a dark blue band containing $Cp_3Rh_3(CO)(C_2Ph_2)$,[6] which was isolated as a blue-black solid and recrystallized from methylene chloride/methanol to yield large prisms (145 mg, 77%): IR (CH_2Cl_2) 1797 (w), 1693 (sh), 1678 (s cm^{-1}; ^1H NMR (25 °C, $CDCl_3$) δ 7.3–6.8 (m, 10 H), 5.18 (s, 15 H); mass spectrum, *m/z* 710 (M^+). $Cp_3Rh_3(CO)(PhC_2(p\text{-tol}))$ was prepared and isolated similarly from the reaction of $Cp_3Rh_3(CO)_3$ with phenyl-*p*-tolylacetylene: IR (CH_2Cl_2) 1851 (m), 1794 (m), 1691 (sh), 1676 (s) cm^{-1} ^1H NMR ($CDCl_3$, 25 °C) δ 7.3–6.8 (m, 9 H), 5.20 (s, 15 H), 2.27 (s, 3 H); mass spectrum, *m/z* 724 (M^+).

Synthesis of $Cp_3Ir_3(CO)(C_2Ph_2)$. Following the above procedure, an initially purple solution of $Cp_3Ir_3(CO)_3$ (94 mg, 0.11 mmol) and diphenylacetylene (200 mg, 1.12 mmol) in benzene (ca. 100 mL) was photolyzed for 24 h, resulting in a color change to dark red. Chromatography and recrystallization as described above afforded $Cp_3Ir_3(CO)(C_2Ph_2)$ (23 mg, 21%) as a red crystalline solid: IR (CH_2Cl_2) 1736 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 25 °C) δ 6.9 (m, 10 H), 5.39 (s, 5 H), 5.27 (s, 10 H); mass spectrum, *m/z* 980 (M^+, ^{193}Ir).

FVP Experiments. The theory and methodology of FVP have been described elsewhere in detail.[15] The pyrolysis experiments were accomplished by vacuum sublimation ($\lesssim 10^{-5}$ torr) of the organometallic clusters through a resistively heated quartz tube (1 cm × 10 cm) followed by condensation of the products on a cold finger at −196 °C. The products were brought into solution by vacuum distillation of appropriate solvents onto the cold finger, which was then slowly warmed to melt the frozen solvent. The resulting solutions were manipulated under a nitrogen atmosphere using standard techniques.

FVP of $Cp_3Rh_3(CO)(C_2Ph_2)$. This compound (23 mg, 0.032 mmol) was subjected to FVP at 500 °C, resulting in the deposition of a dark green black product on the cold finger. The ^1H NMR spectrum of this product in $CDCl_3$ showed only one new cyclopentadienyl singlet at δ 5.02 and a new aromatic multiplet at δ 7.8–7.6 in addition to resonances due to $Cp_3Rh_3(CO)(C_2Ph_2)$. The mixture was separated by column chromatography over neutral alumina. Elution with benzene developed a yellow band which was isolated as an oily orange residue. Continued elution with benzene/methylene chloride (4:1) developed a dark blue band of $Cp_3Rh_3(CO)(C_2Ph_2)$ (8.5 mg, 37% recovery). Further purification of the orange compound by recrystallization from methylene chloride/methanol resulted in the isolation of $Cp_3Rh_3(CPh)_2$[6] as orange needle crystals (9.4 mg, 43% yield): ^1H NMR (CD_2Cl_2, 25 °C) δ 7.8–7.6 (m, 4 H), 7.3–7.1 (m, 6 H), 5.06 (s, 15 H); mass spectrum, *m/z* 682 (M^+). In a similar experiment $Cp_3Rh_3(CO)(C_2Ph_2)$ was subjected to FVP at 500 °C and the product was washed from the cold finger at low temperature under an atmosphere of carbon monoxide. No new metal carbonyl bands were detected in the IR spectrum of the resulting solution. Chromatography on neutral alumina yielded $Cp_3Rh_3(CO)(C_2Ph_2)$ and $Cp_3Rh_3(CPh)_2$ as the only products.

FVP of $Cp_3Rh_3(CO)(C_2PhTol)$. Pyrolysis of this compound (11 mg) according to the same procedure used for $Cp_3Rh_3(CO)(C_2Ph_2)$ resulting in the isolation of $Cp_3Rh_3(CO)(C_2PhTol)$ (4.3 mg, 39% recovery) and $Cp_3Rh_3(CPh)(CTol)$ (4.8 mg, 45% yield): ^1H NMR ($CDCl_3$, 25 °C) δ 7.8–7.5 (m, 4 H), 7.3–6.8 (m, 5 H), 5.03 (s, 15 H), 2.32 (s, 3 H); mass spectrum, *m/z* 696 (M^+). No other products were observed.

FVP of $Cp_3Ir_3(CO)(C_2Ph_2)$. This compound (14 mg) was pyrolyzed by FVP at 560 °C. Separation of the resultant mixture as described above afforded $Cp_3Ir_3(CO)(C_2Ph_2)$ (8.0 mg, 57% recovery) and $Cp_3Ir_3(CPh)_2$ as a yellow solid (2.8 mg, 20% yield): ^1H NMR ($CDCl_3$, 25 °C) δ 7.7–7.4 (m, 4 H), 7.3–7.0 (m, 6 H), 5.00 (s, 15 H); mass spectrum, *m/z* 956 (M^+, ^{193}Ir). In a similar experiment, the pyrolysis product was washed from the cold finger under an atmosphere of 90% ^{13}C enriched carbon monoxide. The mass spectrum of the recovered $Cp_3Ir_3(CO)(C_2Ph_2)$ did not show a detectable amount of ^{13}CO enrichment. As little as 5% enrichment would have been detected by this method.

Results

Synthesis and Flash Vacuum Pyrolysis. Photolysis of a benzene solution of C_{3v}-$Cp_3Rh_3(CO)_3$ containing excess diphenylacetylene results in formation of $Cp_3Rh_3(CO)(C_2Ph_2)$, which can be isolated in 77% yield after column chromatography. The analogous reaction of $Cp_3Ir_3(CO)_3$ affords $Cp_3Ir_3(CO)(C_2Ph_2)$ (20% isolated yield). On the basis of IR and ^1H NMR, we propose a structure for $Cp_3Ir_3(CO)(C_2Ph_2)$ related to II. The higher carbonyl stretching frequency observed for Cp_3Ir_3-

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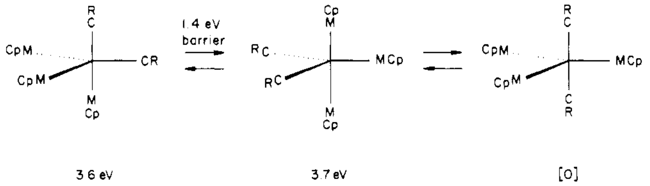
[15] Flash vacuum pyrolysis has been used by organic chemists for many years. See, for example: (a) Wiersum, U. E. *Recl.: J. R. Neth. Chem. Soc.* **1982**, *101*, 317–332. (b) Seybold, G. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 365–373.

[16] Colvin, E. W.; Hamill, B. J. *J. Chem. Soc., Perkin Trans. 1* **1977**, 869–874.

Scheme I

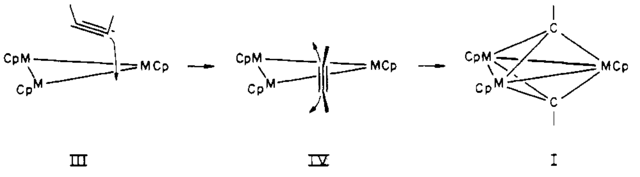


$(CO)(C_2Ph_2)$ (1736 cm^{-1}) suggests a lower degree of interaction with the third metal atom. The room temperature ^1H NMR spectrum of $Cp_3Ir_3(CO)(C_2Ph_2)$ exhibits two singlets for the cyclopentadienyl ligands (2:1 ratio); therefore, the barrier for alkyne rotation is higher than that for $Cp_3Rh_3(CO)(C_2Ph_2)$.[6b]

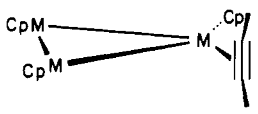
Flash vacuum pyrolysis of $Cp_3Rh_3(CO)(C_2Ph_2)$ at 500 °C results in the formation of a greenish-black deposit on the cold finger. The material is soluble in organic solvents, and the ^1H NMR of the resulting solution exhibits resonances due to $Cp_3Rh_3(CO)(C_2Ph_2)$, together with a second compound shown to be $Cp_3Rh_3(CPh)_2$. Column chromatography of this mixture results in blue $Cp_3Rh_3(CO)(C_2Ph_2)$ (32% recovery) and orange $Cp_3Rh_3(CPh)_2$ (42% yield). The yield of $Cp_3Rh_3(CPh)_2$ is independent of various amounts of rhodium metal predeposited in the hot tube. Furthermore, pyrolysis of the unsymmetrical alkyne complex $Cp_3Rh_3(CO)(C_2PhTol)$ yields only the unsymmetrical dialkylidyne complex $Cp_3Rh_3(CPh)(CTol)$. No metathesis is observed. If the pyrolysis product is washed from the cold finger under carbon monoxide atmosphere at low temperature and slowly warmed to room temperature, the resulting solution does not show any new carbonyl bands in the infrared spectrum. Therefore, no significant amounts of reactive cyclopentadienyl rhodium fragments, which should lead to observable $CpRh(CO)_2$ or $Cp_2Rh_2(CO)_3$, are formed under the conditions of the pyrolysis.

Flash vacuum pyrolysis of $Cp_3Ir_3(CO)(C_2Ph_2)$ at 560 °C followed by chromatography on neutral alumina resulted in a 57% recovery of starting material and a 20% yield of the new dialkylidyne complex $Cp_3Ir_3(CPh)_2$. Although a higher temperature is necessary to effect decarbonylation of $Cp_3Ir_3(CO)(C_2Ph_2)$ relative to $Cp_3Rh_3(CO)(C_2Ph_2)$, the reaction appears to proceed similarly in that decarbonylation is accompanied by alkyne cleavage. In order to test for the presence of "$Cp_3Ir_3(C_2Ph_2)$" in the product mixture, the pyrolysis product was washed from the cold finger at −95 °C under an atmosphere of ^{13}CO (90% enriched) and slowly warmed to room temperature. Under these conditions any "$Cp_3Ir_3(C_2Ph_2)$" present should be converted to $Cp_3Ir_3(^{13}CO)(C_2Ph_2)$, resulting in ^{13}C enrichment of the recovered starting material. The mass spectrum of the recovered $Cp_3Ir_3(CO)(C_2Ph_2)$, however, showed no detectable ^{13}C enrichment (5% detection limits).

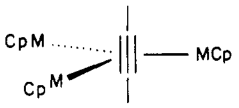
Theory. Our theoretical analysis was based on extended Hückel calculations and qualitative considerations of the electronic structure of possible reaction paths and intermediates. We began by looking at several pathways for scission of C_2H_2, starting from III. The first has the alkyne moving over and coordinating to an edge of the triangle, IV, before splitting.[17] The second pathway has the alkyne moving to vertex coordination V. We also examined way point VI, which one can think of as an alkyne in the center, coordinated by three MCp groups.



III   IV   I



V



VI

The edge "pathways" is calculated to have IV as a transition state, with the alkyne bonded to only two of the metals. This bonding arrangement resembles the metal–alkyne bonding in $Co_2(CO)_6(C_2R_2)$,[18] with the third MCp as a bridging ligand. For the electron count we need, IV has a very small HOMO–LUMO gap and is about 3.5 eV above III.

The "vertex" pathway has an intermediate VI which has the alkyne bonded to only one metal. Serious steric crowding arises between the acetylene and the Cp on the same vertex and between Cp's on different vertices. The calculated energy of the intermediate is very high, >10 eV relative to I.

The "centered" alternative VI is interesting in that its energy is comparable to that of IV. But we were unable to find any reaction path between VI and an alkyne complex that did not involve severe steric problems between the alkyne hydrogens and the metal and Cp ligands.

Only the "edge" pathway maintains the integrity of the metal triangle with a reasonable barrier, ≤3.5 eV. There is, however, an orbital crossing along the path, so that the reaction is formally "forbidden". The crossing occurs near geometry IV.

The trigonal-bipyramidal geometry of the product I leads one naturally to think of a Berry pseudorotation of MCp and CR groups around a phantom center. The sequence is illustrated in Scheme I, which also contains relative energies of the various species from an extended Hückel calculation. We made the restrictive but simple approximation that the distances from the phantom center to C or M were constant along the pseudorotation coordinate and identical with those in the product I.

The trigonal bipyramids in Scheme I resemble some of the possible intermediates discussed earlier. Thus the left trigonal bipyramid is like III: the one of the middle is like IV. But the metal–metal and C–C distances are quite different for these assumed way points on a pseudorotation pathway. The calculated activation energy is not high, but in reality it will be much higher when the left-hand trigonal bipyramid is allowed to relax to the acetylene complex III.

The reaction explored in this paper starts from II. This

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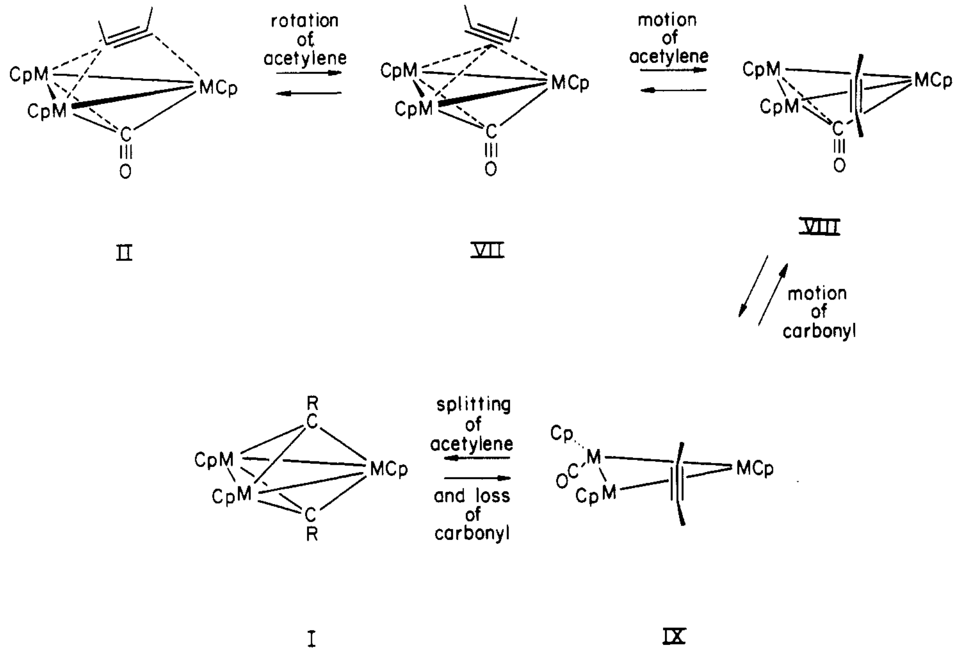
[17] Note in this connection the facile equilibrium between a pentalene bound in one case to the face of a trinuclear complex, in the other case to an edge: Howard, J. A. K.; Knox, S. A. R.; McKinney, R. J.; Stansfield, R. F. D.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1976**, 557–558. Knox, S. A. R.; McKinney, R. J.; Riera, V.; Stone, F. G. A.; Stary, A. C. *J. Chem. Soc., Dalton Trans.* **1979**, 1801–1811.

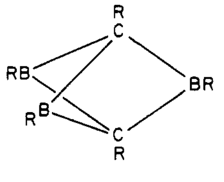
[18] See: Hoffman, D. M.; Hoffmann, R.; Fisel, C. R. *J. Am. Chem. Soc.* **1982**, *104*, 3858–3875, especially ref 13.

Scheme II



molecule has a parallel-bonded alkyne and an extra carbonyl relative to I. Let us examine the hypothetical mechanism of Scheme II. The rotation of the alkyne II → VII and the motion over the edge are "allowed" processes and have barriers of ~0.5 eV. These structures should all be in equilibrium with one another. The CO motion to the third metal has a barrier of 1.5 eV, but level crossing occurs along the way. IX → I is "allowed", with a very small barrier, <0.2 eV. If the motion of the carbonyl to the third metal and acetylene splitting are combined, the net barrier will be much lower than 1.5 eV. We think this is the way the reaction proceeds.

Before leaving this section we would like to mention some connections to boron chemistry. First the incorporation of alkynes into boron cages has been nicely discussed by DeKock, Fehlner, Wade, and co-workers.[19] The isolobal analogy[20] allows one to move between the realms of borane and transition-metal cluster chemistry. A second point emerges by application of that analogy to I, which can be related to a known carborane, X. Since CoCp is



X

isolobal with BH, the bonding of X is as shown. Each boron only has six electrons, two in each bond, and the boron–boron bonding is small. Similarly, our calculation of I shows only a partial cobalt–cobalt bond. The Co–Co Mulliken reduced overlap population is only 0.06, compared to 0.11–0,13 for a single Co–Co bond. In contrast, the cobalt–carbon overlap population is 0.51, indicating a strong single bond. There is also a very large HOMO–LUMO gap, suggesting kinetic stability. We think that the Co–Co interactions in I, while certainly bonding, are less than those in a normal Co–Co single bond.

Discussion

The flash vacuum pyrolysis studies of $Cp_3Rh_3(CO)(C_2Ph_2)$, $Cp_3Rh_3(CO)(C_2PhTol)$, and $Cp_3Ir_3(CO)(C_2Ph_2)$ show that decarbonylation and alkyne cleavage occur with no detectable fragmentation of the metal trinuclear unit. However, the experimental evidence indicates that CO loss is rate determining or does not occur until after the rate-determining step. No evidence for "$Cp_3M_3(C_2Ph_2)$" was found.

These results contrast sharply with the behavior of $Os_3(CO)_{10}(C_2Ph_2)$, which is isoelectronic with $Cp_3Ir_3(CO)(C_2Ph_2)$. Subjecting the trisomium compound to FVP at 250 °C results in clean decarbonylation *without* alkyne cleavage, yielding the coordinatively unsaturated species $Os_3(CO)_9(C_2Ph_2)$.[21] Further thermal or photochemical treatment of $Os_3(CO)_9(C_2Ph_2)$ results only in decomposition. Since the $Cp_3M_3(CO)(C_2Ph_2)$ compounds resist carbonyl loss to higher temperatures, yet ultimately form the $Cp_3M_3(CPh)_2$ products in a very clean reaction, the carbonyl ligand is implicated in reducing the barrier of the carbon–carbon bond breaking process. The theoretical analysis illuminates this role.

As shown in Scheme I the transformation of $Cp_3M_3(C_2R_2)$ into $Cp_3M_3(CR)_2$ can be viewed as a sequence of Berry pseudorotations of a trigonal-bipyramidal M_3C_2 core. However, species IV, with an edge-coordinated alkyne, is particularly high in energy and therefore is not an attractive intermediate.

In contrast, Scheme II provides a mechanism that is consistent with the experimental results and does not pass through any high energy species. Rotation of the alkyne (II → VII) is known experimentally to be facile for $Cp_3Rh_3(CO)(C_2Ph_2)$.[6b] Movement of the alkyne to edge coordination (VII → VIII) in this case is calculated to have only a small barrier, and CO mobility (VIII → IX) should likewise be facile (cf. C_s-$Cp_3Rh_3(CO)_3$[11b]). The key intermediate is IX. In the pathway without the CO (Scheme I) IV is a high-energy intermediate. In the pathway with

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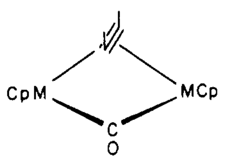
the CO IX is not significantly higher in energy than other intermediate configurations. Comparing IV and IX, it is clear that the major difference is that in IX each metal center is formally saturated (18 e), whereas in IV the third, equatorial metal center is formally unsaturated (only 16 e). Thus, the extra CO in IX serves to stabilize the metal center not involved in bonding to the edge-coordinated alkyne.

Recently, Vollhardt and co-workers[22] reported evidence for an intramolecular "deck shift" reaction (eq 3). This

$$R_3SiC{\equiv}C{-}C[Co_3Cp_3]C{-}C[Co_3Cp_3]CSiR_3 \rightarrow R_3SiC[Co_3Cp_3]C{-}C{\equiv}C{-}C[Co_3Cp_3]CSiR_3 \quad (3)$$

was interpreted in terms of an alkylidyne coupling/decoupling sequence involving structures related to I → IV → III → IV → I. The reconstituted alkyne ligand, however, is necessarily a conjugated diyne, and the second alkyne center can provide the two electrons needed for a saturated intermediate analogous to IX. The accessibility of an unsaturated structure such as IV remains to be determined experimentally.

In other work we have shown that alkyne scission in an "allowed" process on a d^9–d^9 M_2L_6 template.[1] In the case of IX the CpM(CO) fragment is a d^8 ML_4 isolobal with CH_2 isolobal with CO. Therefore, IX is isolobal with XI, a



XI

complex very similar to those we have discussed in the binuclear case.

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Registry No. I (M = Rh, R = Ph), 88801-72-3; I (M = Ir, R = Ph), 88801-74-5; $Cp_3Rh_3(CO)(C_2Ph_2)$, 39346-10-6; $Cp_3Ir_3(CO)(C_2Ph_2)$, 88801-70-1; $Cp_3Rh_3(CO)_3$, 12148-54-8; $Cp_3Ir_3(CO)_3$, 80630-37-1; $Cp_3Rh_3(CO)(C_2PhTol)$, 88801-71-2; $Cp_3Rh_3(CPh)(CTol)$, 88801-73-4; C_2Ph_2, 501-65-5; C_2PhTol, 3287-02-3; Rh, 7440-16-6; Ir, 7439-88-5.

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Cluster Synthesis. 5. Synthesis and Crystal and Molecular Structures of $Os_6(CO)_{19}(\mu_3\text{-}S)$ and $Os_6(CO)_{17}(\mu_4\text{-}S)$

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The cluster compounds $Os_3(CO)_{10}(\mu_3\text{-}S)$ (I) and $Os_3(CO)_{10}(NCMe)_2$ (II) combine when refluxed in benzene solvent to yield the new cluster compound $Os_6(CO)_{19}(\mu_3\text{-}S)$ (III) in 31% yield and the known cluster $Os_5(CO)_{15}(\mu_4\text{-}S)$ (IV) in 18% yield. The structure of III was determined by single-crystal X-ray diffraction methods: space group $P\bar{1}$, $a = 11.119$ (2) Å, $b = 11.357$ (3) Å, $c = 12.904$ (2) Å, $\alpha = 104.51$ (2)°, $\beta = 91.12$ (1)°, $\gamma = 108.80$ (1)°, $V = 1484.4$ (11) Å^3, $Z = 2$, $\rho_{calcd} = 3.82$ g/m^3. The structure was solved by direct methods and refined with 3847 reflections ($F^2 \geq 3.0\sigma(F^2)$) to yield the final residuals $R_1 = 0.038$ and $R_2 = 0.045$. The structure consists of a butterfly tetrahedron of four osmium atoms with two additional osmium tetracarbonyl groups bridging adjacent edges of the butterfly tetrahedron. A triply bridging sulfido ligand bridges one of the open triangular faces of the cluster. When refluxed in toluene solvent, III loses 2 mol of CO and is converted into the new cluster compound $Os_6(CO)_{17}(\mu_4\text{-}S)$ (V) in 23% yield. The structure of V was also determined by a single-crystal X-ray diffraction analysis: space group $Pna2_1$, $a = 11.371$ (3) Å, $b = 16.550$ (3) Å, $c = 14.140$ (3) Å, $V = 2661$ (2) Å^3, $Z = 4$, $\rho_{calcd} = 4.12$ g/cm^3. The structure was solved by direct methods and refined with 1887 reflections ($F^2 \geq 3.0\rho(F^2)$) to yield the final residuals $R_1 = 0.029$ and $R_2 = 0.030$. The structure consists of a capped square pyramid of six osmium atoms with a quadruply bridging sulfido ligand spanning the base of the square pyramid. The observed structure is in accord with the skeletal electron pair theory, but the metal–metal bonding to the capping group is highly distorted. Both the shortest (2.625 (1) Å) and longest (2.930 (1) Å) metal–metal bonds in the molecule involve the capping group. This can be rationalized by a combination of resonance structures, one of which includes a multiple bond at the shortest bond distance and no bond at the longest distance.

Introduction

The widespread interest in the chemistry of transition-metal cluster compounds has stimulated efforts to synthesize them by systematic procedures.[1-4] While redox condensation[2,3] and pyrolytic decarbonylation processes[5] have been employed with considerable success, condensation reactions promoted by bridging ligands have recently attracted attention.[6-14]

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