

event, the phenomenon of decreasing exchange rate associated with the addition of a relatively good donor toward Na^+ is observed with both Me_2SO and HMPA, although at this time less is known about the details of solvation of Na^+ by Me_2SO .

The implications of our proposals for the preparation of mixed aluminates are significant. In the case of $\text{MAIH}_4/\text{MAI}(\text{alkyl})_4$ mixtures,⁵ exchange rates are insignificant in THF alone but become appreciable on addition of $\text{Al}(\text{alkyl})_3$. Hydride exchange in LiAlH_4 has been proposed in the case involving toluene/THF as solvent ($\text{THF}:\text{LiAlH}_4 = 2:1$) but not in pure THF.⁹ We observe alkyl exchange rates which are a function of HMPA: NaAlR_4 ratio. Clearly the best possibility for preparation of stable mixed aluminates, whether containing H or alkyl groups will be under conditions where there is maximum coordination of the cation. Other evidence from our laboratories indicates that the best commonly available donor toward Na^+ is HMPA. It may be possible to control the rates of a wide variety of organometallic exchange processes by making use of the excellent coordinating ability of HMPA. Indeed, the $(\text{AlMe}_3)_2/\text{NaAlEt}_4$ exchange, which is immeasurably fast in benzene, even after some HMPA is added, is very much slower in pure HMPA as solvent.

Experimental Section

Sodium tetraethylaluminate was prepared by a previously reported procedure.¹⁸ Sodium tetramethylaluminate was prepared by adding 0.2 mol of trimethylaluminum dropwise to 0.2 mol of sodium dispersion in 250 mL of toluene and refluxing for 3 h under argon. The mixture was allowed to cool, and the black product was separated by filtration through a fine sintered glass

(18) Frey, F. W., Jr.; Kobetz, P.; Robinson, G. C.; Sistruck, T. O. *J. Org. Chem.* 1961, 26, 2950.

funnel and washed with toluene and hexane. The sodium tetramethylaluminate dissolved on stirring with ether, and the solution was filtered through a sintered glass funnel. The solution was concentrated by evaporation of the solvent and NaAlMe_4 precipitated by adding toluene. This process of dissolution in ether and precipitation with the addition of toluene was repeated twice. Finally the solid white NaAlMe_4 was obtained by evaporation of ether under vacuum. Both sodium tetramethylaluminate and tetraethylaluminate are highly sensitive to atmospheric oxygen and moisture, and hence all operations were performed under an argon atmosphere or in an argon atmosphere drybox.

Kinetic Runs. Benzene was refluxed for 24 h over calcium hydride prior to distillation under a nitrogen atmosphere onto sodium wire. HMPA was refluxed for 48 h over calcium hydride at approximately 0.5 torr prior to distillation. The solutions were prepared in the drybox by weighing the salts in separate containers and adding weighed amounts of HMPA followed by dilution with benzene. The solutions were mixed, and the zero time was noted. The solution separated into two phases immediately. The NMR tube was filled with the lower phase, closed with a pressure cap, taken out of the box, and quenched in liquid nitrogen. The ^1H NMR spectra were run at various time intervals on a Varian HA100 spectrometer equipped with a ^{27}Al decoupler. The peaks were cut out, and the area under the NaAlMe_4 peak was normalized with respect to the total area of the peaks in this region (including the peaks for NaAlMe_3Et , $\text{NaAlMe}_2\text{Et}_2$, and NaAlMeEt_3). Spectra were recorded at several HMPA: Na ratios. The insolubility of NaAlMe_4 at lower HMPA concentrations precludes the kinetic studies below a HMPA: Na^+ ratio of 1.0.

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Registry No. NaAlMe_4 , 16060-25-6; NaAlEt_4 , 2397-68-4; Na^+ , 17341-25-2; HMPA, 680-31-9.

Acetylene Additions to Saturated and Unsaturated Clusters: Four-Electron Addition with and without CO Loss

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The unsaturated cluster $(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu\text{-PPh}_2)$ reacts with diphenylacetylene affording a 1:1 adduct, $(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-PhC}\equiv\text{CPh})(\mu\text{-PPh}_2)$, without CO displacement. Crystals are triclinic of space group $P\bar{1}$ with $a = 9.616$ (2) Å, $b = 14.194$ (4) Å, $c = 15.218$ (4) Å, $\alpha = 102.17$ (2)°, $\beta = 102.31$ (2)°, $\gamma = 97.91$ (2)°, and $Z = 2$. X-ray analysis based on 2744 observed ($I \geq 3\sigma(I)$) reflections and refinement to $R = 0.030$ and $R_w = 0.034$ has revealed that the product is a 50-electron cluster with an open triangular framework, μ -hydrido and μ -phosphido bridges, and face-capping μ_3 -acetylene. This reaction is thus an example of four-electron addition without CO loss. The saturated cluster $\text{Ru}_5(\text{CO})_{13}(\mu_4\text{-}\eta^2\text{-C}\equiv\text{CPh})(\mu\text{-PPh}_2)$ also reacts readily to yield a 1:1 complex of formula $\text{Ru}_5(\text{CO})_{12}(\mu_5\text{-}\eta^2\text{-C}\equiv\text{CPh})(\mu_3\text{-}\eta^2\text{-PhC}\equiv\text{CC}\equiv\text{CPh})(\mu\text{-PPh}_2)$ with diphenylbutadiyne. An X-ray structure determination (monoclinic crystals of space group $P2_1/n$ with $a = 11.195$ (1) Å, $b = 25.638$ (3) Å, $c = 16.384$ (2) Å, $\beta = 92.79$ (1)°, $Z = 4$, $R = 0.030$, $R_w = 0.035$ on 4275 reflections) has shown that the acetylene caps an open triangular face as a four-electron ligand. In this case four-electron addition results in Ru-Ru bond cleavage and loss of a single carbonyl group.

Introduction

The intrinsically high reactivity associated with electronic and coordinative deficiency in mononuclear complexes suggests that unsaturated transition-metal clusters should exhibit unique patterns of chemical behavior with potential applications to catalysis.¹ In addition however,

reaction modes are accessible to clusters that have no counterparts in mononuclear chemistry. Of particular

(1) For recent work on coordinatively unsaturated cluster chemistry see: (a) Kulzick, M.; Price, T.; Muettterties, E. L.; Day, V. W. *Organometallics* 1982, 1, 1256. (b) Sivak, A. J.; Muettterties, E. L. *J. Am. Chem. Soc.* 1979, 101, 4878. (c) Fryzuk, M. D. *Organometallics* 1982, 1, 408.

importance is the way in which clusters appear to mimic the reactivity of unsaturated species. This is manifest in reversible metal-metal bond cleavage, several examples of which have recently come to light,² skeletal rearrangement without degradation³ and ligand activation via multisite coordination. Unfortunately, among the more easily studied low to medium nuclearity clusters, relatively few unsaturated species are known⁴ and reactivity studies have been principally restricted to $\text{H}_2\text{Os}_3(\text{CO})_{10}$,⁵ the rhodium clusters $[\text{HRhL}_2]_x$,¹ and more recently $\text{Fe}_4(\text{CO})_{11}(\text{PR})_2$.⁶ Evidence for the uptake of nucleophiles by saturated species, in a process apparently similar in result to that of reaction at an unsaturated site, has recently been observed for a select group of clusters.^{2,3}

In our efforts to examine the reactivity patterns of saturated and unsaturated low nuclearity clusters, we have discovered several examples of facile unsaturated ligand addition without CO loss, suggesting that this reaction mode may be favored for certain cluster systems under mild conditions. We describe herein the addition of diphenylacetylene to the unsaturated 46-electron trinuclear cluster $(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu\text{-PPh}_2)$ (III), a reaction which precisely illustrates several of the features likely to be encountered in unsaturated cluster chemistry; multisite coordination of an unsaturate without CO loss, with metal-metal bond cleavage and reorganization of the ligand envelope. Similar characteristics are also displayed in the reaction of diphenylbutadiyne with the formally saturated 74-electron cluster $\text{Ru}_5(\text{CO})_{13}(\mu_4\text{-}\eta^2\text{-C}\equiv\text{CPh})(\mu\text{-PPh}_2)$ (V) where Ru-Ru bond cleavage accompanies four-electron addition. In this case, however, one CO molecule is lost in a net two-electron addition.

Experimental Section

Synthesis of $\text{Ru}_3(\text{CO})_{11}(\text{PPh}_2\text{H})$ (I). Complex I was obtained via the method of Bruce et al.,⁷ the only modification being the use of warm freshly distilled THF to aid dissolution of $\text{Ru}_3(\text{CO})_{12}$. This procedure also enhanced the speed of the substitution reaction and minimized the formation of multisubstituted products: IR (C_6H_{12}) $\nu(\text{CO})$ 2096 (w), 2045 (vs), 2028 (s), 2014 (vs), 1993 (w), 1985 (w), 1975 (sh), 1959 (w sh) cm^{-1} .

Synthesis of $(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}(\mu\text{-PPh}_2)$ (II). A solution of I (0.5 g, 0.63 mmol) in *n*-heptane (50 mL) was heated at 60 °C for 10 h. Care was taken not to exceed 60 °C, to inhibit fragmentation and redistribution reactions. Chromatography on Florisil (100–200 mesh) with a $\text{C}_7\text{H}_{16}/\text{C}_6\text{H}_6$ (70:30) eluant yielded an initial orange band which on fractional crystallization from heptane/benzene afforded orange crystals of II (0.41 g, 85%). II is moderately soluble in hydrocarbon solvents and very soluble in polar organic solvents. Though stable in the solid state it decomposed slowly in solution to yield III among other products.^{9,18}

(2) See for example: (a) Huttner, G.; Schneider, J.; Muller, H. D.; Mohr, G.; Von Seyerl, J.; Wohlfahrt, L. *Angew. Chem., Int. Ed. Engl.* 1979, 18, 76. (b) Richter, F.; Vahrenkamp, H. *Organometallics* 1982, 1, 756. (c) Carty, A. J.; MacLaughlin, S. A.; Taylor, N. J. *J. Organomet. Chem.* 1981, 204, C27. (d) Johns, R. A.; Wright, T. C.; Atwood, J. L.; Hunter, W. E. *Organometallics* 1983, 2, 470. (e) MacLaughlin, S. A.; Taylor, N. J.; Carty, A. J. *Organometallics* 1983, 2, 1194.

(3) Several notable examples of cluster skeletal rearrangements accompanying Lewis base additions have been reported. See for example: (a) Bruce, M. I.; Matisons, J. G.; Rodgers, J. R.; Wallis, R. C. *J. Chem. Soc., Chem. Commun.* 1981, 1070. (b) Farrar, D. H.; Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; Nicholls, J. K. N.; McPartlin, M. *Ibid.* 1981, 415.

(4) Johnson, B. F. G.; Lewis, J. *Adv. Inorg. Chem. Radiochem.* 1981, 24, 225.

(5) (a) Deeming, A. J.; Hasso, S.; Underhill, M. *J. Chem. Soc., Dalton Trans.* 1975, 1614. (b) Jackson, W. G.; Johnson, B. F. G.; Kelland, J. W.; Lewis, J.; Schorpp, K. T. *J. Organomet. Chem.* 1975, 87, C27. (c) Keister, J. B.; Shapley, J. R. *Ibid.* 1975, 85, C27.

(6) Vahrenkamp, H.; Wolters, D. *Organometallics* 1982, 1, 874.

(7) Bruce, M. I.; Kehoe, D. C.; Matisons, J. G.; Nicholson, B. K.; Rieger, P. H.; Williams, M. L. *J. Chem. Soc., Chem. Commun.* 1982, 442.

Table I. Summary of Crystal Data for Complexes IV and V

	IV	V
formula	$\text{Ru}_3\text{PO}_9\text{C}_{42}\text{H}_{26}$	$\text{Ru}_5\text{PO}_{12}\text{C}_{48}\text{H}_{25}$
mol wt	1008.44	1329.77
cryst class	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
cell dimens		
<i>a</i> , Å	9.616 (2)	11.195 (1)
<i>b</i> , Å	14.194 (2)	25.638 (3)
<i>c</i> , Å	15.218 (4)	16.384 (2)
α , Å	102.17 (2)	
β , Å	102.31 (2)	92.79 (1)
γ , Å	97.91 (2)	
cell vol, Å ³	1947 (1)	4697.2 (9)
Z	2	4
ρ calcd, g cm ⁻³	1.721	1.880
ρ calcd, g cm ⁻³	1.72	1.85
<i>F</i> (000)	994	2576
μ (Mo K α), cm ⁻¹	12.21	16.30
total reflectns measd	3670	6165
no. of reflectns, $I \geq 3\sigma(I)$	2744	4257
std reflectns	040, 013	500, 102
final <i>R</i>	0.030	0.030
final <i>R</i> _w	0.034	0.035

IR (C_6H_{12}) $\nu(\text{CO})$ 2098 (w), 2054 (s), 2048 (m), 2020 (s), 2002 (w), 1996 (m), 1987 (w) cm^{-1} . Anal. Calcd for $\text{Ru}_3\text{C}_{22}\text{H}_{11}\text{PO}_{10}$: C, 34.33, H, 1.44; P, 4.02. Found: C, 34.73; H, 1.46; P, 4.35.

Synthesis of $(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu\text{-PPh}_2)$ (III). Complex II (0.30 g, 0.39 mmol) was dissolved in CH_2Cl_2 (20 mL). A solution of Me_3NO (0.032 g, 0.43 mmol) in ethanol (0.5 mL) and CH_2Cl_2 (4 mL) was added dropwise (1–2 min). Immediately following the addition the mixture was rapidly evaporated to dryness and the residue extracted with heptane/benzene (1:1). Chromatography on Florisil with $\text{C}_7\text{H}_{16}/\text{C}_6\text{H}_6$ (9:1) afforded a small amount of starting material followed by a second, orange-red band of the desired product. Crystallization from heptane at -10 °C yielded 0.20 g of III (70%).^{8,9} III decomposes slowly in the solid state and in solution. In the latter case complex II is obtained, as well as other materials.^{9,18} IR (C_6H_{12}) $\nu(\text{CO})$ 2083 (s), 2055 (vs), 2029 (vs), 2014 (s), 1993 (m), 1986 (m) cm^{-1} . Anal. Calcd for $\text{Ru}_3\text{C}_{21}\text{H}_{11}\text{PO}_9$: C, 34.01; H, 1.50. Found: C, 34.22; H, 1.66.

Synthesis of $(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu\text{-PPh}_2)(\mu_3\text{-}\eta^2\text{-PhC}\equiv\text{CPh})$ (IV). Complex III (0.20 g, 0.27 mmol) and $\text{PhC}\equiv\text{CPh}$ (0.10 g, 0.55 mmol) were dissolved in benzene (10 mL) and allowed to stir at room temperature for 48 h. IR monitoring was used to gauge consumption of the starting material. Column chromatography (Florisil) with a heptane eluant yielded a small amount of II followed by a yellow band, which on workup and crystallization from heptane gave a product analyzing as $(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu\text{-PPh}_2)(\text{PhC}\equiv\text{CPh})_{1.5}$. X-ray analysis (vide infra) revealed that a free molecule of $\text{PhC}\equiv\text{CPh}$ was present in the crystal, lying on a center of symmetry. Complex IV is stable in the solid state. It is soluble in hydrocarbon solvents in which it decomposes slowly. Other products obtained in the reaction were not characterized: IR (C_6H_{12}) $\nu(\text{CO})$ 2094 (w), 2074 (vs), 2047 (vs), 2023 (s), 2019 (m), 1992 (w), 1955 (w), 1930 (w) cm^{-1} . Anal. Calcd for $\text{Ru}_3\text{C}_{42}\text{H}_{26}\text{PO}_9$: C, 49.99; H, 2.59. Found: C, 50.19; H, 2.75.

Synthesis of $\text{Ru}_5(\text{CO})_{12}(\mu_5\text{-}\eta^2\text{-C}\equiv\text{CPh})(\mu_3\text{-}\eta^2\text{-PhC}\equiv\text{CPh})(\mu\text{-PPh}_2)$ (VI). $\text{Ru}_5(\text{CO})_{13}(\mu\text{-PPh}_2)(\mu_4\text{-}\eta^2\text{-C}\equiv\text{CPh})$ (V)^{15,18} (0.10 g, 0.87 mmol) was mixed with diphenylbutadiyne (0.06 g, 0.3 mmol) in tetrahydrofuran (15 mL) at room temperature under a nitrogen atmosphere. After 24 h a $\nu(\text{CO})$ IR spectrum showed consumption of the starting material. The mixture was evaporated and chromatographed on Florisil with a mixed $\text{C}_7\text{H}_{16}/\text{C}_6\text{H}_6$ (1:1) eluant to yield two products. The major product VI was crystallized from heptane as purple-red prisms: IR (C_6H_{12}) $\nu(\text{CO})$ 2081 (m), 2065 (vs), 2060 (sh), 2036 (vs), 2028 (s), 2018 (vs), 2006 (m),

(8) The cluster $\text{HRu}_3(\text{CO})_9(\text{PPh}_2)$ was previously obtained in modest yield (~30%) via the reduction of $\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}\equiv\text{C-}t\text{-Bu})(\text{PPh}_2)$ by molecular hydrogen.⁹ The present method is simpler and gives much improved yields.

(9) MacLaughlin, S. A.; Carty, A. J.; Taylor, N. J. *Can. J. Chem.* 1982, 60, 87.

Table II. Atomic Positions (Fractional, $\times 10^4$) and Hydrogen Atom Thermal Parameters ($\times 10^3$) for $(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-PhC}\equiv\text{CPh})\cdot 0.5\text{PhC}\equiv\text{CPh}$

A. Non-Hydrogen Atoms									
atom	x	y	z	atom	x	y	z		
Ru(1)	1097.6 (7)	3760.4 (4)	2540.3 (4)	C(16)	-1696 (9)	1527 (6)	-1251 (5)		
Ru(2)	-1537.9 (7)	3341.8 (5)	3030.6 (4)	C(17)	-1562 (8)	1736 (6)	-318 (5)		
Ru(3)	832.3 (7)	1638.1 (4)	2047.1 (4)	C(18)	-2182 (8)	3558 (5)	985 (5)		
P	-912 (2)	1763 (1)	2951 (1)	C(19)	-1631 (9)	4178 (5)	502 (5)		
O(1)	3912 (6)	4179 (5)	1945 (4)	C(20)	-2530 (10)	4494 (6)	-171 (7)		
O(2)	611 (7)	5791 (4)	2418 (5)	C(21)	-4011 (11)	4164 (7)	-395 (6)		
O(3)	2489 (7)	4522 (4)	4614 (4)	C(22)	-4589 (10)	3558 (7)	91 (6)		
O(4)	-4653 (6)	2560 (5)	2942 (4)	C(23)	-3675 (9)	3270 (6)	773 (6)		
O(5)	-2395 (8)	5334 (5)	2970 (5)	C(24)	-323 (8)	1635 (5)	4127 (5)		
O(6)	-624 (7)	3892 (4)	5174 (4)	C(25)	1111 (10)	2004 (6)	4656 (6)		
O(7)	2423 (7)	417 (5)	3224 (4)	C(26)	1507 (11)	2076 (7)	5591 (6)		
O(8)	-1059 (6)	-194 (4)	635 (4)	C(27)	488 (11)	1756 (8)	6024 (6)		
O(9)	3207 (6)	1685 (4)	977 (4)	C(28)	-898 (10)	1390 (8)	5549 (6)		
C(1)	2833 (8)	3978 (6)	2136 (6)	C(29)	-1313 (9)	1339 (8)	4609 (6)		
C(2)	742 (9)	5007 (6)	2442 (6)	C(30)	-2392 (8)	688 (5)	2407 (5)		
C(3)	1928 (9)	4244 (5)	3852 (6)	C(31)	-2257 (9)	-208 (6)	2602 (6)		
C(4)	-3456 (9)	2839 (6)	2973 (5)	C(32)	-3254 (10)	-1043 (7)	2111 (8)		
C(5)	-2026 (9)	4602 (6)	2981 (6)	C(33)	-4414 (10)	-987 (7)	1425 (7)		
C(6)	-989 (8)	3693 (6)	4374 (6)	C(34)	-4564 (9)	-103 (6)	1239 (6)		
C(7)	1847 (9)	885 (6)	2797 (6)	C(35)	-3557 (8)	719 (6)	1705 (5)		
C(8)	-354 (8)	471 (6)	1164 (5)	C(36) ^a	5104 (13)	452 (8)	5181 (8)		
C(9)	2321 (8)	1693 (5)	1364 (5)	C(37) ^a	5276 (10)	1500 (7)	5581 (8)		
C(10)	-318 (8)	2565 (5)	1312 (5)	C(38) ^a	5160 (11)	2127 (8)	5014 (8)		
C(11)	-1285 (8)	3121 (5)	1657 (5)	C(39) ^a	5297 (13)	3076 (9)	5369 (11)		
C(12)	-358 (8)	2362 (5)	311 (5)	C(40) ^a	5569 (17)	3445 (10)	6317 (16)		
C(13)	709 (9)	2775 (6)	-59 (5)	C(41) ^a	5714 (16)	2792 (17)	6875 (10)		
C(14)	555 (10)	2593 (7)	-1018 (6)	C(42) ^a	5592 (12)	1803 (11)	6519 (8)		
C(15)	-657 (10)	1964 (8)	-1608 (6)						

B. Hydrogen Atoms									
atom	x	y	z	U, Å ²	atom	x	y	z	U, Å ²
H(1)	168	289	284	55 (19)	H(27)	80	184	664	71 (32)
H(13)	149	325	34	50 (27)	H(28)	-170	111	587	49 (30)
H(14)	143	299	-126	74 (27)	H(29)	-205	116	434	48 (32)
H(15)	-80	192	-222	78 (30)	H(31)	-146	-27	306	79 (25)
H(16)	-265	115	-168	51 (27)	H(32)	-309	-163	220	70 (32)
H(17)	-224	145	-6	47 (24)	H(33)	-508	-151	114	86 (30)
H(19)	-56	452	65	66 (24)	H(34)	-539	-9	69	77 (27)
H(20)	-212	501	-48	92 (28)	H(35)	-363	124	158	55 (27)
H(21)	-460	436	-81	48 (30)	H(38)	475	181	415	119 (32)
H(22)	-557	333	-12	43 (29)	H(39)	522	355	506	76 (44)
H(23)	-405	287	107	42 (27)	H(40)	559	392	652	148 (51)
H(25)	171	211	432	41 (28)	H(41)	604	287	730	92 (52)
H(26)	259	233	596	46 (29)	H(42)	559	135	701	109 (38)

^a Represents the half molecule of PhC≡CPh of crystallization.

1989 (m), 1965 (w), 1941 (vw) cm⁻¹. Anal. Calcd for Ru₅C₄₈H₂₆PO₁₂: C, 43.33; H, 1.89. Found: C, 42.98; H, 1.78.

X-ray Analyses. (i) $(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-PhC}\equiv\text{CPh})(\mu\text{-PPh}_2)\cdot 0.5\text{PhC}\equiv\text{CPh}$ (IV). Crystal data for complex IV are given in Table I. Intensity data were collected on a crystal of dimensions $0.09 \times 0.17 \times 0.18$ mm using θ - 2θ scans ($3.2 \leq 2\theta \leq 42.0^\circ$) with a variable scan speed of 2.0 - 29.3° mm⁻¹ and a scan width of 0.8° below $K\alpha_1$ to 0.8° above $K\alpha_2$ on a Syntex P2₁ diffractometer. From a total of 3670 measured reflections, 2744 had $I \geq 3\sigma(I)$ and were used in the structure solution and refinement. Two standard reflections (040, 013) monitored after every 100 measurements showed no change in intensity over the course of data collection. With $\mu = 12.21$ cm⁻¹ for these atoms no absorption correction was deemed necessary. Transmission factors varied between 0.79 and 0.90. The structure was solved by standard Patterson and Fourier techniques. Refinement of all non-hydrogen atoms with isotropic parameters gave an R value ($R = \sum |F_o| - |F_c| / \sum |F_o|$) of 0.050. Anisotropic refinement reduced R to 0.037. A difference map at this stage allowed location of all hydrogen atoms. These were included in subsequent refinements but with only the isotropic thermal parameters allowed to vary. Convergence was achieved with R and R_w ($R_w = \sum w|F_o| - |F_c| / \sum w|F_o|$) values of 0.030 and 0.034. A final difference map was featureless ($E_{\text{max}} = 0.5$ e Å⁻³). Scattering factors were taken from ref 10, and for hydrogen, scattering factors were taken

from the data of Stewart et al.¹¹ Both real and imaginary components of anomalous dispersion were applied to corrections for the ruthenium atoms. Computer programs used have been described in detail elsewhere.¹² Atomic positions are listed in Table II and a selection of bond lengths and angles in Table III. Thermal parameters, remaining bond lengths and angles, and structure factors (Tables S1-S3) have been deposited.

(ii) $\text{Ru}_5(\text{CO})_{12}(\mu_5\text{-}\eta^2\text{-C}\equiv\text{CPh})(\mu_3\text{-}\eta^2\text{-PhC}\equiv\text{CC}\equiv\text{CPh})(\mu\text{-PPh}_2)$ (VI). Crystal data for complex VI are given in Table I. Intensity data were collected on a crystal of dimensions $0.27 \times 0.25 \times 0.25$ mm using θ - 2θ scans ($3.2 \leq 2\theta \leq 45^\circ$) with a variable scan speed of 2.93 - 29.3° min⁻¹ and a scan width of 0.75° below $K\alpha_1$ to 0.75° above $K\alpha_2$ on a Syntex P2₁ diffractometer. From a total of 6165 measured reflections, 4257 had $I \geq 3\sigma(I)$ and were used in the structure solution and refinement. Two standard reflections (500, 102) monitored after every 100 measurements fell in intensity by 10%. These were used to scale the data to a common level. With $\mu = 16.30$ cm⁻¹ for these atoms, no ab-

(10) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1975; Vol. IV.

(11) Stewart, R. F.; Davidson, E.; Simpson, W. *J. Chem. Phys.* **1968**, *42*, 3175.

(12) Carty, A. J.; Mott, G. N.; Taylor, N. J.; Yule, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 3051.

Table III. A Selection of Bond Lengths (Å) and Angles (deg) for $(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu\text{-PPh}_2)(\mu_3\text{-}\eta^2\text{-PhC}\equiv\text{C-Ph})\cdot 0.5\text{PhC}\equiv\text{CPh}$

A. Important Bond Lengths			
Ru(1)-Ru(2)	2.813 (1)	Ru(1)-Ru(3)	2.908 (1)
Ru(2)-Ru(3)	3.838 (1)	Ru(2)-P	2.385 (2)
Ru(3)-P	2.387 (2)	Ru(1)-C(1)	1.908 (8)
Ru(1)-C(2)	1.878 (9)	Ru(1)-C(3)	1.920 (8)
Ru(2)-C(4)	1.860 (9)	Ru(2)-C(5)	1.923 (9)
Ru(2)-C(6)	1.935 (9)	Ru(3)-C(7)	1.931 (9)
Ru(3)-C(8)	1.934 (8)	Ru(3)-C(9)	1.942 (8)
Ru(1)-C(10)	2.274 (7)	Ru(1)-C(11)	2.341 (8)
Ru(2)-C(11)	2.118 (8)	Ru(3)-C(10)	2.168 (7)
Ru(1)-H(1)	1.54	Ru(3)-H(1)	1.89
P-C(24)	1.815 (7)	P-C(30)	1.846 (8)
C(1)-O(1)	1.152 (10)	C(2)-O(2)	1.143 (11)
C(3)-O(3)	1.128 (10)	C(4)-O(4)	1.152 (11)
C(5)-O(5)	1.146 (11)	C(6)-O(6)	1.154 (11)
C(7)-O(7)	1.139 (11)	C(8)-O(8)	1.127 (10)
C(9)-O(9)	1.135 (10)	C(10)-C(11)	1.415 (11)
C(10)-C(12)	1.481 (10)	C(11)-C(18)	1.487 (10)
B. Important Bond Angles			
Ru(2)-Ru(1)-Ru(3)	84.2 (0)	Ru(2)-Ru(1)-C(1)	176.3 (2)
Ru(2)-Ru(1)-C(2)	90.3 (2)	Ru(2)-Ru(1)-C(3)	85.2 (2)
Ru(2)-Ru(1)-C(10)	75.5 (1)	Ru(2)-Ru(1)-C(11)	47.5 (1)
Ru(2)-Ru(1)-H(1)	94	Ru(3)-Ru(1)-C(1)	93.1 (2)
Ru(3)-Ru(1)-C(2)	158.7 (2)	Ru(3)-Ru(1)-C(3)	108.8 (2)
Ru(3)-Ru(1)-C(10)	47.5 (1)	Ru(3)-Ru(1)-C(11)	73.7 (1)
Ru(3)-Ru(1)-H(1)	36	C(1)-Ru(1)-C(2)	91.2 (3)
C(1)-Ru(1)-C(3)	98.2 (3)	C(1)-Ru(1)-C(10)	100.8 (3)
C(1)-Ru(1)-C(11)	129.3 (3)	C(1)-Ru(1)-H(1)	85
C(2)-Ru(1)-C(3)	91.1 (3)	C(2)-Ru(1)-C(10)	111.2 (3)
C(2)-Ru(1)-C(11)	87.5 (3)	C(2)-Ru(1)-H(1)	166
C(3)-Ru(1)-C(10)	150.2 (3)	C(3)-Ru(1)-C(11)	132.6 (3)
C(3)-Ru(1)-H(1)	76	C(10)-Ru(1)-C(11)	35.7 (2)
C(10)-Ru(1)-H(1)	83	C(11)-Ru(1)-H(1)	106
Ru(1)-Ru(2)-P	82.8 (0)	Ru(1)-Ru(2)-C(4)	162.1 (2)
Ru(1)-Ru(2)-C(5)	94.2 (2)	Ru(1)-Ru(2)-C(6)	103.9 (2)
Ru(1)-Ru(2)-C(11)	54.5 (2)	P-Ru(2)-C(4)	91.4 (2)
P-Ru(2)-C(5)	174.8 (2)	P-Ru(2)-C(6)	92.4 (2)
P-Ru(2)-C(11)	84.5 (2)	C(4)-Ru(2)-C(5)	90.2 (3)
C(4)-Ru(2)-C(6)	93.2 (3)	C(4)-Ru(2)-C(11)	108.2 (3)
C(5)-Ru(2)-C(6)	92.5 (3)	C(5)-Ru(2)-C(11)	90.3 (3)
C(6)-Ru(2)-C(11)	158.4 (3)	Ru(1)-Ru(3)-P	80.7 (0)
Ru(1)-Ru(3)-C(7)	125.5 (2)	Ru(1)-Ru(3)-C(8)	141.3 (2)
Ru(1)-Ru(3)-C(9)	93.1 (2)	Ru(1)-Ru(3)-C(10)	50.7 (1)
Ru(1)-Ru(3)-H(1)	29	P-Ru(3)-C(7)	91.7 (2)
P-Ru(3)-C(8)	92.5 (2)	P-Ru(3)-C(9)	173.6 (2)
P-Ru(3)-C(10)	84.8 (2)	P-Ru(3)-H(1)	82
C(7)-Ru(3)-C(8)	92.6 (3)	C(7)-Ru(3)-C(9)	90.9 (3)
C(7)-Ru(3)-C(10)	175.2 (3)	C(7)-Ru(3)-H(1)	97
C(8)-Ru(3)-C(9)	93.2 (3)	C(8)-Ru(3)-C(10)	90.9 (3)
C(8)-Ru(3)-H(1)	169	C(9)-Ru(3)-C(10)	92.2 (3)
C(9)-Ru(3)-H(1)	92	C(10)-Ru(3)-H(1)	79
Ru(2)-P-Ru(3)	107.1 (0)	Ru(2)-P-C(24)	108.1 (2)
Ru(2)-P-C(30)	116.9 (2)	Ru(3)-P-C(24)	115.8 (2)
Ru(3)-P-C(30)	106.6 (2)	C(24)-P-C(30)	102.7 (3)
Ru(1)-C(1)-O(1)	174.6 (3)	Ru(1)-C(2)-O(2)	175.7 (3)
Ru(1)-C(3)-O(3)	176.2 (3)	Ru(2)-C(4)-O(4)	177.6 (3)
Ru(2)-C(5)-O(5)	175.5 (3)	Ru(2)-C(6)-O(6)	178.0 (3)
Ru(3)-C(7)-O(7)	178.1 (3)	Ru(3)-C(8)-O(8)	178.2 (2)
Ru(3)-C(9)-O(9)	176.6 (3)	Ru(1)-H(1)-Ru(3)	116
Ru(1)-C(10)-Ru(3)	81.8 (0)	Ru(1)-C(10)-C(11)	74.8 (3)
Ru(1)-C(10)-C(12)	131.0 (2)	Ru(3)-C(10)-C(11)	123.9 (3)
Ru(3)-C(10)-C(12)	114.3 (2)	C(11)-C(10)-C(12)	119.7 (4)
Ru(1)-C(11)-Ru(2)	78.0 (0)	Ru(1)-C(11)-C(10)	69.6 (3)
Ru(1)-C(11)-C(18)	127.3 (2)	Ru(2)-C(11)-C(10)	124.5 (3)
Ru(2)-C(11)-C(18)	119.5 (2)	C(10)-C(11)-C(18)	116.0 (4)

sorption correction was deemed necessary. Transmission factors varied between 0.59 and 0.74. The five ruthenium atoms were located in a Patterson synthesis and light atoms via subsequent Fourier maps. Refinement of all non-hydrogen atoms with isotropic parameters gave an R value of 0.051. Refinement with anisotropic coefficients reduced R to 0.036. At this stage, all the hydrogen atoms were located from a difference Fourier map. These were included in subsequent refinements. The converged R and R_w values were 0.030 and 0.035, respectively ($w^{-1} = 1.50 - 0.01|F_o| + 0.00007|F_o|^2$). A final difference map was featureless

with maximum residuals of $0.5 \text{ e } \text{Å}^{-3}$ in the vicinity of the ruthenium atoms. Atomic positions are listed in Table IV and a selection of bond lengths and angles in Table V and VI, respectively. Anisotropic thermal parameters, remaining bond lengths and angles, and structure factors are available as supplementary material (Tables S4-S6).

Results and Discussion

Although we have previously described a synthetic route

Table IV. Atomic Positions (Fractional, $\times 10^4$) and Hydrogen Atom Thermal Parameters ($\times 10^2$) for $\text{Ru}_3(\text{CO})_{12}(\mu\text{-PPh}_2)(\mu_3\text{-}\eta^2\text{-C}\equiv\text{CPh})(\mu_3\text{-}\eta^2\text{-PhC}\equiv\text{CC}\equiv\text{CPh})$

A. Non-Hydrogen Atoms

atom	x	y	z	atom	x	y	z
Ru(1)	-358.1 (5)	1457.2 (2)	2535.9 (4)	C(16)	1946 (6)	810 (2)	2836 (4)
Ru(2)	1665.1 (5)	909.9 (2)	4107.6 (3)	C(17)	2903 (6)	465 (3)	2636 (4)
Ru(3)	2077.8 (5)	1662.1 (2)	2900.6 (3)	C(18)	3684 (6)	167 (3)	2510 (4)
Ru(4)	452.7 (5)	2417.7 (2)	3344.5 (4)	C(19)	-1158 (6)	1117 (3)	4348 (4)
Ru(5)	2053.9 (5)	1996.3 (2)	4504.9 (3)	C(20)	-1862 (6)	678 (3)	4232 (5)
P	1849.0 (17)	2848.4 (7)	4142.7 (11)	C(21)	-2816 (7)	595 (3)	4724 (5)
O(1)	-1580 (6)	425 (2)	2102 (4)	C(22)	-3090 (7)	936 (4)	5322 (5)
O(2)	-658 (6)	1995 (2)	872 (4)	C(23)	-2387 (8)	1365 (4)	5447 (6)
O(3)	-2763 (5)	1978 (3)	2897 (4)	C(24)	-1426 (7)	1461 (3)	4980 (5)
O(4)	624 (5)	-182 (2)	3865 (4)	C(25)	1323 (6)	845 (3)	1358 (4)
O(5)	1256 (5)	932 (2)	5951 (3)	C(26)	1181 (7)	310 (3)	1173 (5)
O(6)	4257 (5)	602 (2)	4573 (4)	C(27)	1325 (8)	126 (4)	378 (6)
O(7)	2523 (6)	2443 (2)	1581 (4)	C(28)	1614 (9)	474 (4)	-228 (6)
O(8)	4763 (5)	1629 (3)	3158 (4)	C(29)	1766 (9)	983 (4)	-52 (5)
O(9)	-1754 (5)	2895 (2)	4014 (4)	C(30)	1616 (8)	1169 (3)	725 (5)
O(10)	230 (7)	3168 (2)	1900 (4)	C(31)	4609 (7)	-195 (3)	2332 (5)
O(11)	4670 (5)	1913 (2)	5048 (4)	C(32)	4723 (8)	-381 (3)	1547 (6)
O(12)	1539 (7)	2148 (3)	6271 (4)	C(33)	5623 (9)	-722 (4)	1360 (7)
C(1)	-1154 (7)	816 (3)	2250 (5)	C(34)	6423 (9)	-878 (4)	1953 (8)
C(2)	-489 (7)	1793 (3)	1480 (5)	C(35)	6316 (10)	-713 (5)	2746 (8)
C(3)	-1852 (7)	1814 (3)	2801 (5)	C(36)	5415 (8)	-356 (4)	2906 (6)
C(4)	1014 (6)	212 (3)	3987 (5)	C(37)	1374 (6)	3322 (3)	4908 (4)
C(5)	1392 (6)	961 (3)	5277 (5)	C(38)	416 (7)	3197 (3)	5374 (5)
C(6)	3322 (7)	726 (3)	4384 (5)	C(39)	37 (9)	3541 (4)	5949 (6)
C(7)	2308 (7)	2156 (3)	2085 (5)	C(40)	607 (10)	4000 (4)	6078 (6)
C(8)	3737 (7)	1662 (3)	3076 (5)	C(41)	1561 (10)	4134 (3)	5630 (6)
C(9)	-901 (8)	2716 (3)	3768 (5)	C(42)	1973 (7)	3790 (3)	5042 (4)
C(10)	329 (7)	2889 (3)	2435 (5)	C(43)	2983 (6)	3191 (3)	3597 (4)
C(11)	3677 (8)	1948 (3)	4847 (4)	C(44)	4141 (8)	3033 (3)	3609 (6)
C(12)	1715 (8)	2094 (3)	5605 (5)	C(45)	4977 (9)	3291 (4)	3133 (7)
C(13)	579 (6)	1652 (2)	3805 (4)	C(46)	4622 (11)	3715 (5)	2693 (7)
C(14)	-140 (5)	1235 (2)	3834 (4)	C(47)	3488 (10)	3889 (4)	2675 (6)
C(15)	1197 (6)	1019 (2)	2213 (4)	C(48)	2646 (8)	3619 (3)	3127 (5)

B. Hydrogen Atoms

atom	x	y	z	U, Å ²	atom	x	y	z	U, Å ²
H(20)	-1624	459	3741	6 (2)	H(35)	7072	-745	3131	15 (3)
H(21)	-3343	312	4559	8 (2)	H(36)	5380	-262	3451	13 (3)
H(22)	-3775	877	5731	11 (3)	H(38)	-37	2849	5238	5 (2)
H(23)	-2537	1591	5855	9 (3)	H(39)	-603	3419	6243	6 (2)
H(24)	-944	1772	4961	4 (2)	H(40)	418	4205	6546	11 (3)
H(26)	867	80	1573	9 (3)	H(41)	2080	4443	5809	5 (2)
H(27)	833	-328	207	16 (3)	H(42)	2684	3911	4691	8 (2)
H(28)	1550	426	-807	14 (3)	H(44)	4470	2724	3944	5 (2)
H(29)	1971	1235	-512	8 (2)	H(45)	5818	3120	3197	10 (3)
H(30)	1760	1553	796	11 (3)	H(46)	5187	3851	2389	11 (3)
H(32)	4059	-240	1096	9 (2)	H(47)	3178	4133	2337	13 (3)
H(33)	5784	-834	748	14 (3)	H(48)	1891	3794	3073	5 (2)
H(34)	7287	-1137	1810	10 (3)					

to the formally unsaturated cluster III via the destructive hydrogenation of $\text{Ru}_3(\text{CO})_8(\mu_3\text{-}\eta^2\text{-C}\equiv\text{C}-t\text{-Bu})(\mu\text{-PPh}_2)$,⁹ a more convenient synthesis of this interesting molecule involves the decarbonylation of $(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}(\mu\text{-PPh}_2)$ (II) which is readily available from $\text{Ru}_3(\text{CO})_{12}$ and diphenylphosphine. The most interesting structural feature of III is the presence of a P-C(Ph) unit blocking an axial coordination site on the unique ruthenium atom. In view of the formal 46-electron configuration of III reaction of a Lewis base might be expected to lead to adduct formation with the unusual PPh_2 group being displaced to its normal edge bridging role. Such is indeed the case with CO where III is converted rapidly to II. In fact an adduct is also formed in the reaction of III with diphenylacetylene. Analytical and spectroscopic data (Table I) as well as a single-crystal X-ray study (vide infra) revealed that crystalline IV has the formula $(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-PhC}\equiv\text{CPh})(\mu\text{-PPh}_2)\cdot 0.5\text{PhC}\equiv\text{CPh}$.

The structure of IV, drawn so as to illustrate the skeletal stereochemistry, is shown in Figure 1. Whereas in $(\mu\text{-$

$\text{H})\text{Ru}_3(\text{CO})_9(\mu\text{-PPh}_2)$ ⁹ the phosphido group bridges a ruthenium-ruthenium bond (Ru(1)-Ru(3) = 2.9049 (5) Å) and is tipped over the Ru_3 triangle such that a P-Ph group blocks an axial site on Ru(2), in IV the PPh_2 bridge spans an "open" edge (Ru(2)-Ru(3) = 3.838 (1) Å) with the hydride located along the Ru(1)-Ru(3) vector. The Ru(1)-Ru(3) bond (2.908 (1) Å) bridged by the hydride ligand is significantly longer than Ru(1)-Ru(2) (2.813 (1) Å). This is a frequently encountered feature of hydrido-bridged clusters.¹³

The obtuse Ru(2)-P-Ru(3) angle (107.1 (0)°) is notable, particularly since the ³¹P (PPh_2) chemical shift is at high field (δ +13.8). This is another example of the utility of $\delta(^{31}\text{P})$ as a probe of changes in M...M distance and M-P-M angles. In $(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu\text{-PPh}_2)$ $\delta(^{31}\text{P})$ is +134.2.

An unexpected bonus in this structure is the presence

(13) See for example: (a) Churchill, M. R. *Adv. Chem. Ser.* 1978, No. 167, 36. (b) Kaesz, H. D.; Humphries, P. *Prog. Inorg. Chem.* 1981, 25, 145. (c) Teller, R. G.; Bau, R. *Struct. Bonding (Berlin)* 1981, 44, 1.

Table V. A Selection of Bond Lengths (Å) for $Ru_3(CO)_9(\mu-PPh_2)(\mu_3-\eta^2-C\equiv CPh)(\mu_3-\eta^2-PhC\equiv CC\equiv CPh)$

(i) M-M			
Ru(1)-Ru(2)	3.6280 (7)	Ru(2)-Ru(5)	2.8884 (7)
Ru(1)-Ru(3)	2.8127 (7)	Ru(3)-Ru(4)	2.8878 (7)
Ru(1)-Ru(4)	2.9200 (7)	Ru(3)-Ru(5)	2.7660 (6)
Ru(2)-Ru(3)	2.8163 (7)	Ru(4)-Ru(5)	2.7682 (7)
(ii) M-P and M-C			
Ru(4)-P	2.275 (2)	Ru(5)-P	2.272 (2)
Ru(1)-C(1)	1.918 (8)	Ru(3)-C(7)	1.868 (8)
Ru(1)-C(2)	1.932 (8)	Ru(3)-C(8)	1.866 (8)
Ru(1)-C(3)	1.972 (8)	Ru(3)-C(13)	2.292 (6)
Ru(1)-C(13)	2.336 (6)	Ru(3)-C(15)	2.202 (6)
Ru(1)-C(14)	2.204 (6)	Ru(3)-C(16)	2.192 (6)
Ru(1)-C(15)	2.159 (6)	Ru(4)-C(9)	1.862 (8)
Ru(2)-C(4)	1.938 (7)	Ru(4)-C(10)	1.918 (8)
Ru(2)-C(5)	1.960 (8)	Ru(4)-C(13)	2.106 (6)
Ru(2)-C(6)	1.946 (8)	Ru(5)-C(11)	1.880 (8)
Ru(2)-C(13)	2.299 (6)	Ru(5)-C(12)	1.876 (8)
Ru(2)-C(14)	2.212 (6)	Ru(5)-C(13)	2.154 (6)
Ru(2)-C(16)	2.138 (7)		

(iii) C-C			
C(13)-C(14)	1.340 (9)	C(16)-C(17)	1.439 (9)
C(14)-C(19)	1.480 (9)	C(17)-C(18)	1.187 (10)
C(15)-C(16)	1.397 (9)	C(18)-C(31)	1.431 (10)
C(15)-C(25)	1.483 (9)		

(iv) C-O			
C(1)-O(1)	1.130 (10)	C(7)-O(7)	1.140 (10)
C(2)-O(2)	1.130 (10)	C(8)-O(8)	1.153 (10)
C(3)-O(3)	1.123 (10)	C(9)-O(9)	1.150 (10)
C(4)-O(4)	1.114 (9)	C(10)-O(10)	1.133 (10)
C(5)-O(5)	1.124 (9)	C(11)-O(11)	1.147 (10)
C(6)-O(6)	1.123 (10)	C(12)-O(12)	1.128 (10)

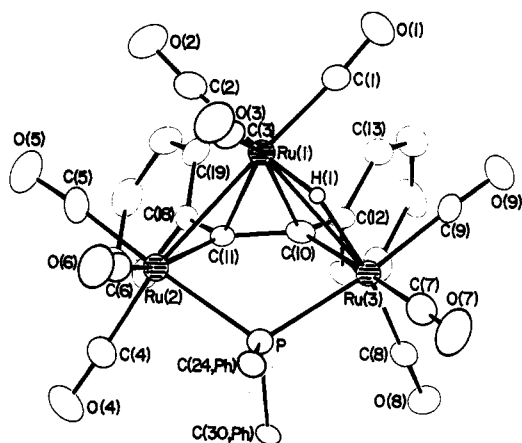


Figure 1. A perspective view of the molecular structure of $(\mu-H)Ru_3(CO)_9(\mu-PPh_2)(\mu_3-\eta^2-PhC\equiv CPh)\cdot 0.5PhC\equiv CPh$. The half molecule of diphenylacetylene of crystallization is not shown.

of a half molecule of $PhC\equiv CPh$ of crystallization per asymmetric unit, which allows a direct internal comparison of $-C\equiv C-$ bond lengthening on $\mu_3-\eta^2$ -coordination. The $C(36)-C(36')$ distance in the $PhC\equiv CPh$ of crystallization is 1.253 (16) Å and the $C(10)-C(11)$ length in IV is 1.415 (11) Å, giving $\Delta(C\equiv C) = 0.162$ Å. The acetylene is involved in parallel interactions with Ru(2) and Ru(3) and an η^2 bond to Ru(1). The $C(10)-C(11)$ distance compares favorably with the value in $Os_3(CO)_{10}(PhC_2Ph)$ (1.439 (10) Å)¹⁶ where a four-electron ($2\sigma + \pi$)-acetylene-metal interaction is present.

The saturated 74-electron cluster $Ru_5(CO)_{13}(\mu_4-\eta^2-C\equiv CPh)(PPh_2)$ (V) is known to undergo facile reactions with Lewis bases leading to adduct formation.^{2e} In this case however, addition of a two-electron donor results in cleavage of an Ru-Ru bond generating open double but-

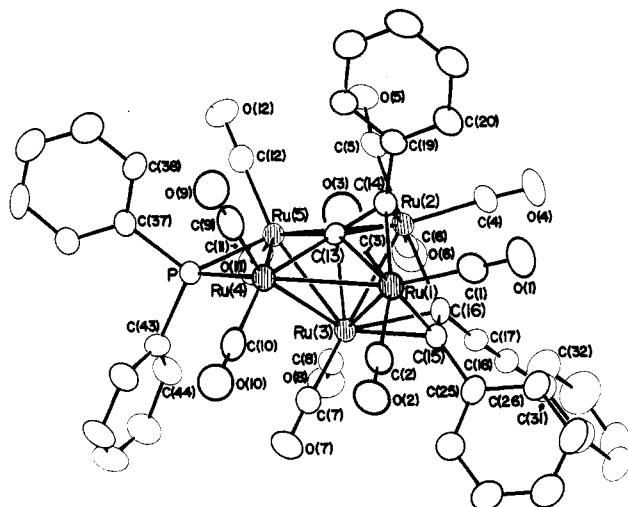
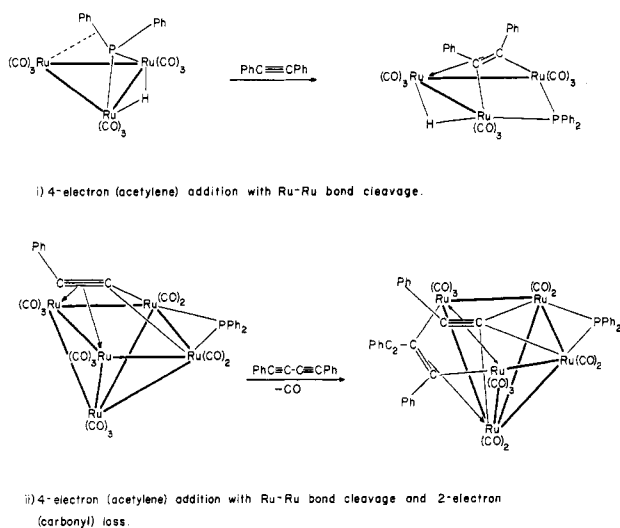


Figure 2. The structure of $Ru_5(CO)_{12}(\mu_5-\eta^2-C\equiv CPh)(\mu_3-\eta^2-PhC\equiv C-C\equiv CPh)(\mu-PPh_2)$ drawn to illustrate the coordination modes of acetylide and diacetylene.

Scheme I



terfly, triangulated polyhedra. The reaction of V with diphenylbutadiyne gave a deep red solution which afforded on chromatography red-purple crystals of VI as the major product.

The structure of VI was revealed by single-crystal X-ray diffraction, and an ORTEP II plot of the structure is shown in Figure 2. Addition of the acetylene to V has occurred at the triangular face of the cluster opposite to that bridged by the phosphido group. The $Ru(1)-Ru(2)$ distance in V (2.8165 (9) Å) has increased to the ostensibly nonbonding value of 3.6280 (7) Å in VI, and a single carbonyl ligand has been displaced from the apical atom Ru(3). Whereas in V C(13), the α -carbon atom of the acetylide, caps a closed square face of the cluster, opening of the framework along the $Ru(1)-Ru(2)$ edge on reaction with the acetylene forces Ru(3) and C(13) into closer proximity such that C(13) is within bonding distance of all five metal atoms. The alkyne $PhC\equiv CC\equiv CPh$ is coordinated in a manner entirely analogous to that found in IV. Thus the C-C axis of the bound group is roughly parallel to the nonbonded Ru-Ru edge, and an η^2 -interaction is present between the unique atom Ru(3) of the open triangular face $Ru(1)-Ru(2)-Ru(3)$.

Structural changes from precursor clusters III and V to products IV and VI are shown in Scheme I. In both cases the acetylenes adopt a triangular face capping bonding

Table VI. A Selection of Bond Angles (deg) for $\text{Ru}_5(\text{CO})_{12}(\mu\text{-PPh}_2)(\mu_3\text{-}\eta^2\text{-C}\equiv\text{CPh})(\mu_3\text{-}\eta^2\text{-PhC}\equiv\text{CC}\equiv\text{CPh})$

(i) M-M-M					
Ru(3)-Ru(1)-Ru(4)	58.0 (0)	Ru(2)-Ru(3)-Ru(4)	99.3 (0)	Ru(3)-Ru(4)-Ru(5)	59.8 (0)
Ru(3)-Ru(2)-Ru(5)	58.0 (0)	Ru(2)-Ru(3)-Ru(5)	62.3 (0)	Ru(2)-Ru(5)-Ru(3)	59.7 (0)
Ru(1)-Ru(3)-Ru(2)	80.3 (0)	Ru(4)-Ru(3)-Ru(5)	59.9 (0)	Ru(2)-Ru(5)-Ru(4)	97.8 (0)
Ru(1)-Ru(3)-Ru(4)	63.0 (0)	Ru(1)-Ru(4)-Ru(3)	59.1 (0)	Ru(3)-Ru(5)-Ru(4)	60.3 (0)
Ru(1)-Ru(3)-Ru(5)	101.9 (0)	Ru(1)-Ru(4)-Ru(5)	99.2 (0)		
(ii) M-M-P					
Ru(1)-Ru(4)-P	149.3 (0)	Ru(5)-Ru(4)-P	52.5 (0)	Ru(3)-Ru(5)-P	93.2 (0)
Ru(3)-Ru(4)-P	92.8 (0)	Ru(2)-Ru(5)-P	148.9 (0)	Ru(4)-Ru(5)-P	52.5 (0)
(iii) M-P-M, M-P-C, and C-P-C					
Ru(4)-P-Ru(5)	75.0 (0)	Ru(4)-P-C(43)	115.5 (2)	Ru(5)-P-C(43)	122.0 (2)
Ru(4)-P-C(37)	119.9 (2)	Ru(5)-P-C(37)	119.0 (2)	C(37)-P-C(43)	104.4 (3)
(iv) M-C-O					
Ru(1)-C(1)-O(1)	176.7 (3)	Ru(2)-C(5)-O(5)	172.2 (2)	Ru(4)-C(9)-O(9)	178.2 (3)
Ru(1)-C(2)-O(2)	174.5 (3)	Ru(2)-C(6)-O(6)	176.3 (3)	Ru(4)-C(10)-O(10)	178.5 (3)
Ru(1)-C(3)-O(3)	172.5 (3)	Ru(3)-C(7)-O(7)	175.3 (3)	Ru(5)-C(11)-O(11)	179.1 (3)
Ru(2)-C(4)-O(4)	175.5 (3)	Ru(3)-C(8)-O(8)	175.3 (3)	Ru(5)-C(12)-O(12)	178.3 (3)
(v) M-C-M, M-C-C, and C-C-C					
Ru(1)-C(13)-Ru(2)	103.0 (0)	Ru(4)-C(13)-Ru(5)	81.1 (0)	Ru(3)-C(15)-C(16)	71.1 (2)
Ru(1)-C(13)-Ru(3)	74.8 (0)	Ru(4)-C(13)-C(14)	136.6 (2)	Ru(3)-C(15)-C(25)	130.4 (2)
Ru(1)-C(13)-Ru(4)	82.0 (0)	Ru(5)-C(13)-C(14)	138.9 (2)	C(16)-C(15)-C(25)	119.5 (3)
Ru(1)-C(13)-Ru(5)	149.4 (0)	Ru(1)-C(14)-Ru(2)	110.5 (0)	Ru(2)-C(16)-Ru(3)	81.2 (0)
Ru(1)-C(13)-C(14)	67.5 (2)	Ru(1)-C(14)-C(13)	78.3 (2)	Ru(2)-C(16)-C(15)	123.7 (2)
Ru(2)-C(13)-Ru(3)	75.7 (0)	Ru(1)-C(14)-C(19)	123.3 (2)	Ru(2)-C(16)-C(17)	116.2 (2)
Ru(2)-C(13)-Ru(4)	151.0 (0)	Ru(2)-C(14)-C(13)	76.3 (2)	Ru(3)-C(16)-C(15)	71.9 (2)
Ru(2)-C(13)-Ru(5)	80.8 (0)	Ru(2)-C(14)-C(19)	122.0 (2)	Ru(3)-C(16)-C(17)	125.0 (2)
Ru(2)-C(13)-C(14)	69.2 (2)	C(13)-C(14)-C(19)	131.6 (3)	C(15)-C(16)-C(17)	119.8 (3)
Ru(3)-C(13)-Ru(4)	78.2 (0)	Ru(1)-C(15)-Ru(3)	80.3 (0)	C(16)-C(17)-C(18)	176.4 (4)
Ru(3)-C(13)-Ru(5)	76.9 (0)	Ru(1)-C(15)-C(16)	118.9 (2)	C(17)-C(18)-C(31)	178.1 (4)
Ru(3)-C(13)-C(14)	119.5 (2)	Ru(1)-C(15)-C(25)	120.2 (2)		
(vi) M-M-C					
Ru(3)-Ru(1)-C(1)	130.2 (2)	Ru(5)-Ru(2)-C(13)	47.4 (1)	Ru(5)-Ru(3)-C(15)	133.9 (1)
Ru(3)-Ru(1)-C(2)	97.9 (2)	Ru(5)-Ru(2)-C(14)	79.0 (1)	Ru(5)-Ru(3)-C(16)	110.5 (1)
Ru(3)-Ru(1)-C(3)	133.7 (2)	Ru(5)-Ru(2)-C(16)	107.9 (1)	Ru(1)-Ru(4)-C(9)	106.0 (2)
Ru(3)-Ru(1)-C(13)	51.9 (1)	Ru(1)-Ru(3)-C(7)	98.1 (2)	Ru(1)-Ru(4)-C(10)	99.7 (2)
Ru(3)-Ru(1)-C(14)	77.4 (1)	Ru(1)-Ru(3)-C(8)	168.6 (2)	Ru(1)-Ru(4)-C(13)	52.4 (1)
Ru(3)-Ru(1)-C(15)	50.5 (1)	Ru(1)-Ru(3)-C(13)	53.3 (1)	Ru(3)-Ru(4)-C(9)	160.0 (2)
Ru(4)-Ru(1)-C(1)	164.7 (2)	Ru(1)-Ru(3)-C(15)	49.2 (1)	Ru(3)-Ru(4)-C(10)	105.0 (2)
Ru(4)-Ru(1)-C(2)	92.3 (0)	Ru(1)-Ru(3)-C(16)	75.0 (1)	Ru(3)-Ru(4)-C(13)	53.9 (1)
Ru(4)-Ru(1)-C(3)	76.0 (2)	Ru(2)-Ru(3)-C(7)	178.3 (2)	Ru(5)-Ru(4)-C(9)	114.6 (2)
Ru(4)-Ru(1)-C(13)	45.6 (1)	Ru(2)-Ru(3)-C(8)	95.0 (2)	Ru(5)-Ru(4)-C(10)	143.1 (2)
Ru(4)-Ru(1)-C(14)	76.3 (1)	Ru(2)-Ru(3)-C(13)	52.3 (1)	Ru(5)-Ru(4)-C(13)	50.2 (1)
Ru(4)-Ru(1)-C(15)	108.3 (1)	Ru(2)-Ru(3)-C(15)	76.3 (1)	Ru(2)-Ru(5)-C(11)	97.8 (2)
Ru(3)-Ru(2)-C(4)	129.3 (2)	Ru(2)-Ru(3)-C(16)	48.6 (1)	Ru(2)-Ru(5)-C(12)	108.1 (2)
Ru(3)-Ru(2)-C(5)	132.8 (2)	Ru(4)-Ru(3)-C(7)	80.2 (2)	Ru(2)-Ru(5)-C(13)	51.8 (1)
Ru(3)-Ru(2)-C(6)	98.1 (2)	Ru(4)-Ru(3)-C(8)	128.3 (2)	Ru(3)-Ru(5)-C(11)	102.0 (2)
Ru(3)-Ru(2)-C(13)	52.1 (1)	Ru(4)-Ru(3)-C(13)	47.9 (1)	Ru(3)-Ru(5)-C(12)	165.0 (2)
Ru(3)-Ru(2)-C(14)	77.3 (1)	Ru(4)-Ru(3)-C(15)	111.9 (1)	Ru(3)-Ru(5)-C(13)	53.8 (1)
Ru(3)-Ru(2)-C(16)	50.3 (1)	Ru(4)-Ru(3)-C(16)	131.6 (1)	Ru(4)-Ru(5)-C(11)	144.6 (2)
Ru(5)-Ru(2)-C(4)	164.8 (2)	Ru(5)-Ru(3)-C(7)	118.5 (2)	Ru(4)-Ru(5)-C(12)	116.9 (2)
Ru(5)-Ru(2)-C(5)	75.1 (2)	Ru(5)-Ru(3)-C(8)	84.8 (2)	Ru(4)-Ru(5)-C(13)	48.7 (1)
Ru(5)-Ru(2)-C(6)	92.8 (2)	Ru(5)-Ru(3)-C(13)	49.3 (1)		
(vii) P-M-C and C-M-C					
P-Ru(4)-C(9)	97.8 (2)	C(13)-Ru(1)-C(14)	34.2 (2)	C(14)-Ru(2)-C(16)	91.4 (2)
P-Ru(4)-C(10)	99.4 (2)	C(13)-Ru(1)-C(15)	89.8 (2)	C(7)-Ru(3)-C(8)	86.5 (3)
P-Ru(4)-C(13)	102.4 (1)	C(14)-Ru(1)-C(15)	92.8 (2)	C(7)-Ru(3)-C(13)	126.9 (2)
P-Ru(5)-C(11)	103.0 (2)	C(4)-Ru(2)-C(5)	95.0 (3)	C(7)-Ru(3)-C(15)	102.4 (2)
P-Ru(5)-C(12)	95.7 (2)	C(4)-Ru(2)-C(6)	98.6 (3)	C(7)-Ru(3)-C(16)	130.7 (2)
P-Ru(5)-C(13)	101.0 (1)	C(4)-Ru(2)-C(13)	123.3 (2)	C(8)-Ru(3)-C(13)	131.0 (2)
C(1)-Ru(1)-C(2)	98.6 (3)	C(4)-Ru(2)-C(14)	89.5 (2)	C(8)-Ru(3)-C(15)	119.7 (2)
C(1)-Ru(1)-C(3)	93.6 (3)	C(4)-Ru(2)-C(16)	82.1 (2)	C(8)-Ru(3)-C(16)	94.1 (2)
C(1)-Ru(1)-C(13)	125.7 (2)	C(5)-Ru(2)-C(6)	88.9 (3)	C(13)-Ru(3)-C(15)	89.9 (2)
C(1)-Ru(1)-C(14)	92.4 (2)	C(5)-Ru(2)-C(13)	92.8 (2)	C(13)-Ru(3)-C(16)	88.3 (2)
C(1)-Ru(1)-C(15)	82.2 (2)	C(5)-Ru(2)-C(14)	89.3 (2)	C(15)-Ru(3)-C(16)	37.1 (2)
C(2)-Ru(1)-C(3)	87.9 (3)	C(5)-Ru(2)-C(16)	176.9 (2)	C(9)-Ru(4)-C(10)	90.1 (3)
C(2)-Ru(1)-C(13)	135.5 (2)	C(6)-Ru(2)-C(13)	137.6 (2)	C(9)-Ru(4)-C(13)	106.9 (3)
C(2)-Ru(1)-C(14)	168.4 (2)	C(6)-Ru(2)-C(14)	171.8 (2)	C(10)-Ru(4)-C(13)	150.0 (2)
C(2)-Ru(1)-C(15)	92.2 (2)	C(6)-Ru(2)-C(16)	90.8 (2)	C(11)-Ru(5)-C(12)	87.7 (3)
C(3)-Ru(1)-C(13)	93.1 (2)	C(13)-Ru(2)-C(14)	34.5 (2)	C(11)-Ru(5)-C(13)	146.8 (2)
C(3)-Ru(1)-C(14)	87.9 (2)	C(13)-Ru(2)-C(16)	89.4 (2)	C(12)-Ru(5)-C(13)	112.4 (3)
C(3)-Ru(1)-C(15)	175.8 (2)				

mode and hence contribute four electrons to the clusters. Although in principle alkynes can behave as two- or four-electron donors, the latter property is dominant in cluster chemistry, as seen in the thermal or photochemical reactions of $M_3(CO)_2$ with $RC\equiv CR$.^{14,16} It is significant that while four-electron donor character is exhibited by both $PhC\equiv CPh$ and $PhC\equiv CC\equiv CPh$ in their respective reactions with III and V, there is no carbonyl displacement from III and only a single CO group is substituted in V. Clearly Ru-Ru bond cleavage is a favored reaction pathway under these mild conditions.

The stereochemical changes from III to IV also provide a nice illustration of the application of the skeletal electron counting rules to cluster reactions.¹⁷ Addition of $PhC\equiv CPh$ to the nido cluster III based on a tetrahedron with one vertex missing (five skeletal electron pairs) generates

an arachno cluster IV with a geometry derived from that of a pentagonal bipyramid with two missing vertices (eight skeletal pairs, five vertices). In this case the two PhC fragments are part of the cluster framework and the skeleton can be readily related to the seven-vertex polyhedron. The closo cluster V (seven skeletal pairs, six vertices; C(13) is a skeletal atom) might be expected, from the counting rules to undergo skeletal expansion to a closo polyhedron with two more skeletal atoms on addition of an acetylene with loss of one CO group. Alternatively, if V is considered as a nido octahedron with one missing vertex (C(13) not considered a skeletal atom), addition of an acetylene and CO loss should afford a nido eight-vertex polyhedron. The skeletal geometry of VI counting C(15) and C(16) as skeletal atoms is difficult to relate to a regular polyhedron. The structure is best viewed in terms of the edge opening of a square-pyramidal 74-electron species on two-electron addition.

Registry No. I, 87984-98-3; II, 80800-57-3; III, 82055-65-0; IV, 87985-00-0; V, 78179-75-6; VI, 87985-01-1.

Supplementary Material Available: Tables of thermal parameters, remaining bond lengths and angles, and structure factors for IV and VI (44 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of Metallophosphenium Ion Complexes Derived from Aminohalophosphites. Crystal and Molecular Structure of $Mo(\eta^5-C_5H_5)(CO)_2[POCH_2CH_2NC(CH_3)_3]$

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The reactions of $RNCH_2CH_2OPX$ ($R = CH_3, C_2H_5, C(CH_3)_3, C_6H_5$; $X = F, Cl$) with $NaMo(\eta^5-C_5H_5)(CO)_3$ in THF at 25 °C result in the formation of a series of metallophosphenium ion complexes $Mo(\eta^5-C_5H_5)(CO)_2[POCH_2CH_2NR]$. The complexes have been characterized by infrared and 1H , ^{13}C , and ^{31}P NMR spectroscopy, and a single-crystal X-ray diffraction analysis of $Mo(\eta^5-C_5H_5)(CO)_2[POCH_2CH_2NC(CH_3)_3]$ has been completed. The compound crystallizes in the monoclinic space group $P2_1/n$ with $a = 12.072$ (2) Å, $b = 9.957$ (2) Å, $c = 13.349$ (3) Å, $\beta = 108.09$ (1)°, $Z = 4$, $V = 1525.2$ (5) Å³, and $\rho = 1.58$ g cm⁻³. Least-squares refinement gave $R_f = 3.5\%$ and $R_wR_f = 3.0\%$ on 2310 unique reflections with $I > 2.5\sigma(I)$. The molecular structure displays a pseudooctahedral molybdenum atom bonded to a ($\eta^5-C_5H_5$) ring, two terminal carbonyls, and the phosphorus atom of the phosphonium ion $[POCH_2CH_2NC(CH_3)_3]^+$. The phosphonium ion is planar and the Mo-P bond distance, 2.207 (1) Å, is short.

Introduction

The reactions of metal carbonyl anions with diamino-halophosphines in a strongly polar solvent (THF)¹ produce a series of molecular metallophosphenium ion complexes that can be considered to contain a dicoordinate diaminophosphenium ion, $(R_2N)_2P^+$, covalently bonded to an anionic organometallic fragment.²⁻⁴ The structures and properties of these complexes are found to be very dependent upon the orbital templates and electronic prop-

erties of the constituent species. For example, toward six d-electron (16 valence electron) metal fragments of the type $MCp(CO)_2^-$ ($M = Cr, Mo, W$) a diamino-phosphenium ion acts as a terminal ligand, and a planar MPN_2 structural unit is formed in the complexes.² The cation σ donates an in-plane phosphorus lone pair to an empty d_{z^2} orbital on the metal fragment while the metal back-donates electron density to the out-of-plane $PN_2 \pi^*$ orbital on the cation. The resulting metal-phosphorus bond distances are unusually short, and the P-N bond distances are longer than is found in $\{[(i-Pr)_2N]_2P^+\}[AlCl_4^-]$.⁵ On the other hand, the eight d-electron (18 valence electron) fragment $MCp(CO)_2^-$ ($M = Fe$) is unable to accept a phosphorus lone pair. Consequently, the phosphorus atom rehybridizes to

(1) Abbreviations used in the text include: THF = tetrahydrofuran; $Cp = \eta^5-C_5H_5$; $Cp^* = (CH_3)_5C_5$.

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