Heterobinuclear Hydrido, Alkyl, and Related Complexes of Rh/Os. Site-Specific Reductive Elimination of Methane from a Rh/Os Core and the Structures of $[RhOs(CH_2CN)(CO)_3(dppm)_2]$ and $[RhOs(CH_3)(CO)_3(dppm)_2]$

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Abstract: This paper reports the synthesis and characterization of a series of hydrido, alkyl, alkenyl, and related heterobimetallic complexes of Rh and Os and the site-specific reductive elimination of methane from hydrido methyl complexes. Reaction of $[RhOs(CO)_3(NCMe)(\mu\text{-}H)(dppm)_2]^{2+}$ (**3**, dppm = $Ph_2PCH_2PPh_2$) with NaC≡CH in acetonitrile yields the acetylide complex $[RhOs(C_2H)(CO)_3(dppm)_2]$ (**6**) and the cyanomethyl complex $[RhOs(CH_2CN)(CO)_3(dppm)_2]$ (**7**). The same reaction under CO instead results in deprotonation of one dppm group to give $[RhOs(CO)_4(dppm\text{-}H)(dppm)]$ (**8**, dppm-H = bis(diphenylphosphino)methanide). The methanide carbon can be alkylated to give $[RhOs(CO)_4(Ph_2PCH(CH_3)PPh_2)(dppm)]^+$ (**9**) or protonated to give the known compound $[RhOs(CO)_4(dppm)_2]^+$ (**2**). The methyl complex $[RhOs(CH_3)(CO)_3(dppm)_2]$ (**10**) is prepared by several routes, and upon protonation yields $[RhOs(CO)_3(\mu\text{-}H)(\mu^2\text{-}\eta^3\text{-}(o\text{-}C_6H_4)PhPCH_2PPh_2)(dppm)]^+$ (**14**) via methane loss. If the reaction is carried out at −80 °C and slowly warmed, three hydrido methyl intermediates are observed at different temperatures, yielding information about the reductive elimination from these heterobinuclear species, which appears to occur from the Os center. An alkenyl complex analogous to the alkyl species **7** and **10** can be obtained by the reaction of $[RhOsH(CO)_3(dppm)_2]$ (**1**) with dimethyl acetylenedicarboxylate resulting in insertion into the Os−H bond and migration of the resulting alkenyl group to Rh yielding $[RhOs(MeO_2CC{=}C(H)CO_2Me)(CO)_3(dppm)_2]$ (**18**). Protonation of **18** yields $[RhOs(R)(CO)_3(\mu\text{-}H)(dppm)_2]^+$ (**19**) and alkylation yields $[RhOs(R)(CH_3)(CO)_3(dppm)_2]^+$ (**20**, R = $MeO_2CC{=}C(H)CO_2Me$). Compound **20** has the vinylic moiety bound to Rh with the methyl group on Os. The structures of **7** and **10** have been established by X-ray crystallography. Compound **7** crystallizes in the monoclinic space group $C2/c$ with a = 18,313(3) Å, b = 13.279(2) Å, c = 22.492(5) Å, β = 115.89(1)°, and Z = 4; compound **10** crystallizes in the triclinic space group $P\bar{1}$ with a = 11,102(2) Å, b = 11.684(3) Å, c = 10.954(3) Å, α = 111.79(2)°, β = 93.16(2)°, γ = 68.18(2)°, and Z = 1. Both compounds are disordered at an inversion center, although only the metals and the carbonyl and alkyl groups are disordered. Both models refined acceptably: R = 0.046, R_w = 0.058 (**7**); R = 0.047, R_w = 0.077 (**10**). The geometries of the two complexes are almost identical, having the cyanomethyl or methyl group terminally bound to Rh and having the three carbonyls on Os. One carbonyl forms a semibridging interaction with Rh.

Introduction

Organometallic complexes containing two or more different metal types[1] offer tremendous scope for future development. Although currently a number of multi-[2] or bimetallic[3] catalysts are used industrially, little is understood about the functions of the different metals involved. Consequently, studies on even the simplest mixed-metal systems, the heterobinuclear complexes, can address a number of important concepts that can improve our understanding of mixed-metal catalysts. Concepts of interest range from the nature of the metal−metal or the different metal−ligand interactions to ligand mobilities over the bimetallic core, ultimately focussing on the metal−metal cooperativity effects that are possible in the activation of substrate molecules. It is the aspect of metal−metal cooperativity that has elicited the most interest in this area, on the supposition that mixed-metal complexes should display unique reactivity as a result of the combination of the different metals, each having its own unique properties.

Although much of the interest in heterobinuclear complexes has been directed at species that involve disparate metals,[1d,4] the so-called early−late metal combinations, in order to make use of the very different metal properties, there has also been considerable interest in combinations of similar metals, either from within the same triad[5] or from adjacent triads.[6] Our interest in combinations of metals from the Fe and Co triads was sparked by reports of ethylene glycol formation from synthesis gas using bimetallic catalysts based on Rh and Ru complexes.[7] In this paper we report our preliminary studies on organometallic complexes involving the Rh/Os combination of metals. We are interested in the nature of the metal−alkyl interactions in Rh/Os systems, in the migratory-insertion reactions that result, and in binuclear reductive eliminations involving hydrido−alkyl and dialkyl ligand combinations.

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(1) For recent reviews see: (a) Gladfelter, W. L.; Geoffroy, G. L. *Adv. Organomet. Chem.* **1980**, *18*, 207. (b) Roberts, D. A.; Geoffroy, G. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Eds; Pergamon: Oxford, 1982; Vol. 6, Chapter 40. (c) Muetterties, E. L.; Kause, M. J. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 135. (d) Stephan, D. W. *Coord. Chem. Rev.* **1989**, *95*, 41.

(2) Dowden, D. A. *Catalysis*; Kemball, C., Dowden, D. A., Eds.; Specialist Periodical Report, The Chemical Society: London, 1978; Vol. 2, p 1.

(3) Sinfelt, J. H. *Bimetallic Catalysts: Discoveries, Concepts and Applications*; John Wiley and Sons: New York, 1983.

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Experimental Section

General Comments. All solvents were dried and deoxygenated immediately before use. Sodium benzophenone was used as the drying agent for all of the solvents except dichloromethane, which was distilled over P_2O_5, and acetonitrile, which was distilled over calcium hydride, The solvents were distilled under an atmosphere of prepurified nitrogen or argon. Rhodium(III) chloride trihydrate was purchased from Johnson Matthey Ltd., $Os_3(CO)_{12}$ was purchased from Sudtek, and $Ph_2PCH_2PPh_2$ (dppm), $HBF_4{\cdot}Et_2O$, $MeO_2CC{\equiv}CCO_2Me$ (DMAD), and $[(Ph_3P)_2N]Cl$ were obtained from Aldrich as were THF solutions of CH_3MgCl, CH_3MgI, and CH_3Li. Sodium acetylide as an 18% slurry in a mixture of xylenes and light mineral oil was also purchased from Aldrich; this reagent was used shortly after receipt and was stored under dinitrogen. The 99% carbon-13-enriched carbon monoxide was purchased from Isotec Inc. The compounds $[RhOsH(CO)_3(dppm)_2]$ (**1**)[8] and $[RhOs(CO)_4(dppm)_2][BF_4]$ (**2**)[9] were prepared by published procedures.

The ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$, NMR spectra were recorded on a Bruker AM-400 spectrometer operating at 400,1, 162.0, and 100.6 MHz for the respective nuclei. The internal deuterated solvent served as a lock for the spectrometer. All infrared spectra were run on a Nicolet 7199 Fourier transform interferometer as solids in Nujol or dichloromethane casts on KBr. The elemental analyses were performed by the microanalytical service within the department. Spectroscopic data for all compounds are given in Table 1.

Preparation of the Compounds. (a) $[RhOs(CO)_3(NCCH_3)(\mu\text{-}H)(dppm)_2][BF_4]_2{\cdot}CH_3CN$ (3). A solution of $HBF_4{\cdot}Et_2O$ (15 μL, 17 mg, 0.105 mmol) in 20 mL of acetonitrile was added dropwise over 1 h to a rapidly stirring solution of $[RhOs(CO)_4(dppm)_2][BF_4]$ (**2**) (100 mg, 0.079 mmol) in 20 mL of acetonitrile, causing the mixture to gradually change from yellow to orange. After all the acid had been added, the mixture was stirred for an additional hour and the solvent volume was reduced to *ca.* 1 mL under vacuum, The addition of 20 mL of diethyl ether to the solution caused the immediate formation of small yellow crystals of **3** (83 mg, 0.059 mmol). Yield 75%. Anal. Calcd for $C_{57}H_{51}N_2B_2F_8O_3OsP_4Rh$: C, 48.81; H, 3.67; N, 2.00. Found: C, 48.73; H, 3.59; N, 1.88.

(b) $[RhOs(CO)_3(CN^tBu)(\mu\text{-}H)(dppm)_2][BF_4]_2$ (4). A stirred solution of **3** (0.100 g, 0.071 mmol) in 10 mL of CH_2Cl_2 was charged with 9 μL of neat ^{t}BuNC (7 mg, 0,080 mmol), resulting in an immediate color change from orange to pale yellow. After 1 h of stirring the solvent was removed under vacuum, leaving a pale yellow solid which was dissolved in 10 mL of THF and precipitated from solution through addition of 20 mL of Et_2O and 20 mL of hexanes. Dissolution of the precipitate in 3 mL of CH_2Cl_2 followed by the slow addition of Et_2O to the resulting solution afforded very pale yellow crystals of the desired product (0.071 g, 0.051 mmol). Yield 72%. Anal. Calcd for $C_{58}H_{54}NB_2F_8O_3OsP_4Rh$: C, 49.63; H, 3.88; N, 1.00. Found: C, 49.60; H, 3.99; N, 0.89.

(c) $[RhOs(I)(CO)_3(\mu\text{-}H)(dppm)_2][BF_4]$ (5). Acetone (20 mL) was added directly to a flask containing NaI (11 mg, 0.0715 mmol) and compound **3** (100 mg, 0.0713 mmol). Both solids rapidly dissolved to form a yellow solution. After the mixture was stirred for 2 h the solvent was removed in vacuo, leaving a yellow solid which was dissolved in 20 mL of CH_2Cl_2 and filtered. The solvent was removed in vacuo and the residue was recrystallized from CH_2Cl_2/Et_2O to give a yellow crystalline solid (67 mg). Yield 69%. Anal. Calcd for $C_{53}H_{45}BF_4IO_3OsP_4Rh$: C, 46.78; H, 3.33; I, 9.33. Found: C, 46.89; H, 3.43; I, 9.72.

(d) Reaction of 3 with NaC≡CH. Forty microliters of a 0.18 g/mL (7 mg, 0.146 mmol) suspension of freshly obtained NaC≡CH in xylenes and mineral oil was added via syringe to a stirred, yellow solution of **3** (100 mg, 0.0713 mmol) in 20 mL of acetonitrile causing an immediate change in color to orange-red, and finally to yellow-brown. After 1 h of stirring, the solvent was removed in vacuo, leaving a yellow-brown residue, CH_2Cl_2 (15 mL) was added forming a cloudy orange solution which was filtered. Evaporation of the filtrate gave an orange-brown oil which was washed with 2 × 20 mL of hexanes and kept under vacuum for 6 h. Recrystallization of the residue from a 20:1 mixture of Et_2O/CH_2Cl_2 afforded 31 mg of yellow-brown crystalline solid which proved to be a 1:1 mixture of $[RhOs(\eta^1\text{-}C{\equiv}CH)(CO)_3(dppm)_2]{\cdot}\,^1/_2CH_2Cl_2$ (**6**) and $[RhOs(\eta^1\text{-}CH_2CN)(CO)_3(dppm)_2]$ (**7**). Essentially pure samples of **7** were obtained in yields ranging from 50 to 70% when 4 equiv of NaC≡CH were used in the above procedure. Compound **7** is orange in the crystalline state. Anal. Calcd for $C_{55}H_{46}NO_3OsP_4Rh$: C, 55.70; H, 3.91; N, 1.18. Found: C, 55.65; H, 3.94; N, 0.76.

Compound **6** was obtained as the predominant product (>90%) when 10 equiv of NaC≡CH were added to acetonitrile solutions of **3** having concentrations greater than 0.02 g/mL. Yellow crystals of **6** containing cocrystallized CH_2Cl_2 were grown from CH_2Cl_2/Et_2O. Anal. Calcd for $C_{55.5}H_{46}ClO_3OsP_4Rh$: C, 54.94; H, 3.82. Found: C, 54.90; H, 3.85.

(e) $[RhOs(CO)_4(\mu\text{-}Ph_2PCHPPh_2)(dppm)]$ (8). Method i. To a stirred solution of **3** (100 mg, 0.0713 mmol) in 10 mL of acetonitrile under a stream of CO gas was added a suspension of NaC≡CH (7 mg. 0.146 mmol) in 40 μL of xylene, causing a slight change in color from yellow to brighter yellow. The mixture was stirred with constant CO purge for 2 h, during which time a bright yellow solid precipitated from solution. NMR studies showed essentially quantitative conversion to compound **8**. The solid was allowed to settle, the pale yellow supernatant was discarded, and 15 mL of dichloromethane was added, forming a cloudy yellow solution which was filtered. The solvent volume was reduced to 1 mL under vacuum and 60 mL of Et_2O was added causing the gradual formation of yellow crystals (39 mg). Isolated yield 47%. Anal. Calcd for $C_{54}H_{43}O_4OsP_4Rh$: C, 55.30; H, 3.70. Found: C, 55.88; H, 3.94.

Method ii. Compound **2** (50 mg, 0.040 mmol) was dissolved in THF (30 mL) to which were added three 0.1-mL portions of 1.7 M ^{t}BuLi in pentane (0.51 mmol) at 2-h intervals. The resulting solution was stirred for 24 h and the solvent was removed in vacuo. The yellow residue was redissolved in 15 mL of CH_2Cl_2 and filtered. The solvent was removed in vacuo and $^{31}P\{^1H\}$ NMR spectra of the solid showed **8** as the only phosphorus-containing product. The residue was redissolved in *ca.* 1 mL of CH_2Cl_2 and addition of 30 mL of hexanes caused precipitation of a yellow powder. Yield 22 mg (47%).

(4) For representative papers see: (a) Langrick, C. R.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1985**, *511*. (b) Sartain, W. J.; Selegue, J. P. *Organometallics* **1989**, *8*, 2153. (c) Powell, J.; Sawyer, J. F.; Stainer, M. V. R. *Inorg. Chem.* **1989**, *28*, 4401. (d) Casey, C. P. *J. Organometallics Chem.* **1990**, *400*, 205. (e) Choukroun, R.; Dahan, F.; Gervais, D.; Rifai, C. *Organometallics* **1990**, *9*, 1982. (f) Baker, R. T.; Fultz, W. C.; Marder, T. B.; Williams, I. D. *Organometallics* **1990**, *9*, 2357. (g) Baxter, S. M.; Wolczanski, P. T. *Organometallics* **1990**, *9*, 2498. (h) Chetcuti, M. J.; Grant, B. E.; Fanwick, P. E. *Organometallics* **1990**, *9*, 1345. (i) Tsai, J.-C.; Wheeler, R. A.; Khan, M. A.; Nicholas, K. M. *Organometallics* **1991**, *10*, 1344. (j) Antonelli, D. M.; Cowie, M. *Organometallics* **1991**, *10*, 2550. (k) Dick, D. G.; Hou, Z.; Stephan, D. W. *Organometallics* **1992**, *11*, 2378. (l) Mague, J. T.; Lin, Z. *Organometallics* **1992**, *11*, 4139. (m) Kalck, P.; Serra, C.; Machet, C.; Broussier, R.; Gautheron, B.; Delmas, G.; Trouvé, G.; Kubicki, M. *Organometallics* **1993**, *12*, 1021. (n) Hostetler, M. J.; Butts, M. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 2743. (o) Selent, D.; Beckhaus, R.; Pickardt, J. *Organometallics* **1993**, *12*, 2857. (p) Berenguer, J. R.; Falvello, L. R.; Forniés, J.; Lalinde, E.; Tomás, M. *Organometallics* **1993**, *12*, 6.

(5) For representative papers see: (a) Pringle, P.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1983**, 889. (b) Albinati, A.; Lehner, H.; Venanzi, L. M. *Inorg. Chem.* **1985**, *24*, 1483. (c) Horváth, I. *Organometallics* **1986**, *5*, 2333. (d) McDonald, R.; Cowie, M. *Inorg. Chem.* **1990**, *29*, 1564. (e) Elliot, D. J.; Ferguson, G.; Holah, D. G.; Hughes, A. N.; Jennings, M. C.; Magnuson, V. R.; Potter, D.; Puddephatt, R. J. *Organometallics* **1990**, *9*, 1336. (f) Garland, M.; Horváth, I.; Bor, G. *Organometallics* **1991**, *10*, 513. (g) Garland, M. *Organometallics* **1993**, *12*, 535.

(6) For representative papers see: (a) Cullen, W. R.; Kim, T.-J.; Einstein, F. W. B.; Jones, T. *Organometallics* **1983**, *2*, 714. (b) Iggo, J. A.; Markham, D. P.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Chem. Commun.* **1985**, 432. (c) Turpin, R.; Dagnac, P.; Poilblanc, R. *J. Organomet. Chem.* **1987**, *319*, 247. (d) Arndt, L. W.; Bancroft, B. T.; Darensbourg, M. Y.; Janzen, C. P.; Kim, C. M.; Reibenspies, J.; Varner, K. E.; Youngdahl, K. D. *Organometallics* **1988**, *7*, 1302. (e) Mague, J. T. *Organometallics* **1991**, *10*, 513. (f) Hilts, R. W.; Franchuk, R. A.; Cowie, M. *Organometallics* **1991**, *10*, 1297. (g) Schiavo, S. L.; Rotondo, E.; Bruno, G.; Faraone, F. *Organometallics* **1991**, *10*, 1613. (h) Poulton, J. T.; Folting, K.; Caulton, K. G. *Organometallics* **1992**, *11*, 1364. (i) Fong, R. H.; Lin, C.-H.; Idmoumaz, H.; Hersh, W. H. *Organometallics* **1993**, *12*, 503. (j) Stang, P. J.; Cao, D. *Organometallics* **1993**, *12*, 996.

(7) Dombek, B. D. *Organometallics* **1985**, *4*, 1707 and references therein.

(8) Antonelli, D. M.; Cowie, M. *Organometallics* **1990**, *9*, 1818.

(9) Hilts, R. W.; Franchuk, R. A.; Cowie, M. *Organometallics* **1991**, *10*, 304.

Table 1. Spectroscopic Parameters for the Compounds[a]

compd	IR,[b] cm^{-1}	NMR[d] $\delta(^{31}P\{^1H\})$	NMR[d] $\delta(^{13}C\{^1H\})$	NMR[d] $\delta(^1H)$
$[RhOs(CO)_3(NCCH_3)(\mu\text{-}H)(dppm)_2][BF_4]_2 \cdot CH_3CN$ (**3**)	2078 (ss), 2004 (ss), 1819 (ss), 2321 (ws)[e] 2292 (ws)[f,c] 2083, 2015, 1822 (CH_2Cl_2 soln)	27.21 (Rh*P*, $^1J_{Rh-P}$ = 99 Hz); −7.05 (Os*P*)	OsCO: 174.27 (t, 1C, $^2J_{PC}$ < 1 Hz); 176.82 (dt, 1C, $^2J_{CC}$ = 27 Hz, $^2J_{PC}$ = 9 Hz); 224.47 (ddt, 1C, $^2J_{CC}$ = 27 Hz, $^1J_{RhC}$ = 25 Hz, $^2J_{PC}$ = 8 Hz)	PC*H*$_2$P: (AB) 4.09 (dm, 2H), 3.88 (dm, 2H, $^2J_{HH}$ = 14 Hz); Rh*H*Os: −15.18 (dtt, 1H, $^1J_{RhH}$ = 27 Hz, $^2J_{RhP-H}$ = 10 Hz, $^2J_{OsP-H}$ not resolved); NCC*H*$_3$: 1.98 (s, 3H), 1.58 (s, 3H)
$[RhOs(CO)_3(CN^tBu)(\mu\text{-}H)(dppm)_2][BF_4]_2$ (**4**)	2083 (ss), 2002 (sb), 1821 (mb), 2189 (ss)[g,c] 2088, 2022, 1831 (CH_2Cl_2 soln)	27.71 (Rh*P*, $^1J_{RhP}$ = 100 Hz); −5.82 (Os*P*)	OsCO: 173.05 (t, 1C, $^2J_{PC}$ < 1 Hz); 173.29 (dt, 1C, $^2J_{CC}$ = 30 Hz, $^2J_{PC}$ = 9 Hz); 211.56 (m, 1C, $^2J_{CC}$ = 30 Hz)	PC*H*$_2$P: (AB) 4.29 (dm, 2H), 4.05 (dm, 2H, $^2J_{HH}$ = 14 Hz); Rh*H*Os: −11.09 (dtt, 1H, $^1J_{RhH}$ = 21 Hz, $^2J_{RhP-H}$ < 3 Hz, $^2J_{OsP-H}$ = 11 Hz); CNC(C*H*$_3$)$_3$: 0.75 (s, 9H)
$[RhOs(I)(CO)_3(\mu\text{-}H)(dppm)_2][BF_4]$ (**5**)	2066 (ss), 1993 (ss), 1793 (ss)[c] 2060, 2000, 1798 (CH_2Cl_2 soln)	20.08 (Rh*P*, $^1J_{RhP}$ = 104); −7.73 (Os*P*)	OsCO: 175.10 (m, 1C); 175.47 (m, 1C); 226.62 (bm, 1C)	PC*H*$_2$P: (AB) 4.12 (dm, 2H), 3.83 (dm, 2H, $^2J_{HH}$ = 14 Hz); Rh*H*Os: −11.17 (dtt, 1H, $^1J_{RhH}$ = 28 Hz, $^2J_{RhP-H}$ = 8 Hz, $^2J_{OsP-H}$ = 4 Hz)
$[RhOs(\eta^1\text{-}C{\equiv}CH)(CO)_3(dppm)_2] \cdot {}^1/_2CH_2Cl_2$ (**6**)	2014 (ws),[h] 1954 (ss), 1930 (sb), 1835 (w)[c]	31.94 (Rh*P*, $^1J_{RhP}$ = 131); 4.78 (Os*P*)	OsCO: 191.04 (t, 1C, $^2J_{PC}$ = 15 Hz); 218.85 (m, 2C)	PC*H*$_2$P: 3.49 (pq, 4H); RhC≡C*H*: 1.73 (dt, 1H, $^3J_{RhH}$ = $^4J_{RhP-H}$ = 4 Hz)
$[RhOs(\eta^1\text{-}CH_2CN)(CO)_3(dppm)_2]$ (**7**)	1945 (ss), 1927 (ss), 1746 (sh), 1731 (ss), 2190 (m)[i,c]	35.32 (Rh*P*, $^1J_{RhP}$ = 139); 2.65 (Os*P*)	OsCO: 192.55 (td, 1C, $^2J_{PC}$ = 11 Hz, $^2J_{RhC}$ = 3 Hz); 216,34 (m, 2C)	PC*H*$_2$P: 3.59 (pq, 4H); RhC*H*$_2$CN: 0.58 (td, 2H, $^2J_{RhH}$ = 3 Hz, $^3J_{RhP-H}$ = 8 Hz)
$[RhOs(CO)_4(dppm)(\mu\text{-}Ph_2PCHPPh_2)]$ (**8**)	1985 (sh), 1962 (ss), 1926 (ss), 1905 (ss)[c]	P_A: 29.73; P_C = −15.21; P_B: 25.78; P_D: −6.97 $J(P_AP_B)$ = 321, $J(P_AP_C)$ = 159, $J(P_AP_D)$ = 34, $J(P_BP_C)$ = 32, $J(P_BP_D)$ = 96, $J(P_CP_D)$ = 117, $J(RhP_A)$ = 109, $J(RhP_B)$ = 117	OsCO: 184.90 (t, 1C, $^2J_{PC}$ = 10 Hz); 197.14 (t, 2C, $^2J_{PC}$ < 2 Hz); RhCO: 184.61 (dt, $^1J_{RhC}$ = 77 Hz, $^2J_{PC}$ = 14 Hz)	PC*H*$_2$P: 4.16 (dd, 2H, $^2J_{P_BH}$ = $^2J_{P_DH}$ = 11 Hz); PC*H*P: 2.84 (bs, 1H)
$[RhOs(CO)_4(dppm)(\mu\text{-}Ph_2PCH(CH_3)PPh_2]\text{-}[CF_3SO_3]$ (**9**)	1984 (ss), 1952 (ss), 1915 (ss)[c]	P_A: 35.80; P_C: 5.10; P_B: 28.48; P_D: −6.23 $J(P_AP_B)$ = 326, $J(P_AP_C)$ = 86, $J(P_AP_D)$ = 26, $J(P_BP_C)$ = 26, $J(P_BP_D)$ = 84, $J(P_CP_D)$ = 179, $J(RhP_A)$ = 119, $J(RhP_B)$ = 119	OsCO: 179.94 (t, 1C, $^2J_{PC}$ = 10 Hz); 193.39 (m, 1C); 195.87 (m, 1C) RhCO: 181.79 (dt, $^1J_{RhC}$ = 74 Hz, $^2J_{PC}$ = 11 Hz); PCH(*C*H$_3$)P: 14.58 (1C, bs); P*C*H(CH$_3$)P: 48.80 (1C, dd, $^1J_{P-C}$ = 14, 27 Hz); PC*H*$_2$P: 40.58 (1C, dd, $^1J_{P-C}$ = 15, 30 Hz)	PC*H*$_2$P: (AB) 4.44 (ddd, 1H, $^2J_{P_BH}$ = $^2J_{P_DH}$ = 11 Hz), 4.03 (ddd, 1H, $^2J_{P_BH}$ = $^2J_{P_DH}$ = 11 Hz), $^2J_{H-H}$ = 15 Hz; PC*H*(CH$_3$)P: 3.77 (ddq, 1H, $^2J_{P_AH}$ = $^2J_{P_CH}$ = $^3J_{CH_3-H}$ = 7 Hz); PCH(C*H*$_3$)P: 1.34 (ddd, 3H, $^3J_{CH_3-H}$ = 7 Hz, $^3J_{P_AH}$ = $^3J_{P_CH}$ = 10 Hz)
$[RhOsCH_3(CO)_3(dppm)_2]$ (**10**)	1911 (ss), 1858 (ss), 1723 (ss) 1910, 1869, 1740 (CH_2Cl_2 soln)	38.46 (Rh*P*, $^1J_{RhP}$ = 150 Hz); 8.3 (m)	OsCO: 197.5 (m, 1C), 220.2 (m, 2C, $^1J_{Rh-C}$ = 13 Hz, $^2J_{P-Rh-C}$ not resolved)	PC*H*$_2$P: 3.5 (bs, 4H) C*H*$_3$: −0.35 (td, $^2J_{Rh-H}$ = 2 Hz, $^3J_{P-H}$ = 7 Hz)
$[RhOs(CO)_3(\mu\text{-}H)_2(dppm)_2]Cl$ (**11**)		26.7 (Rh*P*, $^1J_{Rh-P}$ = 106 Hz); −1.35 (Os*P*)		PC*H*$_2$P: 4.08 (bs, 4H); Rh*H*Os: −9.95 (dtt, 2H, $^1J_{Rh-H}$ = 21 Hz, $^2J_{P-Os-H}$ = $^2J_{P-Rh-H}$ = 11.5 Hz)
$[RhOsCl(CO)_3(dppm)_2]$ (**12**)	1946 (ss), 1890 (ss), 1728 (ss)	28.4 (Rh*P*, $^1J_{Rh-P}$ = 132 Hz); −1.68 (Os*P*)	OsCO: 184.4 (t, 1C, $^2J_{P-Os-C}$ = 14 Hz), 221.6 (m, 2C, $^1J_{Rh-C}$ = 17 Hz, $^2J_{P-Rh-C}$ not resolved)	PC*H*$_2$P: 3.38 (bs, 4H)

Table 1. (Continued)

compd	IR,[b] cm^{-1}	NMR[d] $\delta(^{31}P\{^1H\})$	NMR[d] $\delta(^{13}C\{^1H\})$	NMR[d] $\delta(^1H)$
$[RhOs(CH_3)(CO)_3(\mu\text{-}H)(dppm)_2][X]$[j] **13a**: X = SO_3CF_3 **13b**: X = BF_4		22.74 (Rh*P*, $^1J_{Rh-P}$ = 112 Hz); −3.32 (Os*P*)	Os*C*O: 181.67 (bs); 179,25 (bs); Rh*C*O: 184.32 (dt, $^1J_{RhC}$ = 75 Hz, $^2J_{PC}$ = 15 Hz)	PCH_2P: (AB) 4.3 (dm, 2H), 4.05 (dm, 2H); OsCH_3: −0.43 (t, 3H, $^3J_{P-Os-H}$ =7.5 Hz) Rh*H*Os: −12.90 (bm)
$[RhOs(CO)_3(\mu\text{-}H)(\mu^2\text{-}\eta^3\text{-}(o\text{-}C_6H_4)PhPCH_2PPh_2)(dppm)][CF_3SO_3]\cdot Et_2O$ (**14b**)	2038 (ss), 2004 (ss), 1914 (ss)[c]	P_A: 25,43; P_C: −4.73; P_B: 22.53; P_D: −20.24 $J(P_AP_B)$ = 302, $J(P_AP_C)$ = 46, $J(P_AP_D)$ = 31, $J(P_BP_C)$ = 9, $J(P_BP_D)$ = 67, $J(P_CP_D)$ = 227, $J(RhP_A)$ = 107, $J(RhP_B)$ = 112	Os*C*O: 177.86 (bs), 178.48 (bs); Rh*C*O: 187.56 (dt, $^1J_{RhC}$ = 78 Hz, $^2J_{PC}$ = 12 Hz)	PCH_2P: 5.06 (dm, 1H, $^2J_{H-H}$ = 15 Hz), 4.89 (dm, 1H, $^2J_{H-H}$ = 15 Hz), 4.44 (dm, 1H, $^2J_{H-H}$ = 15 Hz), 4.14 (dm, 1H, $^2J_{H-H}$ = 15 Hz); Rh*H*Os: −15.18 (dm, 1H, $^1J_{RhH}$ = 21 Hz, $^2J_{RhP-H}$ = 10 Hz, $^2J_{OsP-H}$ not resolved)
$[CH_3RhOs(H)(CO)_3(dppm)_2][BF_4]$ (**15**)[k]		31.6 (Rh*P*, $^1J_{Rh-P}$ = 139 Hz); −0.59 (Os*P*)	Os*C*O: 177.4 (t, $^2J_{P-Os-C}$ = 22 Hz); 210.6 (m); 222 (m)	PCH_2P: (AB) 3.4 (dm, 2H), 3.0 (dm, 2H); RhCH_3: 0.51 (t, $^3J_{P-H}$ = 8 Hz) Os*H*: −7.0 (t, $^2J_{P-H}$ = 21 Hz)
$[CH_3RhOs(CO)_3(\mu\text{-}H)(dppm)_2][BF_4]$ (**16**)[l]		31.3 (Rh*P*, $^1J_{Rh-P}$ = 141 Hz); −4.5 (Os*P*)		PCH_2P: (AB) 3.6 (dm, 2H), 3.4 (dm, 2H); RhCH_3: 0.20 (t, $^3J_{P-H}$ = 8 Hz); Rh*H*Os: −8.95 (bm)
$[RhOsCl_2(CO)_3(\mu\text{-}H)(dppm)_2]$ (**17**)	1945 (ss), 1773 (ws)	22.7 (Rh*P*, $^1J_{Rh-P}$ = 115 Hz); 1.47 (Os*P*)	Os*C*O: 182.4 (t, 1C, $^2J_{P-Os-C}$ = 10 Hz), 210.6 (m, 1C, $^1J_{Rh-C}$ = 16 Hz)	PCH_2P: (AB) 3.95 (dm, 2H), 3.58 (dm, 2H); Rh*H*Os: −14.90 (m, 1H, $^1J_{Rh-H}$ = 29 Hz, $^2J_{P-Rh-H}$ = 12 Hz, $^2J_{P-Os-H}$ = 6 Hz)
$[RhOs(CH_3O_2CC{=}C(H)CO_2CH_3)(CO)_3(dppm)_2]$ (**18**)	1950, 1921, 1895	32.46 (Rh*P*, $^1J_{Rh-P}$ = 143 Hz); 0.81 (Os*P*)	Os*C*O: 190.35 (t, 1C, $^2J_{P-Os-C}$ = 14 Hz), 210.6 (bs, 1C), 225.1 (bs, 1C)	RhC=C*H*: 4.12 (dt, 1H, $^3J_{Rh-H}$ = 2 Hz, $^4J_{P-H}$ = 1 Hz); PCH_2P: (AB) 3.8 (dm, 2H), 3.05 (dm, 2H); CH_3: 3.0 (s, 3H), 2.8 (s, 3H)
$[RhOs(CH_3O_2CC{=}C(H)CO_2CH_3)(CO)_3(\mu\text{-}H)(dppm)_2][BF_4]$ (**19**)	2052 (ss), 1997 (ss), 1959 (sh)	24.8 (Rh*P*, $^1J_{Rh-P}$ = 124 Hz); −6.85 (Os*P*)	Os*C*O: 175.6 (bs, 1C), 180.48 (bs, 1C), 225.6 (bs, 1C)	RhC=C*H*: 3.75 (bs, 1H); PCH_2P: (AB) 3.6 (dm, 2H), 3.4 (dm, 2H); CH_3: 3.15 (s, 3H), 2.80 (s, 3H); Rh*H*Os: −10.2 (m, 1H, $^1J_{Rh-H}$ = 15 Hz, $^2J_{P-Rh-H}$ = 7 Hz, $^2J_{P-Os-H}$ = 11 Hz)
$[RhOsH(CH_3O_2CC{=}C(H)CO_2CH_3)(CO)_3(dppm)_2][BF_4]$ (**20a**)[m]		26.84 (RhP, $^1J_{Rh-P}$ = 120 Hz); −4.23 (Os*P*)		−6.78 (t, $^2J_{P-Os-H}$ = 18 Hz)[n]
$[RhOsH(CH_3O_2CC{=}C(H)CO_2CH_3)(CO)_3(dppm)_2][BF_4]$ (**20b**)[m]		25.63 (RhP, $^1J_{Rh-P}$ = 128 Hz); −2,56 (Os*P*)		−6.28 (t, $^2J_{P-Os-H}$ = 14 Hz)[n]
$[RhOs(CH_3O_2CC{=}C(H)CO_2CH_3)(CH_3)(CO)_3(dppm)_2][SO_3CF_3]$ (**21**)	2055 (ss), 1955 (ss), 1920 (sh)	23.49 (Rh*P*, $^1J_{Rh-P}$ = 129 Hz); −3.03 (Os*P*)	Os*C*O: 180.1 (bs, 1C), 192,6 (bs, 1C), 224.2 (bs, 1C)	RhC=C*H*: 4.73 (dt, 1H, $^3J_{Rh-H}$ = 3 Hz, $^4J_{P-H}$ = 1 Hz); PCH_2P: (AB) 3.59 (dm, 2H), 3.2 (dm, 2H); CH_3: 3.1 (s, 3H), 3.05 (s, 3H); OsCH_3: −0.6 (t, 3H, $^3J_{P-Os-H}$ = 7 Hz)

[a] IR abbreviations: ss = strong sharp, ms = medium sharp, ws = weak sharp, sb = strong broad, mb = medium broad, sh = shoulder, m = medium. NMR abbreviations: t = triplet, dt = doublet of triplets, ddt = doublet of doublets of triplets, m = multiplet, td = triplet of doublets, bs = broad singlet, dd = doublet of doublets, dm = doublet of multiplets, dtt = doublet of triplets of triplets, s = singlet, pq = pseudoquintet, ddq = doublet of doublets of quintets, ddd = doublet of doublets of doublets, bm = broad multiplet. [b] Nujol mull except as indicated. Values quoted are ν(CO) except as indicated. [c] CH_2Cl_2 cast. [d] $^{31}P\{^1H\}$ chemical shifts are referenced vs external 85% H_3PO_4 while ^1H and $^{13}C\{^1H\}$ are referenced vs external TMS. Chemical shifts for the phenyl hydrogens are not given in the ^1H NMR data. [e] ν(CN) for cocrystallized CH_3CN. [f] ν(CN) for coordinated CH_3CN. [g] ν(CN) for ^{t}BuNC. [h] ν(C≡C). [i] ν(CN) for Rh−CH_2CN. [j] −40 °C. [k] −80 °C. [l] −60 °C. [m] Isomers of **19** observed between −80 and −20 °C in the protonation of **18**. [n] Owing to the presence of three isomers (**19**, **20a**, **20b**) other ^1H resonances could not be resolved.

(f) [RhOs(CO)$_4$(dppm)(Ph$_2$PCH(CH$_3$)PPh$_2$)][SO$_3$CF$_3$]·$^1/_2$CH$_2$Cl$_2$ (9). Methyl triflate (8 μL, 0.071 mmol) was added by syringe to a stirred yellow solution of **8** (80 mg, 0.068 mmol) in 10 mL of CH_2Cl_2. No color change was observed. After 1 h of stirring, the solvent volume was reduced to 2 mL under vacuum and 20 mL of Et_2O was mixed into the yellow solution forming a slightly cloudy mixture. Over 12 h small orange crystals formed, The supernatant was removed and the crystals were dried under vacuum. Yield 52 mg (65%). Anal. Calcd for $C_{56.5}H_{47}O_7F_3ClP_4SRhOs$: C, 49.19; H, 3,43. Found: C, 49,33; H, 3.51.

(g) [RhOsCH$_3$(CO)$_3$(dppm)$_2$] (10). Method i. The complex [RhOsCl(CO)$_3$(dppm)$_2$] (**12**) (50 mg, 0.042 mmol) was dissolved in 15 mL of THF and the solvent was degassed with two freeze−pump−thaw cycles. A large excess of CH_3MgCl (*ca.* 0.5 mL of a 3.0 M THF solution) was added via cannula at −78 °C. The mixture was stirred for 1 h at −78 °C and then slowly warmed to room temperature. Diethyl ether (15 mL) was added and the mixture was washed with 3 × 25 mL of degassed water, The solvent was removed in vacuo and the residue was recrystallized from THF/hexanes and washed with 2 × 15 mL of hexanes. Yield 17 mg (35%). Anal. Calcd for

$C_{54}H_{47}O_3OsP_4Rh$: C, 55.87; H, 4.08. Found: C, 55.03; H, 4.34.

Method ii. Compound **12** (80 mg, 0.0677 mmol) was suspended in 30 mL of THF and cooled to 0 °C. Then 0.58 mL of a 0.14 M THF solution of CH_3Li (0.081 mmol) was added by syringe and within minutes the yellow suspension turned to an orange solution. After 4 h the solution was filtered and the solvent removed in vacuo. The yellow-orange residue was recrystallized from CH_2Cl_2/Et_2O to give 58 mg of yellow solid. ^{31}P NMR showed the solid to be a mixture of **12** (35%) and **10** (65%).

Method iii. Here 0.1 mL of a 1.4 M THF solution of CH_3Li in THF (0.14 mmol) was added to a suspension of **2** (50 mg, 0.0397 mmol) in 50 mL of THF. Upon addition, the yellow crystals gradually dissolved to form a yellow solution. After 3 h of stirring under a slow dinitrogen purge the solvent was reduced to *ca.* 1 mL and 30 mL of hexanes were added to precipitate a bright yellow solid which was washed with 3 × 20 mL of hexane and dried in vacuo. The solid was then extracted into 5 mL of CH_2Cl_2 and filtered. The solvent was reduced to ca. 0.5 mL and 10 mL of Et_2O was slowly added followed by 20 mL of hexane to precipitate bright yellow solid. Yield 25 mg (46%).

(h) [RhOs(CO)$_3$(μ-H)$_2$(dppm)$_2$]Cl (11). *N,N*-Dimethylacetamide hydrochloride (10.8 mg, 0.0875 mmol) and **1** (100 mg, 0.0875 mmol) were dissolved in 5 mL of THF to form a yellow-orange solution. After 2 min a light-yellow precipitate began to settle out. The mixture was stirred for an additional 2 h, the colorless supernatant discarded, and the remaining yellow solid washed with 2 × 10 mL of Et_2O and dried in vacuo. Yield 78 mg (75%). Anal. Calcd for $C_{53}H_{46}ClO_3OsP_4Rh$: C, 53.76; H, 3.88; Cl, 3.00. Found: C, 53.30; H, 3.84; Cl, 3.40.

(i) [RhOsCl(CO)$_3$(dppm)$_2$] (12). A yellow suspension of **11** (100 mg, 0.0845 mmol) in 30 mL of THF was heated under reflux for 4 h. During this time the initial suspension turned to an orange solution. After cooling, the solvent was removed in vacuo and the resulting orange residue was recrystallized from CH_2Cl_2/Et_2O to give a yellow-orange powder which was washed with 2 × 10 mL of Et_2O and dried in vacuo. Yield 67 mg (67%). Anal. Calcd for $C_{53}H_{44}ClO_3OsP_4Rh$: C, 53.88; H, 3.75; Cl, 3.00. Found: C, 53.48; H, 3.81; Cl, 3.34.

(j) [RhOsH(CO)$_3$(μ^2-η^3-(o-C$_6$H$_4$)PhPCH$_2$PPh$_2$)(dppm)][CF$_3$SO$_3$]·Et$_2$O (14b). Neat methyl triflate (20 μL, 0.177 mmol) was syringed directly into a stirred solution of **1** (200 mg, 0.174 mmol) in 15 mL of CH_2Cl_2. The solution gradually changed from orange-red to orange-yellow. After 1 h of stirring the solvent was removed in vacuo and the residue was redissolved in 2 mL of CH_2Cl_2. Slow addition of Et_2O caused immediate precipitation of a bright yellow solid (0.172 g) which was washed with 2 × 20 mL of Et_2O and dried in vacuo. Yield 72%. Anal. Calcd for $C_{58}H_{54}F_3O_7OsP_4RhS$: C, 50.77; H, 3.97. Found: C, 50.90; H, 3.98. Variable-temperature NMR in CD_2Cl_2 showed that the initial product formed at −40 °C is [RhOs(CH$_3$)(CO)$_3$(μ-H)(dppm)$_2$][SO$_3$CF$_3$] (**13b**). Above 0 °C the final product forms.

(k) Reaction of 10 with HBF$_4$. Compound **10** (30 mg, 0.025 mmol) was dissolved in 0.5 mL of CD_2Cl_2 to form a yellow solution. HBF_4·OEt_2 (7 μL, 0.050 mmol) was added by syringe. ^{31}P and ^1H NMR showed that **14** was formed in 100% yield. Variable-temperature NMR shows that the initial product at −80 °C was [(CH$_3$)RhOs(H)(CO)$_3$(dppm)$_2$][BF$_4$] (**15**). At −80 to −60 °C [(CH$_3$)RhOs(CO)$_3$(μ-H)(dppm)$_2$][BF$_4$] (**16**) was formed. Above −50 °C compound **13** was observed, and above 0 °C the final product **14** was formed.

(l) [RhOsCl$_2$(CO)$_2$(μ-H)(dppm)$_2$] (17). Compound **1** (100 mg, 0.084 mmol) was dissolved in 5 mL of benzene and an excess of CCl_4 (0.2 mL) was added by syringe. The yellow-orange solution immediately turned dark orange and was stirred for an additional 5 min after which the solvent was removed in vacuo. The resulting yellow residue was recrystallized from CH_2Cl_2/Et_2O to give a yellow solid which was washed with 2 × 10 mL of Et_2O and dried in vacuo. Yield: 84 mg (81%). Anal. Calcd for $C_{52}H_{45}Cl_2O_2OsP_4Rh$: C, 52.48; H, 3.78; Cl, 5.96. Found: C, 52.00; H, 3.72; Cl, 6.32.

(m) [RhOs(CH$_3$O$_2$CC≡C(H)CO$_2$CH$_3$)(CO)$_3$(dppm)$_2$] (18). Complex **1** (100 mg, 0.0875 mmol) was dissolved in 5 mL of CH_2Cl_2 and the solution was cooled to −78 °C. Dimethyl acetylenedicarboxylate (10.8 μL, 0.0875 mmol) was then added causing the solution to turn immediately from yellow-orange to red. After 5 min of stirring the solution was warmed to room temperature. The solvent was then removed in vacuo and the resulting red residue was recrystallized from CH_2Cl_2/hexanes to give a dark-orange powder which was washed with 2 × 20 mL of hexanes and dried in vacuo. Yield 92 mg (82%). Anal. Calcd for $C_{59}H_{51}O_7OsP_4Rh$: C, 54.98; H, 3.95. Found: C, 54.75; H, 4.07.

(n) [RhOs(CH$_3$O$_2$CC≡C(H)CO$_2$CH$_3$)(CO)$_3$(μ-H)(dppm)$_2$][BF$_4$] (19). The complex **18** (100 mg, 0.077 mmol) was dissolved in 10 mL of CH_2Cl_2, and HBF_4·Et_2O (11.0 μL, 0.077 mmol) was added by syringe. The solution turned a darker shade of red and was then stirred for 5 min and then the solvent was removed in vacuo. The dark red residue was recrystallized from CH_2Cl_2/hexanes to give a light-brown powder which was washed with 2 × 10 mL of hexanes and dried in vacuo. Yield 87 mg (81%). Anal. Calcd for $C_{59}H_{52}BF_4O_7OsP_4Rh$: C, 51.45; H, 3.78. Found: C, 50.90; H, 4.15. Variable-temperature NMR spectra in CD_2Cl_2 showed that the initial products formed at −80 °C were two isomers of [RhOsH(CH$_3$O$_2$CC=C(H)CO$_2$CH$_3$)(CO)$_3$(dppm)$_2$][BF$_4$] (**20a, 20b**). Above −20 °C the final product formed.

(o) [RhOs(CH$_3$O$_2$CC=C(H)CO$_2$CH$_3$)(CO)$_3$(dppm)$_2$][SO$_3$CF$_3$] (21). Complex **18** (100 mg, 0.077 mmol) was dissolved in 10 mL of CH_2Cl_2, and $CH_3SO_3CF_3$ (8.7 μL, 0.077 mmol) was added by syringe. The red solution was stirred for 1 h after which the CH_2Cl_2 was removed in vacuo. The dark red residue was recrystallized from CH_2Cl_2/hexanes and the light-brown product obtained was washed with 2 × 10 mL of hexanes and dried in vacuo. Yield 95 mg (85%). Anal. Calcd for $C_{61}H_{55}SF_3O_{10}OsP_4Rh$: C, 50.37; H, 3.78. Found: C, 49.94; H, 3.73.

X-ray Data Collection. (a) [RhOs(CH$_2$CN)(CO)$_3$(dppm)$_2$] (7). A crystal of compound **7** was mounted in a glass capillary under nitrogen and solvent vapor, to minimize the possibility of decomposition or solvent loss. Data were collected on an Enraf-Nonius CAD4 diffractometer with use of Mo Kα radiation. Unit cell parameters were obtained from a least-squares refinement of the setting angles of 24 reflections in the range $20° < 2\theta < 24°$. The diffraction symmetry and the systematic absences indicated the space groups *Cc* or *C2/c*; the latter was established on the basis of the successful refinement of the structure.

Intensity data were collected at 22 °C with $\theta/2\theta$ scans being employed, covering reflections having indices of the form $+h, +k, \pm l$, to a maximum of 50° in 2θ. Peak backgrounds were measured by extending the scan range by 25% on either side of the scan region. Three reflections were chosen as intensity and orientation standards and were remeasured after every 120 min of exposure time; no appreciable decay of these standards was observed. The data were processed in the usual way, with a value of 0.04 for p[10] employed to downweight intense reflections; 2891 reflections were considered observed ($I \geq 3\sigma(I)$) and were used in subsequent calculations.[11] The data were corrected for absorption by use of an empirical scheme based on the absorption surface (Fourier filtering) method of Walker and Stuart.[12] See Table 2 for crystal and data collection details for both compounds **7** and **10**.

(b) [RhOs(CH$_3$)(CO)$_3$(dppm)$_2$] (10). Data collection for compound **10** proceeded in much the same manner as for **7**. The 2θ range for centering reflections was $18° < 2\theta < 26°$. In this case both space groups $P1$ and $P\bar{1}$ were possible, with the latter being confirmed by the successful refinement of the model. Indices of the form $+h, \pm k, \pm l$ were collected and a linear decay of 14.5% was observed over the span of data collection; the data were corrected for this decay. A total of 3953 unique reflections were observed and used in subsequent calculations.

Structure Solution and Refinement. (a) [RhOs(CH$_2$CN)(CO)$_3$(dppm)$_2$] (7). With four molecules per unit cell and no inversion symmetry in the molecule, two solutions seemed possible: either space group *Cc* with one molecule per asymmetric unit or *C2/c* with the metals lying on the crystallographic 2-fold axes. The Patterson map ruled out the second option and refinement attempts ruled out *Cc*. Instead the molecule is found to be disordered about the inversion centers. The phosphine groups are ordered and well-behaved so that only the metals and the CH_2CN and CO ligands in the equatorial plane are

(10) Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 204.
(11) Programs used were those of the Enraf-Nonius Structure Determination Package by B. A. Frenz, in addition to local programs by R. G. Ball.
(12) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 158.

Table 2. Crystallographic Data

	A. Crystal Data	
compd	$[OsRh(CH_2CN)(CO)_3(dppm)_2]$ (**7**)	$[OsRh(CH_3)(CO)_3(dppm)_2]$ (**10**)
formula	$C_{55}H_{46}NO_3OsP_4Rh$	$C_{54}H_{47}O_3OsP_4Rh$
formula wt	1185,99	1160.98
crystal dimens (mm)	0,40 × 0.35 × 0,20	0,60 × 0.50 × 0.37
space group	*C2/c* (No. 15)	$P\bar{1}$ (No, 2)
unit cell parameters		
a (Å)	18.313(3)	11.102(2)
b (Å)	13.279(2)	11,684(3)
c (Å)	22,492(5)	10.954(3)
α (deg)	90	111.79(2)
β (deg)	115.89(1)	93.16(2)
γ (deg)	90	68.18(2)
V (Å^3)	4921(3)	1219.2(8)
Z	4	1
ϱ(calcd) (g cm^{-3})	1,601	1.584
μ (cm^{-1})	30,842	31.156
	B. Data Collection and Refinement Conditions	
temp (°C)	22	22
radiation (λ [Å])	Mo Kα (0.71069)	Mo Kα (0.71069)
scan type	θ−2θ	θ−2θ
scan rate (deg min^{-1})	6.7−1.4	6.7−1,4
scan width (deg)	0.60 + 0.347 tan θ	0,60 + 0,347 tan θ
max 2θ (deg)	50.0	50,0
unique reflcns meas	4527 ($h\ k \pm l$)	4257 ($h \pm k \pm l$)
range of abs corr factors	0,7147−1,2214	0.7214−1.4355
total observations (NO)	2891 ($F_o^2 \geq 3\sigma(F_o^2)$)	3953 ($F_o^2 \geq 3\sigma(F_o^2)$)
final no. of parameters varied (NV)	285	307
R^a	0,046	0.047
$R_w{}^b$	0.058	0.077
GOF^c	1.846	3,019

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w = [\Sigma w(|F_o| - |F_c|)^2/(\Sigma wF_o^2)]^{1/2}$. ^{c} GOF $= [\Sigma w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$.

Table 3. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for Selected Atoms of $[OsRh(CH_2CN)(CO)_3dppm)_2]$ (**7**)^a

atom	*x*	*y*	*z*	*B*, Å^2
Rh/Os^b	0.25390(2)	0.16357(3)	−0,03123(2)	3,98(1)^c
P(1)	0.3155(1)	0.2450(2)	−0.08707(9)	4.44(6)^c
P(2)	0.3306(1)	0.4279(2)	−0.0026(1)	4.27(5)^c
O(1)^b	0.239(1)	−0.007(1)	−0.1193(8)	10.4(5)
O(2)	0.4014(4)	0.1696(6)	0.0930(3)	7.8(2)
N^b	0.317(1)	0.499(2)	0.192(1)	12.3(7)
C(1)^b	0.2339(9)	0.070(1)	−0,0902(8)	5.3(4)
C(2)^b	0.3481(8)	0.160(1)	0.0440(7)	4,3(3)
C(3)^b	0.1729(8)	0.280(1)	−0.0563(6)	4.1(3)
C(4)^b	0,2292(9)	0.490(1)	0.0722(7)	4.7(3)
C(5)^b	0,2841(8)	0,493(1)	0.1371(7)	4,4(3)
C(6)	0.3807(4)	0.3488(6)	−0.0393(4)	5.0(2)^c

^{a} Numbers in parentheses are estimated standard deviations in the least significant digits for quantities in this and subsequent tables. Parameters for phenyl carbon atoms are given in the supplementary material. ^{b} Atom Rh/Os is half-occupancy in each of Os and Rh, and atoms O(1), N, C(1), C(2), C(3), C(4), and C(5) are half-occupancy owing to disorder. ^{c} Indicates an atom refined anisotropically. Displacement parameters for the anisotropically refined atoms are given in the form of the equivalent isotropic Gaussian displacement parameter, B_{eq}, defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

affected. In spite of the disorder the atom positions resolved well. After locating the disordered metals from the Patterson map, the atoms of the diphosphine ligands were immediately obvious, and the disordered equatorial ligands were also located without difficulty in subsequent difference Fourier maps. Refinement proceeded by full-matrix least-squares techniques minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, with $w = 4F_o^2/\sigma^2(F_o^2)$. The neutral atom scattering factors[13] and anomalous dispersion terms[14] were taken from the usual tabulations. The hydrogen atoms were generated at idealized calculated positions by assuming a C−H bond length of 0.95 Å and the appropriate sp^2 or sp^3 geometry at carbon. All hydrogens were included in the calculations with fixed, isotropic Gaussian displacement parameters of 1.2 times those of the attached atoms and were constrained to "ride" on the attached atoms.

The final model with 285 parameters varied converged to $R = 0.046$ and $R_w = 0.058$. In the final difference Fourier map the ten highest residuals (0.2−0.6 eÅ^{-3}) were located near the metal atoms and the CO and CH_2CN ligands and were judged to be without chemical significance (a typical carbon on earlier maps had a density of *ca.* 2,3 eÅ^{-3}),

(b) $[RhOs(CH_3)(CO)_3(dppm)_2]$ (10). Solution and refinement of **10** proceeded in a manner similar to that for **7**. In the space group $P\bar{1}$ the molecule was again found to be disordered about an inversion center. The orientations of all ligands, even including the orientations of the dppm phenyl groups, were found to be very similar to those in **7**. Refinement of **10** was handled in the same manner as described above for **7**, and converged to $R = 0.047$ and $R_w = 0.077$ with 307 parameters varied. In the final difference Fourier map the 10 highest residuals (0.6−2.6 eÅ^{-3}) were located near the CO and CH_3 ligands and the metals, A typical carbon on earlier maps had a density of *ca.* 5.1 eÅ^{-3}. The positional and isotropic thermal parameters for compounds **7** and **10** are given in Tables 3 and 4, respectively.

Results and Discussion

Monoalkyl and Related Species. Transition-metal hydrido complexes occupy a key position in organometallic chemistry. Their reactions with olefins, alkynes, and other unsaturated substrates yield alkyl, alkenyl, and related species via insertions into the M−H bonds, and hydrido complexes also having σ-bound organic ligands present are important intermediates leading to organic products through the reductive elimination of these fragments from the metal. Clearly such species are pivotal in a variety of catalytic processes in which hydrogen transfer to an unsaturated substrate occurs,[15]

In our investigations into alkyl, alkyl hydrido, and dialkyl derivatives of heterobinuclear complexes of Rh and Os we began

(13) (a) Cromer, D. T.; Waber, J. T. *International Tables for Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A. (b) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(14) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

Table 4. Atomic Coordinates are Equivalent Isotropic Displacement Parameters for Selected Atoms of $[OsRh(CH_3)(CO)_3(dppm)_2]$ (**10**)[a]

atom	*x*	*y*	*z*	*B*, Å^2
Rh/Os[b]	0,07421(3)	−0.13306(3)	−0.06882(3)	3.413(9)[c]
P(1)	0.1517(2)	−0.1647(1)	0.1198(2)	3.73(4)[c]
P(2)	−0.0286(1)	0.1180(1)	0.2741(2)	3.35(4)[c]
O(1)[b]	0.2903(7)	−0.3952(7)	−0.2070(8)	3.3(2)[c]
O(2)	−0.1849(4)	−0.1085(5)	0.0234(6)	6.1(2)[c]
C(1)[b]	0.222(1)	−0.317(1)	−0.169(1)	5.1(3)[c]
C(2)[b]	−0.082(1)	−0.138(1)	−0.024(1)	3.8(3)[c]
C(3)[b]	0.118(1)	0.046(1)	−0.017(1)	3.4(3)[c]
C(4)[b]	−0.151(2)	0.347(1)	0.183(1)	4.7(4)[c]
C(5)	0.0372(5)	−0.0535(5)	0.2674(6)	3.6(2)[c]

[a] Parameters for phenyl carbon atoms are given in the supplementary material. [b] Atom Rh/Os is half-occupancy in each of Os and Rh, and atoms O(1), C(1), C(2), C(3), and C(4) are half-occupancy owing to disorder. [c] Indicates an atom refined anisotropically. Displacement parameters for the anisotropically refined atoms are given in the form of the equivalent isotropic Gaussian displacement parameter, B_{eq}, defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

with the acetonitrile hydrido complex, $[RhOs(NCMe)(CO)_3(\mu\text{-}H)(dppm)_2][BF_4]_2$ (**3**). This species is readily prepared from the known precursor $[RhOs(CO)_4(dppm)_2][BF_4]$ (**2**)[9] by protonation in acetonitrile, as shown in Scheme 1. The IR spectrum of a solid sample of **3** shows two terminal carbonyl bands at 2078 and 2004 cm^{-1}, a lower frequency stretch at 1819 cm^{-1}, suggesting a bridging mode for this carbonyl, and two bands attributed to a coordinated (2292 cm^{-1}) and a co-crystallized solvent acetonitrile (2321 cm^{-1}); in solution the spectrum was almost identical. The $^{13}C\{^1H\}$ NMR spectrum displays three carbonyl resonances at δ 174.27, 176.82, and 224.47, and selective ^{31}P-decoupling experiments establish that the former two signals correspond to carbonyls terminally bound to Os, whereas the low-field signal shows coupling to the Os-bound phosphorus nuclei and to Rh (25 Hz), confirming its position bridging the metals. Although the coupling of this carbonyl to Rh is substantial, it is somewhat less than the 30−35 Hz expected for a symmetrically bridged carbonyl,[4j,16] and this together with the lack of coupling of this group to the Rh-bound phosphorus nuclei leads to its formulation as being more strongly bound to Os, in either an asymmetric or a semibridging mode.[17] This carbonyl also displays coupling (27 Hz) to one of the terminal CO groups, consistent with a mutually trans arrangement. In the ^1H NMR spectrum the hydride resonance at δ −15.18 displays coupling to all four phosphorus atoms and to Rh ($^1J_{Rh-H}$ = 27 Hz) confirming its bridged position.

Compound **3** appeared to be a potentially useful precursor for a variety of organometallic hydride complexes through displacement of the acetonitrile ligand by neutral or anionic organic groups. This reactivity was initially demonstrated by replacement of NCMe by ^{t}BuNC and I$^-$, yielding $[RhOs(^t BuNC)(CO)_3(\mu\text{-}H)(dppm)_2][BF_4]_2$ (**4**) and $[RhOsI(CO)_3(\mu\text{-}H)(dppm)_2][BF_4]$ (**5**), respectively. Both products are structurally analogous to the acetonitrile precursor, having very comparable spectroscopic parameters, The IR spectra of compounds **3**−**5** are closely comparable in both the solid and solution suggesting no major structural difference in the two states. Although the low carbonyl stretch in each compound (1821 (**4**), 1793 cm^{-1} (**5**)) again suggests a bridging interaction, the lack of resolvable $^{103}Rh-^{13}C$ coupling in the ^{13}C NMR implies that the interaction with Rh is weaker than in **3**, indicating a weak semibridging interaction. In **4** the CN stretch of the ^{t}BuNC group (2189 cm^{-1}) is at higher frequency than that of the free ligand (2125 cm^{-1}), indicating that this group functions more as a σ donor than a π acceptor[18] in this dicationic complex.

Attempts to obtain either an alkyne−hydrido complex or an alkenyl species resulting from alkyne insertion into the metal−hydrogen bond of **3** failed, as no reaction was observed with alkynes such as acetylene, diphenylacetylene, dimethyl acetylenedicarboxylate, or hexafluoro-2-butyne. Presumably, substitution of the σ-donor acetonitrile ligand by π acceptors is not favorable, a conclusion that is in line with the observation that ^{t}BuNC functions primarily as a σ donor in the related species, **4**, The acetonitrile ligand in **3** is surprisingly not very labile; no exchange of this ligand with CD_3CN solvent was observed, even after several days.

Reaction of **3** with carbanions also occurs, but invariably these stronger bases result in deprotonation at one or more locations in the complex. With sodium acetylide, reaction of **3** in acetonitrile yields two products (in other solvents a large number of unidentified species resulted). The first product, $[RhOs(\eta^1\text{-}C{\equiv}CH)(CO)_3(dppm)_2]$ (**6**), shown in Scheme 1, is an acetylide complex resulting from deprotonation at the metals and subsequent replacement of the neutral acetonitrile ligand by the second equivalent of acetylide ion. The second product quite unexpectedly is the cyanomethyl complex $[RhOs(CH_2CN)(CO)_3(dppm)_2]$ (**7**), which has apparently resulted from a double deprotonation, removing both the hydrido ligand (as H$^+$) and a hydrogen of the coordinated acetonitrile ligand. This latter deprotonation, although not anticipated, can be rationalized by the comparable acidities of acetylene and acetonitrile,[19] and by the expected increase in the acidity of acetonitrile upon coordination to a dicationic species. The possibility that the reaction occurred by deprotonation of acetonitrile solvent followed by attack on **3** by the resulting acetonitrilide anion is ruled out by the reaction of **3** with NaC≡CH in THF. Although many decomposition products were obtained in this solvent, compound **7** was still obtained in up to 10% yield. Furthermore we saw no evidence of exchange of the coordinated acetonitrile ligand of **3** with solvent THF after 12 h. Further support for deprotonation of coordinated acetonitrile came from the reaction of **3** with NaOH in acetonitrile which again gave **7** in approximately 10% yield together with decomposition products, NaOH is not a strong enough base to deprotonate free acetonitrile to an appreciable extent.[19] Labeling studies using CD_3CN were not carried out owing to the large volumes of labeled solvent required. Both products (**6** and **7**) have NMR spectroscopic parameters that are very similar to those of the related methyl complex **10**, which is well-characterized (vide infra). For **6** the acetylide hydrogen appears as a triplet of doublets at δ 1.73 in the ^1H NMR, displaying coupling to the Rh-bound P nuclei (4 Hz) and to Rh (4 Hz); although we have not seen reports of coupling between an acetylide and Rh or Rh-bound phosphines, the chemical shift of this proton is in agreement with that reported for another Rh−acetylide complex,[20] Compounds **6** and **7** each display one resonance for the dppm methylene protons and have very similar ^{13}C NMR spectra, displaying a resonance for a single carbonyl bound to Os at *ca.* δ 192 and an unresolved multiplet at *ca.* δ 217, integrating as two carbonyls. Although no Rh coupling is obvious in the latter signal, a small coupling could be masked

(15) (a) Pruett, R. L. *Adv. Organomet. Chem.* **1979**, *17*, 1. (b) James, B. R. *Adv. Organomet. Chem.* **1979**, *17*, 319. (c) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407. (d) Parshall, G. W. *Homogeneous Catalysis*; John Wiley & Sons: New York, 1980; Chapters 3, 4, and 8. (e) Halpern, J. A. *Inorg. Chim. Acta* **1981**, *50*, 11.

(16) (a) Jenkins, J. A.; Cowie, M. *Organometallics* **1992**, *11*, 2767. (b) Antwi-Nsiah, F.; Cowie, M. *Organometallics* **1992**, *11*, 3157.

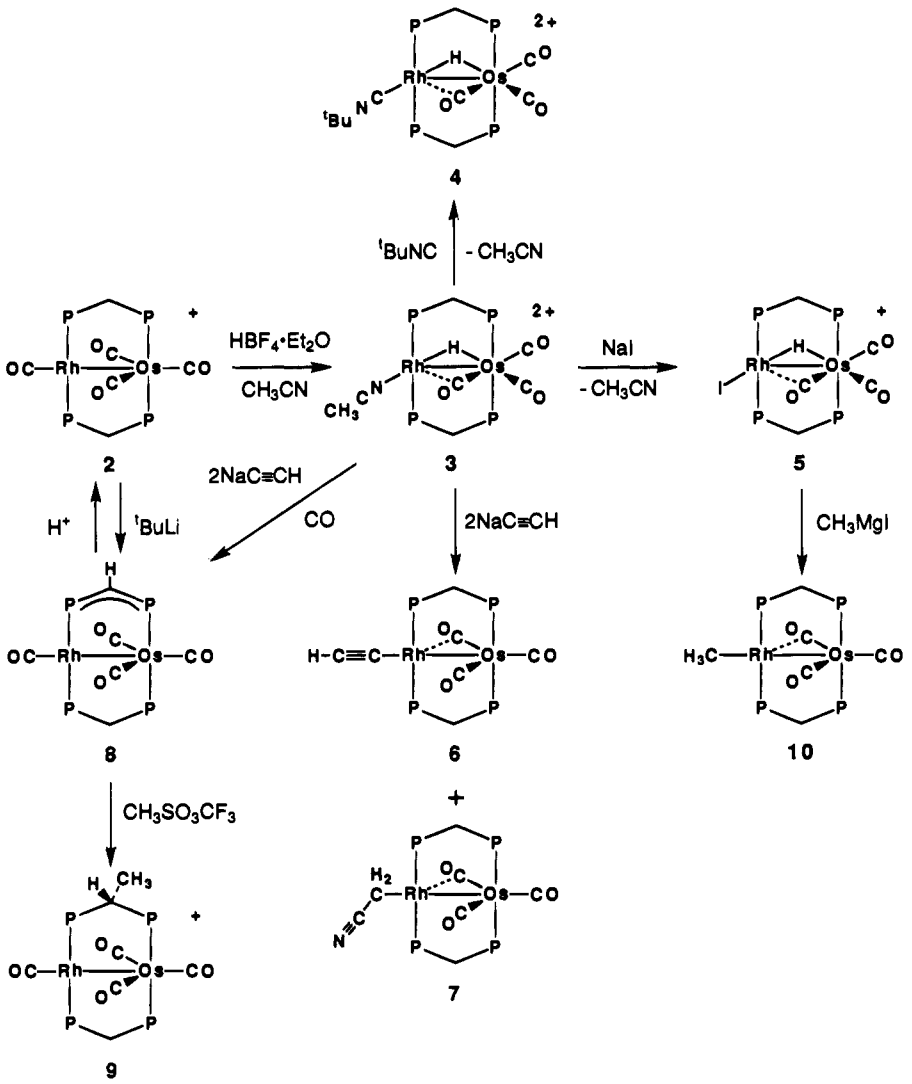
(17) Colton, R.; McCormick, M. J. *Coord. Chem. Rev.* **1980**, *31*, 1.

(18) Treichel, P. M. *Adv. Organomet. Chem.* **1973**, *11*, 21.

(19) March, J. *Advanced Organic Chemistry*; John Wiley & Sons: New York, 1992; Chapter 8.

(20) Stang, P. J.; Crittell, C. M. *Organometallics* **1990**, *9*, 3191.

Scheme 1



by the breadth of the peak. It is noteworthy that for compound **7** the unique carbonyl on Os, opposite the Rh−Os bond, shows weak coupling to Rh of 3 Hz. Coupling of this magnitude, through a metal−metal bond, has previously been observed in related systems,[16a] We suggest that both **6** and **7** have weak semibridging interactions much like that spectrally observed in a methyl analogue (**10**) (vide infra). The structure proposed for **6** is based on the structural determinations for **7** and **10** (vide infra); it appears that an exchange of bonding modes between the semibridging CO and the terminal one on the opposite face is occurring as proposed later for **10**. Compound **7** displays a triplet of doublets for the cyanomethyl group at δ 0.58 (2H) in the ^{1}H NMR spectrum, and this resonance is closely comparable to those observed in a series of related alkyl complexes,[4j,16b,21] including **10** (vide infra). The C≡N stretch of this cyanomethyl group is observed at 2190 cm^{-1} in the IR spectrum and compares favorably to values obtained for a number of cyano−alkyl complexes.[22,23] Confirmation of this formulation comes from the X-ray structure determination.

Although the structure of [RhOs(CH$_2$CN)(CO)$_3$(dppm)$_2$] (**7**) is disordered about the inversion center (see Experimental Section), only the oxygen atoms of two disordered carbonyls and the metals were actually superimposed, so the other disordered atoms were readily resolved. The phosphines themselves were not disordered and are well-behaved. A perspective view of **7** is shown in Figure 1, while relevant parameters are given in Tables 5 and 6. Whether the cyanomethyl and the carbonyl groups are bound to Rh or Os cannot be established crystallographically owing to the nature of the disorder; however, the connectivity shown is unambiguously established from the NMR studies (vide supra). Both diphosphines bridge the metals in the usual trans arrangement perpendicular to the plane of the other ligands. The Os center can be viewed as trigonal bipyramidal, having the three carbonyls in the equatorial plane, with all intercarbonyl angles of approximately 120°. This gives Os its favored 18e configuration. Rh, with only three ligands attached, requires a dative bond from Os to give it a 16-electron configuration; the resulting Rh−Os distance (2.7272(4) Å) is normal. In addition, Rh also forms a semibridging interaction with one carbonyl (C(3)O(2′)) which is σ bound to Os. Although the parameters involving C(3)O(2′) seem to clearly indicate a semibridging geometry for this group, with it being primarily bound to Os (note the Os−C(3)−O(2′) angle of 156.4(9)°), we avoid any detailed discussion of the bonding involving this carbonyl owing to the disorder. Therefore the abnormally long C(3)−O(2′) distance of 1.41(1) Å is probably a consequence of this disorder. The

(21) Graham, T.; Van Gastel, F.; Cowie, M., manuscript in preparation, describing alkyl complexes of RhMo.

(22) Porta, F.; Ragaini, F.; Cenini, S.; Demartin, F. *Organometallics* **1990**, *9*, 929.

(23) Crocco, G. L.; Lee, K. E.; Gladysz, J. A. *Organometallics* **1990**, *9*, 2819.

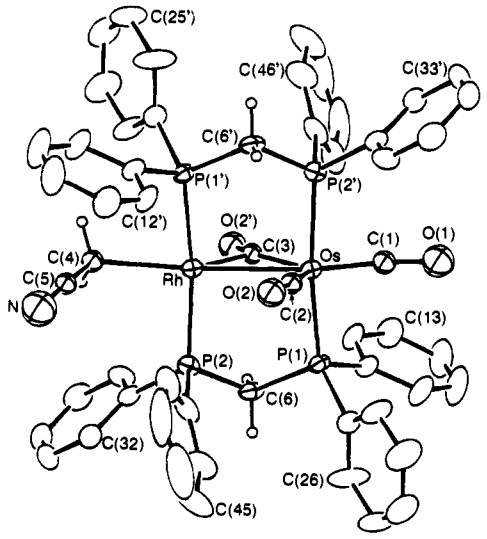


Figure 1. Perspective drawing of $[RhOs(CH_2CN)(CO)_3(dppm)_2]$ (**7**) showing only one of the two disordered molecules. Thermal ellipsoids are shown at the 20% level, except for methylene hydrogens which are shown arbitrarily small and phenyl hydrogens which are omitted.

Table 5. Selected Distances (Å) in $[OsRh(CH_2CN)(CO)_3(dppm)_2]$ (**7**)

atom 1	atom 2	distance	atom 1	atom 2	distance
Os	Rh	2.7272(4)	P(1)	C(6)	1.833(7)
Os	P(1)	2.293(2)	P(2)	C(6)	1.813(7)
Os	P(2')	2.340(2)	O(1)	C(1)	1.24(2)
Os	C(1)	1.73(2)	O(2)	C(2)	1.11(1)
Os	C(2)	1.82(1)	O(2')	C(3)	1.41(1)
Os	C(3)	2.04(1)	N	C(5)	1.11(2)
Rh	C(3)	1.98(1)	C(4)	C(5)	1.36(2)
Rh	C(4)	2.31(1)			

Table 6. Selected Angles (deg) in $[OsRh(CH_2CN)(CO)_3(dppm)_2]$ (**7**)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Rh	Os	P(1)	91,96(5)	Os	Rh	C(4)	173.3(3)
Rh	Os	P(2')	94.51(5)	P(1')	Rh	C(3)	94.9(3)
Rh	Os	C(1)	162.6(5)	P(1')	Rh	C(4)	90.8(3)
Rh	Os	C(2)	77.4(4)	P(2)	Rh	C(3)	97.4(3)
Rh	Os	C(3)	46.4(3)	P(2)	Rh	C(4)	84.0(3)
P(1)	Os	P(2')	167.47(7)	C(3)	Rh	C(4)	125,4(5)
P(1)	Os	C(1)	84.7(5)	Os	P(1)	C(6)	112.5(2)
P(1)	Os	C(2)	91.6(4)	Rh	P(2)	C(6)	112.7(2)
P(1)	Os	C(3)	87.9(3)	Os	C(1)	O(1)	162(2)
P(2')	Os	C(1)	86.0(4)	Os	C(2)	O(2)	170(1)
P(2')	Os	C(2)	100.3(4)	Os	C(3)	Rh	85.2(5)
P(2')	Os	C(3)	88.8(3)	Os	C(3)	O(2')	156.4(9)
C(1)	Os	C(2)	119.7(7)	Rh	C(3)	O(2')	117.5(8)
C(1)	Os	C(3)	116.3(6)	Rh	C(4)	C(5)	107(1)
C(2)	Os	C(3)	123.7(5)	N	C(5)	C(4)	167(2)
Os	Rh	C(3)	48.3(4)	P(1)	C(6)	P(2)	111.9(3)

semibridging nature of this interaction is supported, however, by the almost identical structure of **10**, for which clear evidence of this semibridging interaction also appears in the $^{13}C\{^1H\}$ NMR spectra (vide infra).

The binding mode of the CH_2CN group is shown in Figure 1, and all parameters involving this group are as expected. In particular, the angle at C(4) of 107(1)° is close to the tetrahedral value and the essentially linear C(4)−C(5)−N linkage and the short C(5)−N bond (1.11(2) Å) are consistent with the presence of a C≡N triple bond,[22,23] The Rh−C(4) distance of 2.31(1) Å is slightly longer than expected for a Rh−alkyl bond; however, the disorder of the groups in the equatorial plane precludes an in-depth discussion of their parameters, since their positions are not accurately determined.

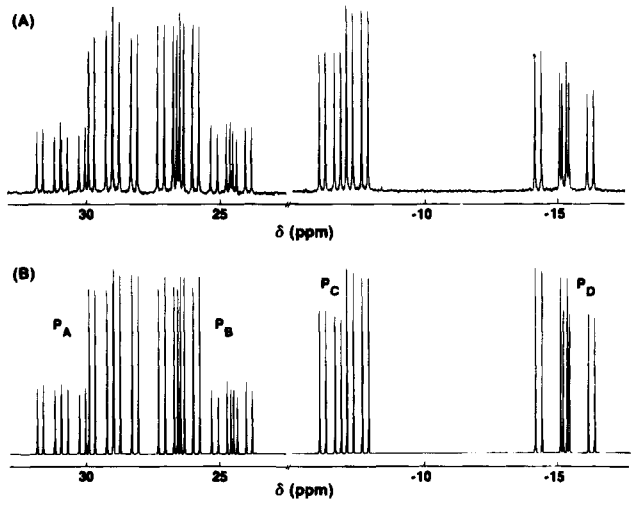


Figure 2. $^{31}P\{^1H\}$ NMR spectra for $[RhOs(CO)_4(Ph_2PCHPPh_2)(dppm)]$ (**8**): (A) observed (in CD_2Cl_2), (B) calculated—see Table 1 for derived parameters.

Although compounds **6** and **7** can be independently obtained in high yield by the above route through variations of the stoichiometries and experimental conditions (see Experimental Section), attempts to obtain these products by more rational routes were unsuccessful, It appears that obtaining a cyanomethyl complex by deprotonation of a coordinated acetonitrile ligand is unusual; more conventional routes involve oxidative addition of an α-halo acetonitrile to a metal,[22] halide displacement from XCH_2CN by anionic complexes,[22,23] or nucleophilic attack by cyanide ion on a methylidene complex.[23] There are also reports of formation of cyanomethyl complexes via C−H activation of acetonitrile,[24]

Under a CO atmosphere the reaction of **3** with sodium acetylide takes a very different and unexpected course, resulting in deprotonation at the metals and at one of the dppm groups, yielding $[RhOs(CO)_4(dppm\text{-}H)(dppm)]$ (**8**) (dppm-H = bis(diphenylphosphino)methanide). The $^{31}P\{^1H\}$ NMR spectrum of **8**, shown in Figure 2, displays a complex pattern of an ABCDX spin system in which all four phosphorus nuclei (ABCD) are chemically inequivalent, Simulation of the spectrum gives values of 321 and 117 Hz for the P−P coupling across Rh and Os, respectively, consistent with a trans arrangement of the phosphines at both metals. The much larger value of trans P−P coupling across Rh than Os appears typical.[25] In addition, the $^2J_{P-P}$ value within the deprotonated dppm group (159 Hz) is greater than that within the normal dppm (96 Hz), consistent with π delocalization over the deprotonated group. The methanide proton appears at higher field (δ 2,84) as a broad resonance compared to the dppm methylene signal, which is an apparent triplet at δ 4.16; such an upfield shift upon deprotonation has previously been observed.[26,27]

We assume that the different reactivity of **3** with sodium acetylide under CO results from substitution of NCMe by CO at some stage of the reaction, leaving the hydrido ligand and

(24) (a) English, A. D.; Herskovitz, T. *J. Am. Chem. Soc.* **1977**, *99*, 1648. (b) Ittel, S. D.; Tolman, C. A.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7577.

(25) (a) Jenkins, J. A. M.Sc. Thesis, Dalhousie University, 1984. (b) Hilts, R. W.; Cowie, M. Unpublished results.

(26) Dominguez, R.; Lynch, T. J.; Wang, F. *J. Organomet. Chem.* **1988**, *338*, C7.

(27) (a) Sharp, P. R.; Ge, Y.-W. *J. Am. Chem. Soc.* **1987**, *109*, 3796. (b) Sharp, P. R.; Ge, Y.-W. *Inorg. Chem.* **1993**, *32*, 94.

the dppm methylene groups as the only remaining acidic sites in the molecule. Although **8** was obtained in only *ca.* 50% isolated yield, spectroscopically monitoring the reaction indicated that conversion of **3** to **8** was essentially quantitative. Sodium acetylide also reacts with the cationic tetracarbonyl **2**, but surprisingly **8** is *not* obtained by deprotonation of a dppm methylene group; instead two other unidentified products result. This indicates that **2** is not an intermediate in the double deprotonation of **3** by NaC≡CH under CO. However, compound **8** can be obtained as the only observable species (by NMR) from **2** through the use of ^{t}BuLi as base. The latter route to **8** is more rational than the serendipitous double deprotonation of **3** by sodium acetylide.

Compound **8** reacts with methyl triflate resulting in alkylation of the methanide carbon to give $[RhOs(CO)_4(dppmMe)(dppm)][SO_3CF_3]$ (**9**). This appears to be the only reported example of substitution of a methylene hydrogen of a *bridged* dppm group by an alkyl group. Prior synthesis of dppmMe and its subsequent coordination to metals has been described,[28-32] and direct alkylation of dppm bound to a single metal has also been reported.[33-35] Although in one report[34] the alkylation of bridging dppm was noted as under investigation, no report has appeared. Surprisingly, the related complex, $[Li(THF)_4][Re_2(CO)_8(dppm\text{-}H)]$, was inert to alkylation of the methanide carbon,[26] and alkylation of a (dppm-H)-bridged dirhodium compound occurred at a bridging amido group and *not* at the methanide carbon of dppm-H.[27b] Apparently in **8** there is no site nucleophilic enough to compete with the methanide carbon.

The $^{31}P\{^1H\}$ NMR spectrum of **9** appears as an ABCDX spin system and derived parameters (Table 1) are consistent with our formulation; in particular, the intraligand P−P coupling within dppm and dppmMe are almost identical. In the ^1H NMR the methyl signal appears at δ 1.34 and the three signals for the protons on the methylenic carbons appear at δ 4.44, 4.03, and 3.77. Owing to the front−back asymmetry in **9**, imposed by the methyl substituent, four distinct carbonyl resonances are also observed in the ^{13}C NMR.

As anticipated, protonation of **8** occurs much as with alkylation, with this electrophile again attacking the methanide carbon of dppm-H to regenerate compound **2**, with the appropriate anion.

The iodo−hydrido complex **5** also appeared to be a potential precursor to hydrido alkyl complexes, via replacement of the iodo ligand by reaction with a Grignard reagent. Again, however, deprotonation occurs readily so no hydride complex is obtained, although the neutral alkyl complex $[RhOs(CH_3)(CO)_3(dppm)_2]$ (**10**) can be isolated in low yield in the reaction of **5** with MeMgI. The ^1H NMR spectrum of **10** shows the methyl resonance as a triplet of doublets at δ −0.35. The coupling of the methyl hydrogens to the adjacent phosphorus atoms ($^3J_{P-H}$ = 7 Hz) and to Rh ($^2J_{Rh-H}$ = 2 Hz) is typical for such species,[4j,16b,21] The spectroscopic properties involving the carbonyls in **10** are similar to those of compounds **6** and **7**, yet they have important minor differences. In the IR spectrum **10** shows a very low carbonyl stretch at 1723 cm^{-1}, consistent with a bridging interaction of this group. In addition, the low-field ^{13}C resonance (δ 220.2), corresponding to two carbonyl ligands, displays coupling to Rh of 13 Hz; this is clearly much less than expected for a symmetrically bridged CO and indicates a semibridging geometry having a weaker, although substantial, interaction with Rh. Although one resonance for two carbonyls implies that both are semibridging, the solid-state structure indicates that only one is semibridging (vide infra), and the solution IR spectrum is almost identical to that in the solid (apart from broader bands in the former), showing three carbonyl stretches of which only one is at low frequency. It appears therefore that a fluxional process exchanges the semibridging CO with the terminal CO on the opposite face of the complex. This exchange is extremely facile since no change in the ^{13}C NMR spectrum was obvious to −80 °C. The presence of at least one accompanying semibridging carbonyl group, which functions as a π acceptor from the electron-rich Rh center, is typical of these A-frame-like alkyls[4j,16b,21] and appears necessary owing to the good donor ability of the methyl group and the absence of another π acceptor on Rh. From this perspective the absence of a strong semibridging carbonyl (as indicated by significant $^{103}Rh-^{13}CO$ coupling) in either **6** or **7** is understandable in view of the acetylide and cyanomethyl groups in the respective compounds being poorer net donors to Rh compared to CH_3, resulting in less π back-donation to the semibridging CO groups. Clearly the cyanomethyl group will be a poorer donor by virtue of the electronegative cyano substituent, and the acetylide ligand has been shown to be a much poorer σ donor than a methyl group.[36] Although one might expect that the electron density at Rh would also be reduced by π back-donation to the acetylide ligand, theoretical[37] and experimental[36] studies suggest that the acetylide group is a poor π acceptor. Although we suggest a weaker semibridging interaction in **7** than in **10**, on the basis of NMR studies, it should be recalled the comparable solid-state structures suggest substantial interactions for both compounds.

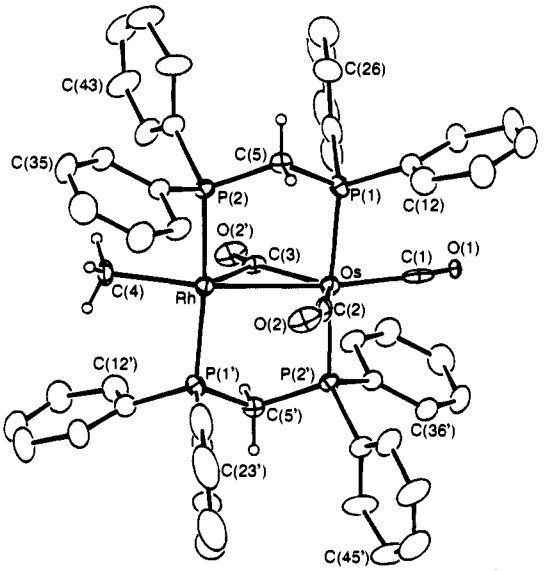


Figure 3. Perspective drawing of $[RhOs(CH_3)(CO)_3(dppm)_2]$ (**10**) showing only one of the disordered molecules. Thermal parameters as in Figure 1. Methyl hydrogens are also drawn artificially small.

The X-ray structure determination of **10** confirms the structural assignment, as shown in Figure 3, and although this structure was also disordered, it was resolved satisfactorily,

(28) Kraihanzel, C. S.; Maples, P. K. *J. Organomet. Chem.* **1976**, *117*, 159.
(29) van der Ploeg, A. M. J.; van Koten, G. *Inorg. Chim. Acta* **1981**, *51*, 225.
(30) Sommer, K. *Z. Anorg. Chem.* **1970**, *376*, 37.
(31) Dean, P. A. W.; Srivastava, R. S. *Can. J. Chem.* **1985**, *63*, 2829.
(32) Lee, C.-L.; Yang, Y.-P.; Rettig, S. J.; James, B. R.; Nelson, D. A.; Lilga, M. A. *Organometallics* **1986**, *5*, 2220.
(33) Al-Jibori, S.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1982**, 286.
(34) Al-Jibori, S.; Shaw, B. L. *Inorg. Chem. Acta* **1982**, *65*, L123.
(35) Al-Jibori, S.; Shaw, B. L. *Inorg. Chem, Acta* **1983**, *74*, 235.
(36) Lichtenberger, D. L.; Renshaw, S. K.; Bullock, R. M. *J. Am. Chem. Soc.* **1993**, *115*, 3276.
(37) Kostić, N. M.; Fenske, R. F. *Organometallics* **1982**, *1*, 974.

Table 7. Selected Distances (Å) in $[OsRh(CH_3)(CO)_3(dppm)_2]$ (**10**)

atom 1	atom 2	distance	atom 1	atom 2	distance
Os	Rh	2.7643(9)	Rh	C(4)	2.183(8)
Os	P(1)	2.298(1)	P(1)	C(5)	1.832(4)
Os	P(2′)	2.333(1)	P(2)	C(5)	1.834(4)
Os	C(1)	2.08(2)	O(1)	C(1)	0.91(1)
Os	C(2)	1.859(8)	O(2)	C(2)	1.151(8)
Os	C(3)	2.183(9)	O(2′)	C(3)	1.244(8)
Rh	C(3)	2.087(8)			

Table 8. Selected Angles (deg) in $[OsRh(CH_3)(CO)_3(dppm)_2]$ (**10**)

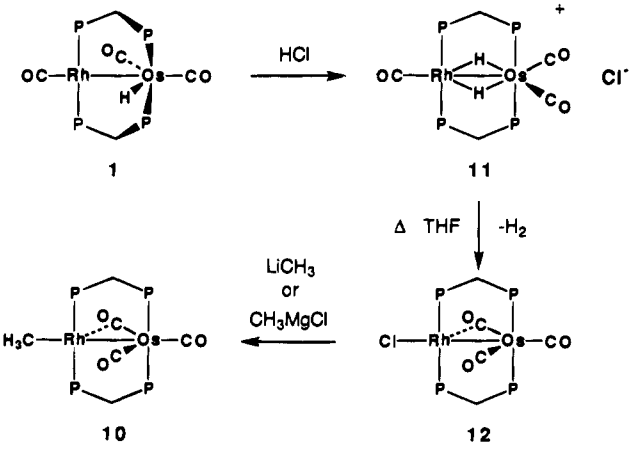
atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Rh	Os	P(1)	92.64(4)	Os	Rh	C(3)	51.2(2)
Rh	Os	P(2′)	93.26(4)	Os	Rh	C(4)	167.7(3)
Rh	Os	C(1)	166.2(3)	P(1′)	Rh	C(3)	91.3(2)
Rh	Os	C(2)	77.5(3)	P(1′)	Rh	C(4)	91.6(3)
Rh	Os	C(3)	48.2(2)	P(2)	Rh	C(3)	97.4(2)
P(1)	Os	P(2′)	171.25(4)	P(2)	Rh	C(4′)	83.9(3)
P(1)	Os	C(1)	85.3(2)	C(3)	Rh	C(4)	117.2(4)
P(1)	Os	C(2)	89.4(3)	Os	P(1)	C(5)	113.1(1)
P(1)	Os	C(3)	92.1(2)	Rh	P(2)	C(5)	113.6(1)
P(2′)	Os	C(1)	87.5(2)	Os	C(1)	O(1)	175.5(9)
P(2′)	Os	C(2)	98.2(3)	Os	C(2)	O(2)	163.0(7)
P(2′)	Os	C(3)	87.0(2)	Os	C(3)	Rh	80.7(2)
C(1)	Os	C(2)	116.0(4)	Os	C(3)	O(2′)	153.9(7)
C(1)	Os	C(3)	118.3(4)	Rh	C(3)	O(2′)	124.9(7)
C(2)	Os	C(3)	125.6(3)	P(1)	C(5)	P(2)	110.6(2)

allowing a meaningful discussion of at least the important structural features. Important structural parameters are given in Tables 7 and 8. At osmium, the geometry is that of a coordinatively-saturated trigonal-bipyramidal $OsL_2(CO)_3$ moiety; the phosphines are essentially trans (171.25(4)°) and the angles between the equatorial carbonyl groups are all close to 120°. Having only a methyl group and two ends of the diphosphines bound to Rh, this metal would have only 14 valence electrons, without a dative bond from Os which is required to give Rh an essentially square planar, 16e configuration. The observed Rh−Os separation of 2.7643(9) Å is clearly consistent with a significant metal−metal interaction associated with a single bond. Donation from Os to Rh in addition to the methyl group, which is also a good donor, and the two diphosphine ligands causes a buildup of electron density at Rh which is alleviated by the semibridging interaction with C(3)O-(2)′. Surprisingly the shorter metal−C(3) distance (2.087(8) Å) is to Rh and not to Os (2.183(9) Å) (much as in **7**), in spite of this carbonyl being significantly more linear with repect to Os (Os−C(3)−O(2)′ = 153.9(7)°, Rh−C(3)−O(2)′ = 124.9-(7)°), which indicates a stronger interaction with Os, The shorter Rh−C(3) distance may in part be due to the smaller radius of Rh^+ compared to that of Os^0,[38] but may also be, in part, a consequence of the disorder. However, we feel that this disorder has been satisfactorily resolved and this and the substantial ^{103}-Rh−^{13}C coupling for this CO in the $^{13}C\{^1H\}$ NMR spectra indicate substantial π donation from Rh to C(3). The structure also shows that exchange of the semibridging and one-terminal carbonyl in solution (vide supra) would require movement of the two carbonyl carbon atoms by only *ca.* 0.4 Å.[39] Although the positions of the disordered methyl and carbonyl ligands are for the most part well-defined, that of C(1) is poorly defined as shown by the long Os−C(1) and short C(1)−O(1) distances and by the elongated thermal ellipsoid of C(1) (see Figure 3),

(38) The radii for the metals are 1.34 Å (Rh) and 1.35 Å (Os) (see: Wells, A. F. *Structural Inorganic Chemistry*; Oxford University Press: London, 1975; p 1020) so that for Rh^+ will be even smaller than that of Os.

(39) This distance was calculated by leaving O(2′) in its observed position and moving C(3) to a position to give a linear Os−C(3)−O(2′) unit.

Scheme 2

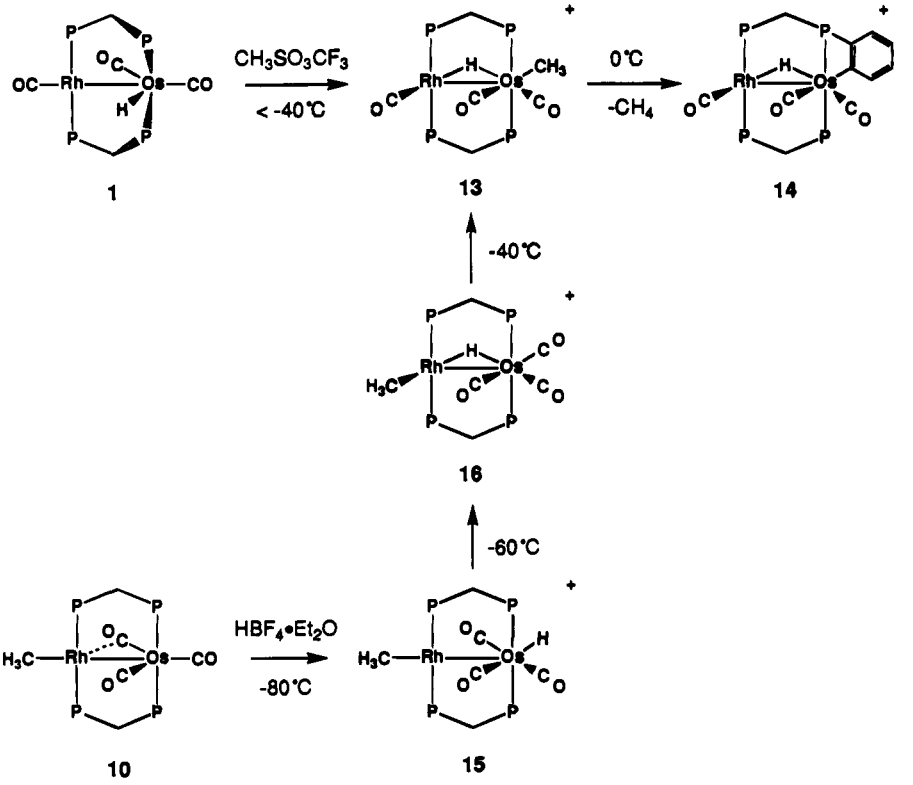


Although both compounds **7** and **10** show disorder of the alkyl and carbonyl ligands, limiting any structural interpretations, the structural parameters of the two compounds are closely comparable, giving us confidence in the gross structural features,

Other far superior routes for synthesizing **10** utilize either the analogous chloro complex, $[RhOsCl(CO)_3(dppm)_2]$ (**12**), or compound **2**. Compound **12** is generated from **1** via protonation with 1 equiv of HCl to give $[RhOs(CO)_3(\mu\text{-}H)_2(dppm)_2][Cl]$ (**11**), followed by H_2 loss under reflux, as diagrammed in Scheme 2, Both **11** and **12** are readily characterized by conventional means, and in particular the spectroscopy of **11** is essentially identical to that of the BF_4^- salt previously described.[9] Compound **10** can be obtained in moderate yields (*ca.* 35%) in the reactions of **12** with either MeMgCl or $LiCH_3$. Of these two routes, that involving the Grignard is the better since we were never able to obtain the methyl compound **10** free from the starting chloride (**12**) via the latter route. Even with the former method the Grignard must be destroyed with water immediately after the reaction to minimize reconversion of the methyl to the chloro compound. Another route to **10**, involving the reaction of **2** (as the BF_4^- salt) with $LiCH_3$, appears to be the best route and is the one currently used.

Hydrido−Methyl Complexes and Reductive Elimination of CH_4. One of our original goals had been the synthesis of binuclear hydrido−alkyl complexes to allow the investigation of the reductive elimination of the alkane fragment from the two metal centers, Two obvious routes to such a species involved the alkylation (using a source of CH_3^+) of the hydrido complex **1** or protonation of the alkyl complex **10**. At −40 °C alkylation of **1** yields a metastable hydrido−alkyl complex $[RhOs(CH_3)(CO)_3(\mu\text{-}H)(dppm)_2][SO_3CF_3]$ (**13b**). At lower temperatures the reaction proceeded slower and did not occur appreciably at −80 °C, Over the temperature range from −80 to −40 °C compound **13b** was the only observed product. The ^1H NMR spectrum of **13b** displays the hydride resonance at δ −12.90 with coupling to all P nuclei and to Rh, indicating a bridged geometry, and the methyl resonance at δ −0.43 with coupling to only the P nuclei on Os (as shown by selective ^{31}P decoupling), indicating that it is terminally bound to this metal, In the $^{13}C\{^1H\}$ NMR spectrum one carbonyl shows 75 Hz coupling to Rh, indicating its terminal coordination to this metal, and two carbonyls appear as broad singlets and are bound to Os, in agreement with the formulation shown in Scheme 3, Allowing a solution of **13b** to warm to ambient temperature results in methane evolution (as detected in the ^1H NMR) to yield the orthometalated product, $[RhOs(CO)_3(\mu^2\text{-}\eta^3\text{-}(o\text{-}C_6H_4)PPhCH_2PPh_2)(\mu\text{-}H)(dppm)][SO_3CF_3]$ (**14b**). The $^{31}P\{^1H\}$ NMR spectrum of this product shows a complex pattern for

Scheme 3

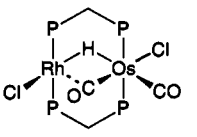


four chemically distinct ^{31}P nuclei, and simulation of this spectrum is consistent with a trans arrangement of phosphines at both metals. The IR, ^{1}H, and ^{13}C NMR spectra are also consistent with the structure shown on Scheme 3. Orthometalation is assumed to be at Os since both signals for the two Rh-bound ^{31}P nuclei in the ^{31}P NMR spectrum are near those in other Rh^{+} systems reported in this paper, whereas the signals for the Os-bound ^{31}P nuclei are widely separated with one at rather high field, consistent with the presence of a strained 4-membered ring[40] involving the orthometalated phenyl group.

Since the hydrido–methyl intermediate **13b**, which preceded methane loss, had the methyl group bound to Os, we undertook the preparation of this species via protonation of **10**, which has the methyl group bound to Rh. It was of interest to determine whether methane elimination from the Rh center might occur in this case or whether rearrangement to **13** would precede methane loss. At −80 °C reaction of **10** with HBF_4•OEt_2 yields a new hydrido–methyl complex $[(CH_3)RhOsH(CO)_3(dppm)_2][BF_4]$ (**15**), which has been shown by ^{1}H and $^{1}H\{^{31}P\}$ experiments to have the methyl group still on Rh while the hydrido ligand is terminally bound to Os. At −60 °C this species transforms to the isomer **16**, which still has the methyl group on Rh but now has the hydrido ligand bridging the metals. At −40 °C compound **16** undergoes another rearrangement to yield **13a**, which is identical to **13b** apart from the BF_4^- anion instead of $SO_3CF_3^-$. No other intermediates are observed when **13a** is warmed to give **14a**. It is significant that reductive elimination does *not* occur from Rh in intermediate **16** even though the hydrido and methyl groups are both bound to this metal. It may be that the mutually trans arrangment of these ligands inhibits their elimination. Analogous diplatinum complexes having a trans arrangement of terminal methyl and bridging hydride ligands have been shown to be remarkably inert toward methane elimination.[41] Instead reductive elimination of methane occurs from the pseudooctahedral Os^{2+} center, in which we assume a cis arrangement of H and CH_3 groups, presumably generating a coordinatively unsaturated Os^0 center which readily orthometalates one of the dppm phenyl groups to give **14**. The absence of resolvable coupling of the methyl protons to Rh in the ^{1}H NMR spectra of both compounds **15** and **16** is not surprising considering that the line widths of these resonances at these temperatures were 4–5 Hz; as noted earlier, Rh–H coupling in methyl complexes such as **10** is generally only *ca.* 2 Hz.

Reaction of the deuterio analogue of **1**, $[RhOsD(CO)_3(dppm)_2]$, with CH_3^+ in CD_2Cl_2 or CH_2Cl_2 at ambient temperature gives CH_3D, as observed in the ^{2}H NMR, and compound **14**, in which no deuterium incorporation was observed, confirming that the hydrogen atom required for conversion of the methyl ligand to methane comes from the hydrido ligand and not from elsewhere, such as the dppm groups, and that the hydrido ligand in the orthometalated product **14** comes from dppm.

Insertion Reactions. Another obvious route to alkyl complexes analogous to **10** involves the insertion of olefins into the Os–H bond of compound **1**. However, a variety of olefins, including ethylene, tetrafluoroethylene, 1,1-difluoroethylene, and dimethyl maleate, did not react. Tetrachloroethylene and *cis*-1,2-dichloroethylene do react, but only to yield the monochloro complex **12** and the dichloro species $[RhOsCl_2(CO)(\mu\text{-}H)(\mu\text{-}CO)(dppm)_2]$ (**17**)

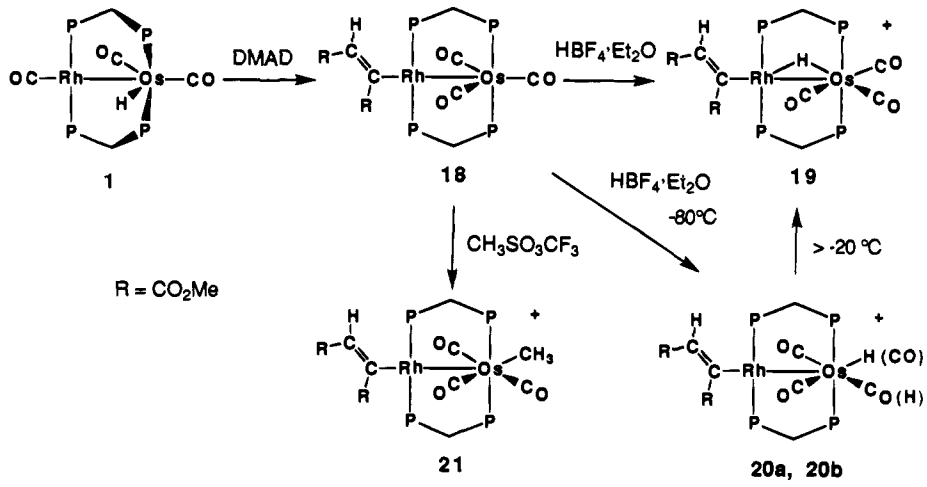


(**17**)

(together with starting material in the latter reaction). The spectroscopic data for **17** are shown in Table 1. The small

(40) (a) Garrou, P. E. *Inorg. Chem.* **1975**, *14*, 1435. (b) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

Scheme 4



$^{103}Rh-^{13}C$ coupling involving one carbonyl group clearly identifies it as semibridging. Compound **17** can be synthesized from **1** in high yield through reaction with CCl_4.

Although olefins failed to yield alkyl complexes in reaction with **1**, an η^1-vinyl complex, analogous to **10**, is obtained from the reaction of **1** with dimethyl acetylenedicarboxylate (DMAD) as shown in Scheme 4. Insertion into the Os–H bond has resulted in a product, $[RhOs(MeO_2CC{=}C(H)CO_2Me)(CO)_3(dppm)_2]$ (**18**), having the resulting vinyl group bound to Rh. The ^1H NMR spectrum shows two resonances for the two sets of methylene protons, a doublet of triplets for the vinyl proton at δ 4.12, showing coupling to Rh of 2 Hz and to the two Rh-bound phosphorus nuclei of 1 Hz, and singlets for the two DMAD methyl groups. All carbonyls are bound to Os, as shown by ^{13}C NMR, and display no coupling to Rh. The absence of $^{103}Rh-^{13}CO$ coupling in the ^{13}C NMR and the absence of a low-frequency carbonyl stretch in the IR suggest the absence of any bridging interaction of the carbonyl groups, although a weak semibridging interaction cannot be ruled out. That the vinyl group in **18** functions as a weaker donor to Rh than the methyl group in **10** is expected, based on the sp^2 hybridization of the α-carbon and on the electron-withdrawing carboxylate groups; therefore strong π donation from Rh to an Os-bound carbonyl appears unnecessary. Attempts to observe an alkyne, hydrido intermediate at low temperature failed, as the reaction proceeds readily to completion, even at −80 °C.

Protonation of **18** yields the hydrido-bridged vinyl complex $[RhOs(MeO_2CC{=}C(H)CO_2Me)(CO)_3(\mu\text{-}H)(dppm)_2][BF_4]$ (**19**). This is the vinyl analogue of intermediate **16**, observed in the low-temperature protonation of the methyl complex **10**. Protonation of **18** at −80 °C gives two additional products together with **19**. These are formulated as **20a** and **20b**, isomers of **19** which are analogous to the intermediate **15** in the protonation of the methyl complex **10**. These species would result from protonation at the two accessible sites on Os. But whereas this gives the same species in **10**, the orientation of the vinyl moiety in **18** gives rise to two isomers upon protonation (on the same or opposite face as the vinylic double bond). These isomers persist until *ca.* −20 °C at which point their conversion to **19** occurs readily. That reductive elimination of dimethyl maleate from **19** does not readily occur is not surprising, since alkyl and alkenyl groups having electronegative substituents are often stable to reductive elimination,[42] owing to a stronger metal–carbon bond. However the failure of **19** to reductively eliminate is also consistent with the earlier discussion of methane elimination which did not occur directly from **16**, but first required rearrangement so that elimination could occur for the Os center. Heating **19** in refluxing THF for 1 h does not result in reductive elimination of the olefin; instead another unidentified hydrido complex is obtained. This species is currently being studied.

Reaction of **18** with methyl triflate yields $[RhOs(MeO_2CC{=}C(H)CO_2Me)(CH_3)(CO)_3(dppm)_2][SO_3CF_3]$ (**21**). The ^1H NMR study shows coupling of the vinylic hydrogen to Rh and coupling of the methyl hydrogens to the Os-bound phosphines, indicating that these groups are bound one to each metal as shown in Scheme 4. Although we cannot rule out the isomer in which one carbonyl is interchanged between the metals and the methyl group, the structure shown is the most likely initial product of alkylation based on access of methyl triflate to the Os center in compound **18**. This proposed structure for **21** is as observed in the recent structure determination of the related species, $[RhOs((CH_3)C{=}C(CH_3)_2)(CH_3)(CO)_3(dppm)_2][SO_3CF_3]$, which was obtained from methyl triflate addition to the trimethylvinyl precursor.[43] Unlike the protonation of **18**, in which two isomers are obtained, alkylation yields only one isomer (**21**). It is also significant that this structure is analogous to that proposed as the initial species in the protonation of **10**. The alkylation of **18** to yield **21** also represents a convenient route into dialkyl complexes of RhOs. Our preliminary studies have indicated that compound **10** also reacts with methyl triflate to give a species having a methyl group on each metal, and this work will be reported in a subsequent paper.[44]

Conclusions

A series of alkyl, alkenyl, and acetylide species of the form $[RhOsR(CO)_3(dppm)_2]$ have been prepared. In all cases the organic group is σ bound to Rh, in spite of our expectation that the Os–C bond is stronger than Rh–C.[45] The observed structures give the metals a Rh^+/Os^0 formulation, whereas having the σ-bound organic group on Os would result in a Rh^0/Os^+ formulation. We suggest that the favored Rh^+/Os^0 combination is one important driving force favoring the structures obtained. The X-ray studies on **7** and **10**, together with the spectroscopic data on related species, indicate that in

(41) (a) Brown, M. P.; Cooper, S. J.; Frew, A. A.; Manojlović-Muir, Lj.; Muir, K. W.; Puddephatt, R. J.; Thompson, M. A. *J. Chem. Soc., Dalton Trans.* **1982**, 299. (b) Azam, K. A.; Puddephatt, R. J. *Organometallics* **1983**, *2*, 1396.
(42) Nakamura, A.; Otsuka, S. *J. Am. Chem. Soc.* **1973**, *95*, 7262.
(43) Sterenberg, B. T.; Cowie, M. Manuscript in preparation.
(44) Sterenberg, B. T.; Cowie, M. Unpublished work.

most cases Rh is involved in at least one semibridging interaction with a carbonyl on Os. It is suggested that this semibridging interaction stabilizes these species by removing excess charge from Rh, which is brought about by the absence of an acceptor ligand on Rh, together with the presence of the donor phosphines and the alkyl group which is also a good donor,[46] In addition, the Os → Rh dative bond required to give Rh a 16e configuration also gives rise to a charge buildup on Rh. In cases in which a semibridging carbonyl is not clearly identified spectroscopically, the Rh-bound alkyl or related group is stabilized by electron-withdrawing substituents.

Reductive elimination of methane from methyl hydride species has been shown to be site specific; even when the methyl group starts out on Rh, reductive elimination occurs from the Os center. This is not the result to be expected on the basis of bond strengths[45] or kinetic labilities,[47] which should favor elimination from the second-row element (Rh). We assume that reductive elimination from Rh is inhibited by the trans arrangement of the hydride and methyl groups in the appropriate intermediate, and by the unfavorable, highly coordinatively unsaturated Rh center which would result, having only two phosphines coordinated. The reductive elimination of methane from Os yields a highly unstable, coordinatively unsaturated Os^0 center which rapidly leads to orthometalation of one of the dppm phenyl rings to give a saturated Os^{2+} center. Facile oxidative addition of a 16e Os^0 center is well-known.[48]

The synthesis of $[RhOs(MeO_2CC{=}C(H)CO_2Me)(CH_3)(CO)_3(dppm)_2][SO_3CF_3]$ (**21**) having a σ-bound organic group on each metal suggests a route to a series of such species in which the roles of the different metals and different organic groups can be probed with respect to their tendencies to undergo migratory-insertion and reductive-elimination reactions. This work is currently underway.[44]

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Supplementary Material Available: Tables of parameters for the dppm phenyl rings and solvent molecules, anisotropic thermal parameters and calculated hydrogen parameters (11 pages); structure factor tables (21 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JA9409366

(45) (a) Ziegler, T.; Tschinke, V. *Bonding Energetics in Organometallic Compounds*; Marks, T. J., Ed.; American Chemical Society: Washington, DC, 1990; Chapter 19. (b) Ziegler, T.; Tschinke, V.; Ursenbach, B. *J. Am. Chem. Soc.* **1987**, *109*, 4825. (c) Armentrout, P. B. *Bonding Energetics in Organometallic Compounds*; Marks, T. J., Ed.; American Chemical Society: Washington, DC 1990; Chapter 2.

(46) Rees, W. M.; Churchill, M. R.; Li, Y.-J.; Atwood, J. D. *Organometallics* **1985**, *4*, 1162.

(47) Shen, J.-K.; Tucker, D. S.; Basolo, F.; Hughes, R. P. *J. Am. Chem. Soc.* **1993**, *115*, 11312 and references therein.

(48) Collman, J. P.; Roper, W. R. *Adv. Organomet. Chem.* **1968**, *7*, 53.