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A Convenient General Route to a Series of Diphosphine-Bridged Heterobinuclear Complexes That Contain Rhodium and Structures of the Mixed-Valent Complexes $[RhM(CO)_4(Ph_2PCH_2PPh_2)_2]$ (M = Mn, Re)

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A convenient route to a series of dppm-bridged complexes has been developed in which the chloride anion in $[RhCl(dppm)_2]$ is displaced by a metal carbonylate anion. This metathesis reaction is accompanied by unwinding of one or both of the chelating dppm groups to adopt a bridging arrangement and by loss of one carbonyl group. In the compounds $[RhCo(CO)_3(dppm)_2]$, $[RhMH(CO)_3(dppm)_2]$ (M = Fe, Ru, Os), $[RhM(CO)_4(dppm)_2]$ (M = Mn, Re), and $[RhMH(CO)_4(dppm)_2]$ (M = Cr, W), both diphosphines adopt a bridging arrangement, whereas in $[RhFeCp(CO)(dppm)_2]$ and $[RhMoCp(CO)_2(dppm)_2]$ only one dppm group bridges the metals while one remains chelating on rhodium. The structures of $[RhM(CO)_4(dppm)_2]$ (M = Mn (**5**), Re (**6**)) have been determined by X-ray methods. The coordination geometries at Mn and Re are not octahedral, but instead (ignoring the Rh atoms), the $[M(CO)_3L_2]$ (L = one end of dppm unit) moieties have trigonal-bipyramidal geometries, suggesting that a M(−I) formulation is appropriate. This $[M(CO)_3L_2]^-$ fragment then functions as a pseudohalide, forming a dative $M \rightarrow Rh$ bond and giving the Rh center a square-planar arrangement consistent with a Rh(+I) formulation. The resulting M–Rh bond lengths are 2.8428 (8) Å (M = Mn) and 2.7919 (6) Å (M = Re). Compound **5** crystallizes in the triclinic space group $P\bar{1}$ with $a = 10.897$ (2) Å, $b = 11.046$ (2) Å, $c = 11.700$ (2) Å, $\alpha = 68.14$ (1)°, $\beta = 67.48$ (1)°, $\gamma = 87.69$ (1)°, $V = 1198.7$ (4) Å^3, and $Z = 1$ and was refined to $R = 0.054$ and $R_w = 0.082$. Compound **6** crystallizes together with one THF molecule in the monoclinic space group $P2_1/c$ with $a = 12.963$ (4) Å, $b = 19.883$ (3) Å, $c = 11.277$ (2) Å, $\beta = 99.12$ (2)°, $V = 2870$ (2) Å^3, and $Z = 2$ and was refined to $R = 0.053$ and $R_w = 0.088$. Both compounds occupy a crystallographic inversion center so the metal carbonyl fragments are disordered, although this disorder, in reality, is readily handled crystallographically, with only two carbonyl carbons having two sets of half-occupancy positions and each metal position being composed of one half-occupancy rhodium atom and one half-occupancy manganese or rhenium atom.

Introduction

The current interest in heterobimetallic complexes arises from their promise of displaying unique chemistry by virtue of the differing properties of the two distinct metals. In such complexes not only can the ligands be varied to achieve a range in reactivities but the metals can also be changed, allowing an even wider reactivity range to be explored.

As pointed out by Geoffroy and co-workers,[1] the metal–metal bond (M–M′) in heterobimetallic complexes is not purely covalent but can have significant donor–acceptor character. Such bonds have been shown to be relatively weak, being readily cleaved by nucleophiles.[2] Although this property is often not desirable when investigating binuclear reactivity, since it results in cleavage to mononuclear fragments, the labile $M \rightarrow M'$ bond does have the benefit of yielding a source of incipient coordinative unsaturation. In order to make use of the labile $M \rightarrow M'$ bond while still maintaining the binuclearity of the complex, we have chosen to use bis(diphenylphosphino)methane (dppm) as a bridging group in order to hold the metals in close proximity during the reactions of interest.

Dppm has been widely used in homobinuclear complexes[3] but has been much less used in heterobinuclear species.[4] Several approaches have been used to synthesize dppm-bridged heterobinuclear complexes,[4] most notably by Shaw and co-workers.[4,5] In one approach, complexes containing chelating dppm groups were used, with unwinding of these groups upon reaction with the second metal to yield the dppm-bridged species.[5a–c]

In this paper we describe a general route to a series of dppm-bridged heterobinuclear complexes through the exchange of the halide ligand in $[RhCl(dppm)_2]$ by a series of metal carbonylate anions. This method yields complexes in which the metals are in low formal oxidation states, in which a potentially labile $M \rightarrow Rh$ dative bond can be formulated. Rhodium is chosen as one of the metals, owing to its tendency to adopt a coordinatively unsaturated 16e configuration.[6] The effect of this site of unsaturation on the chemistry of the other, coordinatively

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Table I. Spectral Data[a]

		NMR	
	IR, cm^{-1}	$\delta(^{31}P\{^1H\})^d$	$\delta(^1H)^e$
[$RhCo(CO)_3(dppm)_2$] (1)	1944 (m), 1922 (s), 1830 (m)^b	35.2 (m), 22.2 (dm, $^1J_{Rh-P}$ = 133 Hz)	
[$RhFeH(CO)_3(dppm)_2$] (2)	1956 (s), 1880 (s), 1830 (m)^b	71.1 (m), 34.1 (dm, $^1J_{Rh-P}$ = 123 Hz)	−12.65 (m, $^1J_{Rh-H}$ = 24 Hz, $^2J_{P(Fe)-H}$ = 37 Hz, $^2J_{P(Rh)-H}$ = 12 Hz)^f
[$RhRuH(CO)_3(dppm)_2$] (3)	1955 (s), 1892 (s), 1849 (m)^b	44.8 (m), 28.3 (dm, $^1J_{Rh-P}$ = 123 Hz)	−9.3 (m, $^1J_{Rh-H}$ = 22 Hz, $^2J_{P(Ru)-H}$ = 14 Hz, $^2J_{P(Rh)-H}$ = 12 Hz)
[$RhOsH(CO)_3(dppm)_2$] (4)	1971 (m), 1925 (m), 1858 (s) [ν(Os–H) 2040 (w)]^b	−9.2 (m), 15.2 (dm, $^1J_{Rh-P}$ = 143 Hz)	−7.4 (t, $^2J_{P(Os)-H}$ = 20 Hz)
[$RhMn(CO)_4(dppm)_2$] (5)	1960 (m), 1891 (m), 1817 (s), 1797 (s)^b	81.6 (m), 28.6 (dm, $^1J_{Rh-P}$ = 131 Hz)	
[$RhRe(CO)_4(dppm)_2$] (6)	1959 (m), 1908 (m), 1838 (m), 1800 (m)^b	6.2 (m), 26.2 (dm, $^1J_{Rh-P}$ = 136 Hz)	
[$RhCrH(CO)_4(dppm)_2$] (7)	1975 (m), 1922 (m), 1824 (s), 1803 (s)^b	70.3 (m), 26.2 (dm, $^1J_{Rh-P}$ = 121 Hz)	−14.8 (m, $^1J_{Rh-H}$ = 23 Hz, $^2J_{P(Cr)-H}$ = 10.1 Hz, $^2J_{P(Rh)-H}$ = 12.2 Hz)
[$RhWH(CO)_4(dppm)_2$] (8)	1978 (m), 1942 (s), 1838 (s), 1818 (s)^c	21.2 (m), 25.5 (dm, $^1J_{Rh-P}$ = 121 Hz)	−10.50 (m, $^1J_{Rh-H}$ = 25.1 Hz, $^2J_{P(W)-H}$ = 5 Hz, $^2J_{P(Rh)-H}$ = 14.2 Hz, $^1J_{W-H}$ = 49 Hz)
[$RhFeCp(CO)(dppm)_2$] (9)	1679 (s)^b	P_A, 34.8 (ddt, $^1J_{Rh-P_A}$ = 160 Hz, $^2J_{P_A-P_B}$ = 136 Hz, $^2J_{P_A-P_C}$ = 16 Hz); P_B, 86.9 (d); P_C, −19.2 (dd, $^1J_{Rh-P_C}$ = 137 Hz)	
[$RhMoCp(CO)_2(dppm)_2$] (10)	1684 (s), 1960 (m)^b	−22.1 (d, $^1J_{Rh-P}$ = 108 Hz)	

[a] Abbreviations used: IR, w = weak, m = medium, s = strong; NMR, m = multiplet, d = doublet, dm = doublet of multiplets, ddt = doublet of doublet of triplets. [b] CH_2Cl_2 solution in KCl cells. [c] Nujol mull in KBr disk. [d] Vs 85% H_3PO_4, −40 °C in CD_2Cl_2 solvent. [e] Vs TMS, 25 °C in CD_2Cl_2 solvent. [f] $J_{P(M)-H}$ is the coupling constant between the phosphorus nuclei bound to M and hydrogen.

saturated metal center will be of subsequent interest. A similar approach has previously been used to prepare a limited number of Pd[7] and Ru[8] complexes.

Experimental Section

General Considerations. All solvents were dried and deoxygenated before use and transferred directly to the reaction flask by cannula. Reactions were conducted with use of standard Schlenk procedures. Prepurified argon was used without further drying or deoxygenating. The hydrated rhodium(III) and ruthenium(III) chlorides were obtained from Johnson Matthey Ltd. and $Co_2(CO)_8$, $Re_2(CO)_{10}$, $Mn_2(CO)_{10}$, $W(CO)_6$, $Cr(CO)_6$, $Os_3(CO)_{12}$, and $Fe(CO)_5$ were purchased from Strem, while $Mo_2Cp_2(CO)_6$, $Fe_2Cp_2(CO)_4$, [$(Ph_3P)_2N$]Cl, and $Ph_2PCH_2PPh_2$ (dppm) were obtained from Aldrich. $Ru_3(CO)_{12}$[9] and [$RhCl(dppm)_2$][10] were prepared by the literature procedures, except that in the latter case the reaction in benzene was allowed to proceed for ca. 1 h; then the benzene was removed and the solid used without further purification. All metal carbonyls were sublimed before use, except for $Fe(CO)_5$, which was vacuum-distilled. The 99% carbon-13-enriched carbon monoxide was obtained from Isotec Inc.

The ^1H, $^1H\{^{31}P\}$, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AM-400 spectrometer, and infrared spectra were run on either a Nicolet 7199 Fourier transform interferometer or a Perkin-Elmer 883 spectrophotometer, either as solids (Nujol mulls on KBr disks) or solutions (KCl windows, 0.5-mm path length). Elemental analyses were performed by the microanalytical service within the department.

The compounds Na[$Co(CO)_4$],[11] Na[$Mn(CO)_5$],[12] Na[$Re(CO)_5$],[13] Na[$FeCp(CO)_2$],[14] and Na[$MoCp(CO)_3$][15] were all prepared by the reduction of the parent metal carbonyl dimers in THF with 2.3% Na/Hg. In all cases the anions were used in situ. The compound (PPN)[$HFe(CO)_4$][16] (PPN = [$(Ph_3P)_2N$]$^+$) was prepared by the reaction of NaOH with $Fe(CO)_5$ in MeOH followed by addition of (PPN)Cl, the salts (PPN)[$HM(CO)_4$] (M = Ru, Os)[17] were prepared by the Na/NH_3 reduction of $M_3(CO)_{12}$ (M = Ru, Os) followed by treatment with MeOH and (PPN)Cl, and the compounds (PPN)[$HM(CO)_5$] (M = Cr, W)[18] were synthesized by the reaction of $M(CO)_5PIP$ (PIP = piperidine) with (PPN)(BH_4) in THF.

Preparation of Compounds. (a) [$RhCo(CO)_3(dppm)_2$] (1). The compound [$RhCl(dppm)_2$] (100 mg, 0.11 mmol) was dissolved in 5 mL of THF, and Na[$Co(CO)_4$] (21 mg, 0.11 mmol) was then added in 10 mL of THF via cannula. The solution gradually turned from light orange to dark orange-brown over $^1/_2$ h. After it was stirred for an additional 18 h, the mixture was filtered under argon to remove NaCl and the THF was removed in vacuo to yield a dark brown solid, which was recrystallized from CH_2Cl_2/Et_2O to yield 82 mg (73%) of a deep brown powder, which was spectroscopically identified as 1. Anal. Calcd for $C_{53}H_{44}CoO_3P_4Rh$: C, 62.68; H, 4.33. Found: C, 62.12; H, 4.16. The spectroscopic parameters for all compounds are given in Table I.

(b) [$RhFe(\mu\text{-}H)(CO)_3(dppm)_2$] (2). The compound [$RhCl(dppm)_2$] (100 mg, 0.11 mmol) was dissolved in 5 mL of THF, to which (PPN)[$HFe(CO)_4$] (78 mg, 0.11 mmol) was added by cannula in 10 mL of THF. The mixture instantly turned dark green, and a white precipitate of (PPN)Cl formed. The mixture was stirred for an additional 4 h, after which the THF was removed in vacuo. The green solid was redissolved in toluene and filtered to remove the (PPN)Cl, and the solvent was removed under vacuum. Recrystallization from CH_2Cl_2/Et_2O yielded 84 mg (76%) of a dark green-brown powder (2). Anal. Calcd for $C_{53}H_{45}FeO_3P_4Rh$: C, 62.81; H, 4.34. Found: C, 62.41; H, 4.13.

(c) [$RhRu(\mu\text{-}H)(CO)_3(dppm)_2$] (3). The compound [$RhCl(dppm)_2$] (100 mg, 0.11 mmol) was dissolved in 5 mL of THF, and (PPN)[$HRu(CO)_4$] (83 mg, 0.11 mmol) was added by cannula in

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10 mL of THF. The mixture turned dark brown immediately, and a white precipitate of (PPN)Cl formed. After 8 h of additional stirring the solvent was removed in vacuo and the residue redissolved in toluene. After this solution was filtered to remove the (PPN)Cl, the toluene was removed in vacuo. The resulting brown residue was recrystallized from CH_2Cl_2 to yield 94 mg (81%) of a dark brown solid (**3**). Anal. Calcd for $C_{53}H_{45}O_3P_4RhRu$: C, 60.12; H, 4.16. Found: C, 59.75; H, 4.01.

(d) [RhOs(H)(CO)$_3$(dppm)$_2$] (4). In a procedure identical with that of part b, 100 mg (0.11 mmol) of [RhCl(dppm)$_2$] was reacted with (PPN)[HOs(CO)$_4$] (92 mg, 0.11 mmol) to yield 109 mg of a fine orange-yellow powder (87%). Anal. Calcd for $C_{53}H_{45}O_3OsP_4Rh$: C, 55.46; H, 3.92. Found: C, 54.89; H, 4.12.

(e) [RhMn(CO)$_4$(dppm)$_2$] (5). The compound [RhCl(dppm)$_2$] (100 mg, 0.11 mmol) was dissolved in 5 mL of THF and treated with 24 mg (0.11 mmol) of Na[Mn(CO)$_5$] in 10 mL of THF. The reaction mixture turned red-orange and was stirred for 8 h, after which time some of the product had precipitated. The addition of CH_2Cl_2 (20 mL) caused the product to redissolve. The solution was then filtered under argon to remove the NaCl, and the solvent was removed in vacuo. Recrystallization of the residue yielded 107 mg (84%) of a yellow powder (**5**). Anal. Calcd for $C_{54}H_{44}MnO_4P_4Rh$: C, 56.39; H, 3.83. Found: C, 56.11; H, 4.07.

(f) [RhRe(CO)$_4$(dppm)$_2$] (6). The compound [RhCl(dppm)$_2$] (100 mg, 0.11 mmol) was dissolved in 5 mL of THF, and Na[Re(CO)$_5$] (38 mg, 0.11 mmol) in 10 mL of THF was added via cannula. The solution turned light orange immediately and was stirred for 6 h. After filtration under argon the solvent was removed in vacuo and the residue was recrystallized from CH_2Cl_2/Et_2O. Owing to the high solubility of **6** in CH_2Cl_2, it is important to use a minimum volume of solvent in this step to maximize the yield; 95 mg (74%) of a bright yellow powder of **6** was obtained. Anal. Calcd for $C_{54}H_{44}O_4P_4ReRh$: C, 55.47; H, 3.76. Found: C, 55.08; H, 4.12.

(g) [RhCr(μ-H)(CO)$_4$(dppm)$_2$] (7). A solution of (PPN)[HCr(CO)$_5$] (80.7 mg, 0.11 mmol) in 10 mL of THF was added via cannula to a solution of [RhCl(dppm)$_2$] (100 mg, 0.11 mmol) in 10 mL of THF. The solution quickly turned dark red-brown over 5 min and was stirred for a total of 8 h. The THF volume was then reduced to 10 mL, and the solution was filtered to remove (PPN)Cl. The THF was then removed in vacuo, and the dark brown residue was recrystallized from THF/Et_2O and washed with 3 × 5 mL of Et_2O, to yield 85 mg (74%) of a dark brown solid. Anal. Calcd for $C_{54}H_{45}CrP_4O_4Rh$: C, 62.56; H, 4.37. Found: C, 62.11; H, 4.51.

(h) [RhW(μ-H)(CO)$_4$(dppm)$_2$] (8). The compound [RhCl(dppm)$_2$] (100 mg, 0.11 mmol) was dissolved in 5 mL of THF, and (PPN)[HW(CO)$_5$] (95 mg, 0.11 mmol) was added by cannula in 10 mL of THF. The solution rapidly turned dark red-brown, and a white precipitate of (PPN)Cl formed. After 6 h of stirring, the THF was removed in vacuo to yield a red-brown residue, which was extracted into toluene. Filtration of the brown solution to remove the insoluble (PPN)Cl followed by the removal of the solvent in vacuo left a red-brown solid, which was recrystallized from CH_2Cl_2/Et_2O to give 101 mg (78%) of a dark red-brown powder. Anal. Calcd for $C_{55}H_{45}O_4P_4RhW$: C, 55.50; H, 3.85. Found: C, 55.17; H, 4.21.

(i) [RhFeCp(μ-CO)(dppm)$_2$] (9). A solution of [RhCl(dppm)$_2$] (100 mg, 0.11 mmol) in 5 mL of THF was treated with a solution of Na[FeCp(CO)$_2$] (22 mg, 0.11 mmol) in 10 mL of THF. The dark green reaction mixture was stirred for 2 h and then filtered under argon. The solvent was removed in vacuo, and the dark green residue was recrystallized from CH_2Cl_2/Et_2O to yield 74 mg (65%) of a dark green-brown powder. Anal. Calcd for $C_{56}H_{49}FeOP_4Rh$: C, 65.89; H, 4.80. Found: C, 65.23; H, 4.99.

(j) [RhMoCp(CO)(μ-CO)(dppm)$_2$] (10). The compound [RhCl(dppm)$_2$] (100 mg, 0.11 mmol) was dissolved in 5 mL of THF. Na[MoCp(CO)$_3$] (29 mg, 0.11 mmol) in 10 mL of THF was added via cannula, and the reaction mixture instantly turned dark brown. After 5 h of stirring, NaCl was removed by filtration under argon and the solvent removed in vacuo. The brown product was recrystallized from CH_2Cl_2/Et_2O to yield 80 mg (67%) of product. Anal. Calcd for $C_{57}H_{49}MoO_2P_4Rh$: C, 62.87; H, 4.50. Found: C, 62.16; H, 4.81.

X-ray Data Collection. Yellow crystals of [RhMn(CO)$_4$(dppm)$_2$] (**5**) were obtained from CH_2Cl_2/Et_2O, and light orange crystals of [RhRe(CO)$_4$(dppm)$_2$]·THF (**6**) were obtained from THF/Et_2O. Suitable crystals were mounted and flame-sealed in glass capillaries under argon to minimize decomposition, which was still quite substantial for the Re compound (vide infra). Unit cell parameters were obtained from least-squares refinements of 25 well-distributed reflections in the ranges $20.0 \leq 2\theta \leq 24.0°$ (compound **5**) and $21.9 \leq 2\theta \leq 25.6°$ (compound **6**). For **5** a triclinic cell was established by the usual peak-search and reflection-indexing programs; the lack of systematic absences established the space group as either $P1$ or $P\bar{1}$. A cell reduction failed to locate a higher symmetry cell. The centrosymmetric space group was established as the more probable one on the basis of the successful refinement of the structure, although with $Z = 1$ in this space group the metal carbonyl moieties are disordered about the inversion center (vide infra). For compound **6** the space group was established as $P2_1/c$ with $Z = 2$, so again the metal carbonyl moieties were found to be inversion-disordered. Although for **6** there were only two THF molecules per unit cell, these were not found to occupy inversion centers but occupy general positions of half-occupancy.

Intensity data for both compounds were collected at 22 °C with use of the $\theta/2\theta$ scan technique to a maximum of $2\theta = 50.0°$. Backgrounds were scanned for 25% of the peak widths on either side of the scans. Three reflections were chosen as intensity standards and remeasured at 120-min intervals of X-ray exposure. For **5** there was no significant systematic decrease in the intensities of the standards, so no correction was applied, but for **6** the intensities decayed by 23.5%, so a correction was applied with the assumption of a linear decay. Data were processed in the usual way with a value of 0.04 for p,[19] and absorption corrections were applied to the data by using the method of Walker and Stuart.[20,21]

Structure Solution. Both structures were solved by conventional Patterson and Fourier techniques, with the assumption that the molecules were statistically disordered about the inversion centers. In fact only two carbonyl groups in each complex are affected, since the diphosphine groups are exactly inversion-related and one carbonyl group on each metal lies along the Rh–M (M = Mn, Re) axis and are therefore inversion-related. Even within the two carbonyl groups (C(2)O(2) and C(3)O(2)′) that do display disorder, the oxygen positions of the disordered pairs are superimposable, so in fact only the carbons of these two carbonyls show up as two sets of positions having half-occupancy. With such minor changes in the carbonyl positions for the two disordered sets it is not surprising that the phenyl ring positions are unaffected and are well behaved.

All non-hydrogen atoms were located. The THF molecule in compound **6** was apparently rotationally disordered, since none of the five ring atoms could be refined acceptably as an oxygen. All five atoms were therefore treated as carbons. Atomic scattering factors[22,23] and anomalous dispersion terms[24] were taken from the usual sources. Hydrogen atoms were included as fixed contributions and were not refined. Their idealized positions were calculated from the geometries of the attached carbon atoms with a C–H distance of 0.95 Å being used. Hydrogens were assigned thermal parameters of 20% greater than the isotropic B's of the attached carbon atoms. A summary of the structure refinements is given in Table II.

Results and Discussion

The reaction of [RhCl(dppm)$_2$] with 1 equiv of Na[Co(CO)$_4$] occurs readily at room temperature, yielding the mixed-metal species [RhCo(CO)$_3$(dppm)$_2$] (**1**). Replacement of the chloride anion by the cobalt carbonylate anion

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Table II. Summary of Crystal Data and Details of Intensity Collection

compd	$[RhMn(CO)_4(dppm)_2]$ (5)	$[RhRe(CO)_4(dppm)_2]\cdot$THF (6)
formula	$C_{54}H_{44}MnO_4P_4Rh$	$C_{58}H_{52}O_5P_4ReRh$
fw	1038.7	1242.1
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a, Å	10.897 (2)	12.963 (4)
b, Å	11.046 (2)	19.883 (3)
c, Å	11.700 (2)	11.277 (2)
α, deg	68.14 (1)	
β, deg	67.48 (1)	99.12 (2)
γ, deg	87.69 (1)	
V, Å^3	1198.7 (4)	2870 (2)
Z	1	2
d_{calcd}, g cm^{-3}	1.439	1.437
temp, °C	22	22
radiation, Å	Mo Kα, 0.71073	Mo Kα, 0.71073
monochromator	graphite	graphite
μ, cm^{-1}	7.91	25.71
transmissn coeff (min, max)	0.758, 1.101	0.845, 1.230
scan width, deg	$0.50 + 0.35 \tan \theta$	$0.60 + 0.35 \tan \theta$
takeoff angle, deg	3.00	3.00
no. of unique data collected	4169	5463
no. of obsd data (NO)	3010	3744
no. of variables (NV)	288	188
R^a	0.054	0.053
$R_w{}^b$	0.082	0.088
error in observn of unit wt (GOF)^c	2.573	2.874

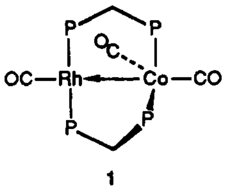
[a] $R = \sum||F_o|-|F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o|-|F_c|)^2/\sum wF_o{}^2]^{1/2}$. [c] GOF = $[\sum w(|F_o|-|F_c|)^2/(NO-NV)]^{1/2}$.

Table III. Positional and Thermal Parameters for $[RhMn(CO)_4(dppm)_2]$ (5)

atom	x	y	z	B, Å$^{2\,a}$
Rm^b	0.08893 (6)	0.06850 (6)	−0.13580 (5)	3.62 (1)
P(1)	0.0443 (1)	0.2671 (1)	−0.1231 (1)	3.23 (3)
P(2)	−0.1549 (1)	0.1215 (2)	0.1574 (1)	3.48 (4)
O(1)	0.2855 (7)	0.2068 (6)	−0.4025 (7)	10.1 (2)
O(2)	−0.1787 (4)	−0.0251 (4)	−0.1079 (4)	5.4 (1)
C(1)	0.2070 (7)	0.1530 (7)	−0.2972 (7)	5.7 (2)
C(2)^b	−0.075 (1)	0.017 (1)	−0.118 (1)	3.52 (2)*
C(3)^b	0.144 (1)	0.041 (1)	0.0101 (9)	3.2 (2)*
C(4)	−0.0293 (5)	0.2658 (6)	0.0457 (5)	3.8 (1)
C(11)	0.1984 (5)	0.3805 (5)	−0.2032 (5)	3.5 (1)
C(12)	0.2229 (6)	0.4932 (6)	−0.3157 (5)	4.4 (2)
C(13)	0.3509 (7)	0.5695 (7)	−0.3858 (6)	5.6 (2)
C(14)	0.4493 (7)	0.5304 (8)	−0.3441 (7)	6.5 (2)
C(15)	0.4271 (7)	0.4143 (8)	−0.2329 (6)	6.1 (2)
C(16)	0.3007 (6)	0.3414 (6)	−0.1613 (6)	4.6 (2)
C(21)	−0.0614 (5)	0.3633 (6)	−0.2041 (5)	3.9 (2)
C(22)	−0.0965 (6)	0.3209 (7)	−0.2865 (6)	5.3 (2)
C(23)	−0.1627 (7)	0.4018 (9)	−0.3609 (7)	8.4 (2)
C(24)	−0.2016 (6)	0.5152 (8)	−0.3491 (8)	7.8 (3)
C(25)	−0.1744 (7)	0.5543 (8)	−0.2648 (8)	6.9 (2)
C(26)	−0.1009 (7)	0.4803 (8)	−0.1909 (7)	6.1 (2)
C(31)	−0.1887 (6)	0.1205 (6)	0.3230 (5)	4.0 (2)
C(32)	−0.0833 (7)	0.1343 (8)	0.3575 (6)	6.0 (2)
C(33)	−0.1080 (7)	0.1217 (8)	0.4890 (6)	6.7 (2)
C(34)	−0.2398 (8)	0.0916 (8)	0.5862 (6)	6.7 (2)
C(35)	−0.3439 (8)	0.0762 (9)	0.5516 (6)	7.4 (3)
C(36)	−0.3206 (7)	0.0928 (8)	0.4210 (6)	6.1 (2)
C(41)	−0.3077 (5)	0.1710 (5)	0.1310 (5)	3.4 (1)
C(42)	−0.3826 (6)	0.0920 (7)	0.1116 (5)	4.9 (2)
C(43)	−0.4977 (6)	0.1274 (8)	0.0934 (6)	6.0 (2)
C(44)	−0.5367 (7)	0.2486 (9)	0.0909 (7)	7.0 (2)
C(45)	−0.4673 (7)	0.3293 (8)	0.1144 (7)	6.2 (2)
C(46)	−0.3497 (8)	0.2918 (7)	0.1334 (6)	5.2 (2)

[a] Starred values indicate atoms refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$. [b] Atom Rm is half-occupancy Rh and half-occupancy Mn, and atoms C(2) and C(3) are half-occupancy owing to disorder. See Experimental Section for details.

has been accompanied by unwinding of the chelating dppm groups, their transformation to the bridging mode, and concomitant loss of one carbonyl group. The $^{31}P\{^1H\}$ NMR spectrum is characteristic of a rhodium-containing heterobimetallic complex in which the metals are bridged by two dppm groups, yielding an AA′BB′X spin system. The broad second-order multiplet (a pseudotriplet) at δ 35.2 corresponds to the phosphorus nuclei bound to Co, and the doublet of pseudotriplets at δ 22.2 represents those bound to Rh ($^1J_{Rh-P}$ = 133 Hz). The low-field chemical shift for the phosphorus nuclei on Co appears to be typical of these species, in which the chemical shifts move to higher field on progressing down a triad. The carbonyl stretches for 1, at 1944, 1922, and 1830 cm^{-1}, are very reminiscent of those observed for the related complexes $[MM'(CO)_3(dppm)_2]$ (M = M′ = Rh,[25] 1940, 1920, 1835 cm^{-1}; M = Rh, M′ = Ir,[26] 1950, 1934, 1861 cm^{-1}; M = M′ = Ir,[27] 1950, 1936, 1857 cm^{-1}); therefore, 1 is formulated



1

as having an analogous structure. The assumption that Rh has the coordinatively unsaturated configuration, as shown, is consistent with the structure observed for $[(PEt_3)_2RhCo(CO)_5]$[28] and that proposed for $[RhCo(CO)_7]$[29] and with the known tendencies of Rh to favor a square-planar 16e configuration[6] and Co to favor 18e species.[30] This formulation very much reflects the method of preparation, with the tetrahedral $[Co(CO)_2L_2]^-$ anion functioning as a pseudohalide in the Vallarino-type complex *trans*-$[RhX(CO)L_2]$ (where L represents one end of the diphosphine unit and X = anionic group). The structure of 1 has recently been determined,[31] confirming the above formulation.

Complex 1, like the analogous Rh_2,[25] RhIr,[26] and Ir_2[27] complexes, displays temperature-dependent fluxionality, as shown by the $^{31}P\{^1H\}$ and ^{13}C NMR spectra. At −40 °C the $^{31}P\{^1H\}$ NMR spectrum is as described earlier, whereas at 23 °C the pseudotriplet corresponding to the Co-bound phosphorus nuclei has collapsed to a broad singlet. The ^{13}C NMR spectrum of a ^{13}CO-enriched sample, taken at −40 °C, displays three equal-intensity resonances at δ 180.4 (doublet of triplets, $^1J_{Rh-C}$ = 70 Hz, $^2J_{P-C}$ = 11 Hz), δ 214.6 (triplet, $^2J_{P-C}$ = 20 Hz), and δ 215.4 (broad singlet). Only the high-field resonance displays Rh coupling, consistent with the structure proposed. At 23 °C the high-field resonance remains essentially unchanged, but the other two have collapsed into a broad singlet at δ 215.6, having

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Table IV. Positional and Thermal Parameters for $[RhRe(CO)_4(dppm)_2]\bullet THF$ (6)

atom	*x*	*y*	*z*	*B*, Å^{2a}
Rr^b	0.07431 (4)	0.04268 (2)	−0.03694 (4)	2.98 (1)
P(1)	0.1720 (2)	−0.0460 (1)	−0.0967 (2)	3.00 (5)
P(2)	0.0265 (2)	−0.1377 (1)	0.0108 (2)	3.04 (5)
O(1)	0.2548 (6)	0.1333 (4)	−0.0804 (8)	6.6 (2)
O(2)	−0.1088 (8)	−0.0213 (5)	−0.2414 (7)	7.2 (2)
C(1)	0.1872 (8)	0.1008 (5)	−0.067 (1)	4.1 (2)
C(2)^b	−0.037 (1)	0.007 (1)	−0.163 (2)	3.4 (4)*
C(3)^b	0.107 (2)	0.033 (1)	0.139 (2)	4.0 (4)
C(4)	0.1021 (7)	−0.1264 (5)	−0.1115 (8)	3.4 (2)
C(5)^c	0.429 (3)	0.103 (2)	0.383 (3)	15.4 (9)*
C(6)^c	0.387 (5)	0.142 (3)	0.296 (6)	14 (2)*
C(7)^c	0.453 (3)	0.182 (2)	0.280 (3)	19 (1)*
C(8)^c	0.373 (3)	0.194 (2)	0.398 (3)	12 (1)*
C(9)^c	0.439 (4)	0.161 (3)	0.458 (5)	10 (2)*
C(11)	0.2037 (8)	−0.0334 (5)	−0.2479 (9)	3.6 (2)*
C(12)	0.1267 (9)	−0.0400 (6)	−0.347 (1)	4.6 (2)*
C(13)	0.147 (1)	−0.0270 (6)	−0.461 (1)	5.2 (3)*
C(14)	0.242 (1)	−0.0058 (6)	−0.479 (1)	5.5 (3)*
C(15)	0.319 (1)	0.0016 (7)	−0.383 (1)	5.8 (3)*
C(16)	0.3006 (9)	−0.0118 (6)	−0.265 (1)	4.7 (2)*
C(21)	0.2978 (8)	−0.0663 (5)	−0.0076 (9)	3.7 (2)*
C(22)	0.3638 (9)	−0.1123 (6)	−0.049 (1)	5.1 (2)*
C(23)	0.460 (1)	−0.1315 (7)	0.023 (1)	6.3 (3)*
C(24)	0.485 (1)	−0.1034 (7)	0.130 (1)	7.3 (4)*
C(25)	0.418 (1)	−0.0577 (7)	0.178 (1)	7.7 (4)*
C(26)	0.324 (1)	−0.0370 (6)	0.103 (1)	5.2 (3)*
C(31)	−0.0433 (7)	−0.2160 (5)	−0.0339 (8)	3.4 (2)*
C(32)	−0.0364 (9)	−0.2723 (6)	0.0411 (9)	4.5 (2)*
C(33)	−0.095 (1)	−0.3298 (7)	0.001 (1)	6.1 (3)*
C(34)	−0.153 (1)	−0.3326 (7)	−0.111 (1)	5.8 (3)*
C(35)	−0.162 (1)	−0.2757 (7)	−0.183 (1)	6.4 (3)*
C(36)	−0.1087 (9)	−0.2168 (6)	−0.146 (1)	4.9 (2)*
C(41)	0.1195 (7)	−0.1646 (5)	0.1385 (8)	3.4 (2)*
C(42)	0.202 (1)	−0.2037 (6)	0.126 (1)	5.3 (3)*
C(43)	0.279 (1)	−0.2239 (7)	0.226 (1)	6.4 (3)*
C(44)	0.262 (1)	−0.2043 (6)	0.336 (1)	5.7 (3)*
C(45)	0.176 (1)	−0.1703 (7)	0.353 (1)	6.2 (3)*
C(46)	0.1038 (9)	−0.1484 (6)	0.253 (1)	4.8 (2)*

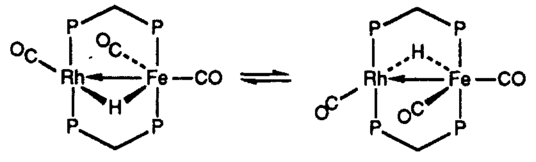
[a] See footnote *a* of Table III. [b] Atom Rr is half-occupancy Rh and half-occupancy Re, and atoms C(2) and C(3) are half-occupancy owing to disorder. See Experimental Section for details. [c] Atoms C(5)–C(9) are the rotationally disordered THF molecule. See Experimental Section for details.

twice the intensity of the high-field signal. These observations are consistent with a scrambling process occurring only at the Co center.

Although CO scrambling over both metals does not occur rapidly on the NMR time scale, addition of ^{13}CO results in enrichment of all carbonyls, indicating complete exchange under these conditions. Scrambling of the carbonyl groups might be expected to proceed through a tetracarbonyl species such as $[RhCo(CO)_4(dppm)_2]$, as was observed for the RhIr[26] and Ir_2[27] analogues. Such a species would be reminiscent of $Co_2(CO)_8$ but has not been observed in this study. Instead, under an excess of CO reversible cleavage of 1 occurs slowly, over a 2–4-h period, as shown in eq 1. Under 1 atm of CO at room temperature, the equilibrium still slightly favors the dinuclear species 1, with the ratio of monomer to dimer being about 1:1.25 as monitored by $^{31}P\{^1H\}$ and ^{13}C NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum for the mononuclear rhodium species displays a doublet at δ 22.0 ($^1J_{Rh-P}$ = 97.5 Hz) essentially as reported,[10] and the ^{13}C NMR spectrum shows a doublet of quintets at δ 198.2 ($^1J_{Rh-C}$ = 72.4 Hz, $^2J_{P-C}$ = 14.1 Hz) for the rhodium monomer and an octet for $[Co(CO)_4]^-$, displaying coupling to ^{59}Co ($I = {}^7/_2$, $^1J_{Co-C}$ = 281.3 Hz). In order to regenerate 1 after enrichment with ^{13}CO, it is necessary to flush the system with argon for approximately 12 h, since re-formation of 1 from the mononuclear fragments is slow. The reaction of 1 with CO confirms the lability of the Rh←Co bond, as previously observed by Geoffroy in an analogous system,[28] although reversible and facile transformation of the bridging dppm mode to the chelating one is highly unusual.

$$[RhCo(CO)_3(dppm)_2] + 2CO \rightleftharpoons [Rh(CO)(dppm)_2]^+ + [Co(CO)_4]^- \quad (1)$$

The compound $[RhCl(dppm)_2]$ also reacts with $[HM(CO)_4]^-$ anions (M = Fe, Ru, Os), as described for $[Co(CO)_4]^-$, to yield the heterobinuclear complexes $[RhMH(CO)_3(dppm)_2]$ (M = Fe (2), Ru (3), Os (4)). As with compound 1 the $^{31}P\{^1H\}$ NMR spectra of compounds 2–4 are typical of those for dppm-bridged heterobinuclear compounds containing Rh. Species 2-4 fall into two structural groups, with the Os complex differing subtly from the Ru and Fe species. This difference shows up clearly in the ^1H NMR spectra. For 2 the high-field region of the ^1H NMR spectrum displays a complex multiplet that can be shown by selectively decoupling the resonances for the Fe- and the Rh-bound phosphorus nuclei (P(Fe) and P(Rh), respectively) to be a triplet of doublet of triplets ($^1J_{Rh-H}$ = 24 Hz, $^2J_{P(Rh)-H}$ = 12 Hz, $^2J_{P(Fe)-H}$ = 37 Hz), corresponding to a hydride ligand that bridges both metals. The large coupling of the hydride ligand to both the Fe-bound and the Rh-bound phosphorus nuclei suggests that this hydride is strongly bound to both nuclei, and the relatively large coupling to Rh also supports a substantial interaction with this nucleus. By comparison, the isoelectronic complex $[RhIr(H)(CO)_3(dppm)_2][BF_4]$[26] has a bridging hydride that appears to have a somewhat weaker association with Rh, having $^1J_{Rh-H}$ = 19.0 Hz and $^2J_{P(Rh)-H}$ = 9.3 Hz. The carbonyl stretches for 2 (1956, 1880, 1830 cm^{-1}) bear a strong resemblance to those of 1 and are again consistent with a mixed-valence formulation with the two lower stretches being associated with the Fe center. These data suggest that 2 has the structure shown,



2

in which a trigonal-bipyramidal (TBP) $[HFe(CO)_2(L)_2]^-$ center forms a dative bond to Rh(+I). This formulation is analogous to that of 1 except that the additional hydride ligand on Fe results in a TBP structure rather than the tetrahedral coordination of Co. Complex 2 is isoelectronic with the cationic species $[MM'(H)(CO)_3(dppm)_2]^+$ (M, M′ = Rh, Ir),[26,32,33] for which there appear to be two structural forms. The homobinuclear complexes[32,33] have doubly bridged A-frame structures in which the metals are bridged by a hydride and a carbonyl group, whereas the RhIr species[26] has a bridging hydride but only terminal carbonyls. Compound 2 appears to have this latter structure. The ^{13}C NMR spectrum of 2 displays only two carbonyl resonances at −40 °C, at δ 225.5 (triplet, J_{P-C} = 18 Hz) and δ 183.8 (doublet of triplets, J_{P-C} = 14 Hz, J_{Rh-C} = 72 Hz) that are integrated as 2:1, respectively. At −80 °C the higher field, Rh-bound carbonyl resonance is unchanged, whereas that at low field appears as a broad (ca. 70 Hz at half-height) unresolved peak. We suggest that compound 2 undergoes the fluxional process shown in which tunneling of the hydride ligand between the metals results in ex-

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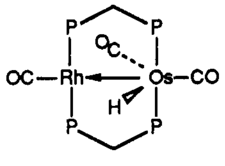
Table V. Selected Bond Lengths (Å) for $[RhMn(CO)_4(dppm)_2]$ (5)[a]

(a) Bonded Lengths			
Rh–Mn[b]	2.8428 (8)	P(1)–C(21)	1.829 (4)
Mn–P(1)[c]	2.275 (1)	P(2)–C(4)	1.838 (4)
Mn–P(2)′	2.263 (1)	P(2)–C(31)	1.823 (4)
Mn–C(1)[c]	1.737 (5)	P(2)–C(41)	1.834 (4)
Mn–C(2)	1.806 (8)	O(1)–C(1)	1.137 (6)
Mn–C(3)	1.936 (7)	O(2)–C(2)	1.188 (8)
P(1)–C(4)	1.819 (4)	O(2)′–C(3)	1.289 (7)
P(1)–C(11)	1.833 (4)		
(b) Nonbonded Lengths			
P(1)–P(2)	2.994 (2)	Rh–C(3)	2.475 (8)
Rh–C(2)	2.707 (8)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Although the Rh and Mn positions are disordered, the atoms are labeled as in Figure 1. [c] Because of disorder Mn–P(1) = Rh–P(1)′; Mn–P(2)′ = Rh–P(2), and Rh–C(1)′ = Mn–C(1).

change of the two Fe-bound carbonyl groups. Although the low-temperature limiting spectrum of 2 was not obtained, we see no evidence of a bridging carbonyl group.

The structure of the Ru analogue (3) appears to be similar to that of 2, as evidenced by the ^{1}H NMR spectrum, which displays a high-field multiplet at δ −9.3. Selective phosphorus decoupling experiments show that, as in 2, the hydride ligand bridges both metals ($^1J_{Rh-H}$ = 22 Hz, $^2J_{P(Ru)-H}$ = 14 Hz, $^2J_{P(Rh)-H}$ = 12 Hz). The IR spectrum of 3 also resembles that of 2. Although ^{13}C NMR spectra have not been obtained for 3, we suggest that it likely undergoes a fluxional process as observed for 2. The osmium analogue (4), however, has a structure different from those of the Fe and Ru species, as shown by the ^{1}H NMR spectra. Compound 4 displays a triplet in the high-field region of the ^{1}H NMR spectrum at δ −7.4. Selective phosphorus-decoupling experiments show that this hydride resonance is coupled only to the Os-bound phosphorus nuclei, with no coupling to Rh or the Rh-bound phosphorus atoms observed. This species is therefore formulated as shown, with a terminal hydride ligand bound to Os. The isomer in which the hydride ligand is opposite the Rh←Os bond can be ruled out, since the ^{13}C NMR spectrum displays three equal-intensity resonances, at δ 183.8 (t, $^2J_{P-C}$ = 13.6 Hz), δ 184.9 (t, $^2J_{P-C}$ = 13.6 Hz), and δ 197.6 (unresolved multiplet), showing that all carbonyl groups are inequivalent. This subtly different structure for 4 also gives rise to carbonyl stretches somewhat different from those of 2 and 3, as shown in Table I. Although for compound 4 an approximately trigonal-bipyramidal geometry for the Os center is shown (ignoring the Os→Rh bond), significant distortions may result through bending of the phosphines toward the sterically undemanding hydride ligand, to give a pseudotetrahedral geometry at Os, not unlike the geometry of Co in compound 1. Such distortions are not uncommon among hydride complexes.[34]



4

Table VI. Selected Angles (deg) for $[RhMn(CO)_4(dppm)_2]$ (5)

Rh–Mn–P(1)[a]	92.10 (3)	Mn–P(1)–C(4)	115.5 (1)
Rh–Mn–P(2)′	91.60 (3)	Mn–P(1)–C(11)	110.9 (1)
Rh–Mn–C(1)	175.6 (2)	Mn–P(1)–C(21)	119.1 (1)
Rh–Mn–C(2)	67.0 (2)	C(4)–P(1)–C(11)	103.5 (2)
Rh–Mn–C(3)	58.9 (2)	C(4)–P(1)–C(21)	103.8 (2)
P(1)–Mn–P(2)′	174.37 (4)	C(11)–P(1)–C(21)	102.3 (2)
P(1)–Mn–C(1)	87.5 (2)	Rh–P(2)–C(4)	114.4 (1)
P(1)–Mn–C(2)	96.9 (2)	Rh–P(2)–C(31)	113.5 (1)
P(1)–Mn–C(3)	84.3 (2)	Rh–P(2)–C(41)	116.4 (1)
P(2)–Mn–C(1)	88.5 (2)	C(4)–P(2)–C(31)	102.6 (2)
P(2)–Mn–C(2)	88.4 (2)	C(4)–P(2)–C(41)	104.8 (2)
P(2)–Mn–C(3)	94.0 (2)	C(31)–P(2)–C(41)	103.8 (2)
C(1)–Mn–C(2)	117.4 (3)	Mn–C(1)–O(1)	179.0 (5)
C(1)–Mn–C(3)	116.8 (3)	Mn–C(2)–O(2)	174.9 (6)
C(2)–Mn–C(3)	125.8 (3)	Mn–C(3)–O(2)′	178.2 (6)

[a] Labeling is as shown in Figure 1.

Table VII. Selected Bond Lengths (Å) for $[RhRe(CO)_4(dppm)_2]\bullet THF$ (6)[a]

(a) Bonded Lengths			
Re–Rh[b]	2.7919 (6)	P(1)–C(21)	1.820 (6)
Re–P(1)	2.331 (1)	P(2)–C(4)	1.829 (6)
Re–P(2)′	2.343 (1)	P(2)–C(31)	1.831 (6)
Re–C(1)	1.936 (7)	P(2)–C(41)	1.806 (6)
Re–C(2)	1.99 (1)	O(1)–C(1)	1.119 (7)
Re–C(3)	1.97 (1)	O(2)–C(2)	1.31 (1)
P(1)–C(4)	1.833 (6)	O(2)′–C(3)	1.18 (1)
P(1)–C(11)	1.834 (6)		
(b) Nonbonded Lengths			
P(1)–P(2)	3.013 (2)	Rh–C(3)	2.88 (1)
Rh–C(2)	2.58 (1)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Labeling is as in Figure 2.

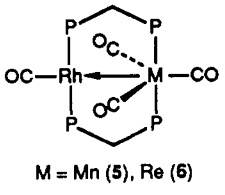
Table VIII. Selected Angles (deg) for $[RhRe(CO)_4(dppm)_2]\bullet THF$ (6)

Rh–Re–P(1)[a]	93.36 (4)	Re–P(1)–C(11)	112.2 (2)
Rh–Re–P(2)′	91.60 (4)	Re–P(1)–C(21)	119.2 (2)
Rh–Re–C(1)	172.5 (2)	C(4)–P(1)–C(11)	102.5 (3)
Rh–Re–C(2)	62.6 (3)	C(4)–P(1)–C(21)	104.1 (3)
Rh–Re–C(3)	72.0 (4)	C(11)–P(1)–C(21)	103.3 (3)
P(1)–Re–P(2)′	170.29 (5)	Rh–P(2)–C(4)	111.8 (2)
P(1)–Re–C(1)	86.7 (2)	Rh–P(2)–C(31)	117.4 (2)
P(1)–Re–C(2)	84.0 (3)	Rh–P(2)–C(41)	117.0 (2)
P(1)–Re–C(3)	100.3 (4)	C(4)–P(2)–C(31)	101.4 (3)
P(2)′–Re–C(1)	89.6 (2)	C(4)–P(2)–C(41)	105.5 (3)
P(2)′–Re–C(2)	90.9 (3)	C(31)–P(2)–C(41)	101.9 (3)
P(2)′–Re–C(3)	89.3 (4)	Re–C(1)–O(1)	177.3 (6)
C(1)–Re–C(2)	124.8 (4)	Re–C(2)–O(2)	174.6 (9)
C(1)–Re–C(3)	100.6 (4)	Re–C(3)–O(2)′	167 (1)
C(2)–Re–C(3)	134.5 (5)	P(1)–C(4)–P(2)	110.8 (3)
Re–P(1)–C(4)	113.8 (2)		

[a] Labeling is as in Figure 2.

Compound 2 is extremely air-sensitive in solution, having a half life of ca. 10 min after even brief exposure to air. Although the Ru complex is almost as air-sensitive as the Fe analogue, the Os species is slightly more robust and can be handled in air for brief periods of time.

This chemistry can also be extended to group VII, and the complexes $[RhM(CO)_4(dppm)_2]$ (M = Mn (5), Re (6)) have been prepared by an exactly analogous route with use of the $[M(CO)_5]^-$ anions. Both products have rather



M = Mn (5), Re (6)

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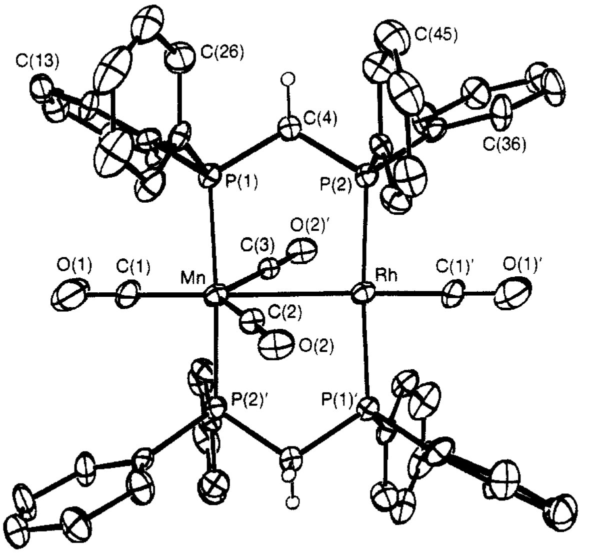

Figure 1. Perspective view of [RhMn(CO)$_4$(dppm)$_2$] (**5**) showing the numbering scheme. Thermal parameters are shown at the 20% level except for hydrogens, which are shown artificially small for the methylene groups but are not shown for the phenyl groups. Although the molecule is inversion-disordered, only one of the two positions for each of C(2) and C(3) is shown and the two disordered Rh/Mn positions are identified as assumed for the ordered structure.

similar $^{31}P\{^1H\}$ NMR and IR spectra (except for the lower field chemical shift for the Mn-bound phosphorus nuclei compared to those on Re) consistent with the formulation shown. This formulation has been confirmed by the X-ray structure determinations of both species. Perspective drawings of both compounds are shown in Figures 1 and 2 with bond lengths and angles given in Tables V–VIII. As noted earlier, the metal carbonyl moieties are disordered; however, only one set of disordered atoms, C(2) and C(3), and one of each of the Rh and Mn (**5**) or Re (**6**) positions are shown in these drawings. Although this disorder involves only the metals and two carbonyl groups, it does in principle cast some doubt on the coordination geometries about the metals. However, the interpretation that is most chemically reasonable and the only one that agrees with the ^{13}C NMR data, which clearly indicate that only one of the four carbonyls is bound to Rh (vide infra), is that in which Rh has a distorted-square-planar arrangement and the Mn and Re atoms have trigonal-bipyramidal coordinations. The $[M(CO)_3L_2]^-$ (M = Mn, Re) moieties are then regarded as functioning as pseudohalide groups. The alternate description, in which both metals are considered to be in the zero oxidation state and joined by a conventional Rh–M covalent bond, would be expected to give rise to octahedral configurations at Mn and Re. Although the geometries about Mn and Re are clearly trigonal bipyramidal (ignoring the M→Rh dative bonds), that about Re is more distorted than that about Mn, with a compressed C(1)–Re–C(3) angle of 100.6 (4)° and an expanded C(2)–Re–C(3) angle of 134.5 (5)°. In contrast the angles between the carbonyl ligands in the Mn complex are close to the idealized values, ranging from 116.8 (3) to 125.8 (3)°. This Mn complex is very reminiscent of the isoelectronic species [PdMnBr(CO)$_3$(dppm)$_2$], which has a similar structure.[35] The slight bending of the carbonyl on Re at C(3) is probably not chemically significant but more likely results from the poorly determined carbon position of this half-occupancy atom and from the single position observed for O(2), which probably represents two closely spaced but unresolved half-occupancy oxygen atoms. The disorder in these compounds negates any detailed comparison of individual metal-ligand bond lengths within each structure, although comparison of the average metal–phosphorus distances is still meaningful. Not unexpectedly, the metal–phosphorus distances in the Re complex (2.331 (1), 2.343 (1) Å) are longer than those in the Mn species (2.263 (1), 2.275 (1) Å, owing to the larger covalent radius of Re. But surprisingly the Rh–Re distance of 2.7919 (6) Å is *shorter* than the Rh–Mn distance (2.8428 (8) Å), indicating a stronger Rh–Re bond. The stronger dative bond involving Re is consistent with its more basic character compared to Mn, as exemplified by the basicities of the $M(CO)_5^-$ (M = Mn, Re) anions,[36] and is again supportive of our mixed-valence formulation. Both distances are significantly shorter than the intraligand P(1)–P(2) distances (2.994 (2) Å (**5**), 3.013 (2) Å (**6**)), indicating substantial attraction of the adjacent metal centers. As noted, the coordination about Rh in both complexes is close to square planar, as expected for Rh(I) species. Although the carbonyls C(2)O(2) and C(3)O(2)' in each compound are in positions to be considered as semibridging and are certainly well within the sum of the van der Waals radii, the contacts involving Rh and these carbonyl carbons (2.475 (8), 2.707 (8) Å (**5**); 2.58 (1), 2.88 (1) Å (**6**)) are not unusually short.[37] In addition the essentially linear M–C–O (M = Mn, Re) linkages suggest that interactions of these groups with Rh is not strong. We therefore tend not to consider these groups as semibridging but rather as being forced close to Rh by virtue of the TBP geometries at Mn and Re. This view is supported by the lack of Rh coupling for these carbonyl resonances in the ^{13}C NMR spectra (vide infra).

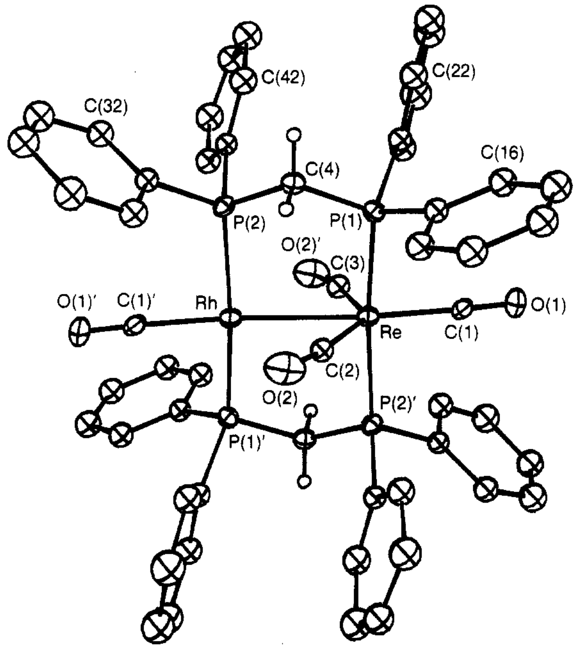

Figure 2. Perspective view of [RhRe(CO)$_4$(dppm)$_2$] (**6**). Thermal parameters and numbering are analogous to those described in Figure 1.

The reaction of compounds **5** and **6** with ^{13}CO results in enrichment of all analogous positions. This facile scrambling over both metals apparently occurs via the pentacarbonyl species [RhM(CO)$_5$(dppm)$_2$], since in the absence of excess CO scrambling in **5** and **6** is not facile

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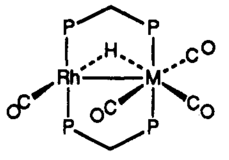
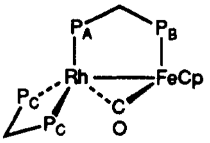
at room temperature. For example, raising the temperature of a solution of 6 from −40 to +30 °C causes the carbonyl resonances at δ 217.6 (t, $^2J_{\text{P-C}}$ = 9 Hz, 2 C), 206.3 (t, $^2J_{\text{P-C}}$ = 10 Hz, 1 C), and 181.5 (dt, $^1J_{\text{Rh-C}}$ = 71 Hz, $^2J_{\text{P-C}}$ = 14 Hz, 1 C) to broaden considerably. However, even at 30 °C coalescence has not occurred, and all three resonances are still distinct. The proposed pentacarbonyl species for Mn has not been observed; however, the Re analogue [RhRe(CO)$_5$(dppm)$_2$] has been characterized in solution[38] (ν(CO) 2010, 1988, 1964, 1918, 1892 cm^{-1}), although it loses the additional carbonyl on Rh in the absence of a CO atmosphere. This species is assumed to have a structure analogous to that of the isoelectronic species [IrOs(CO)$_5$(dppm)$_2$]$^+$, which is related to 6 by an additional carbonyl on Ir, which then has a trigonal-bipyramidal coordination.[39]

Treatment of [RhCl(dppm)$_2$] with the [HM(CO)$_5$]$^-$ (M = Cr, W) anions yields the analogous mixed-metal complexes involving these group 6 metals [RhM(μ-H)(CO)$_4$(dppm)$_2$] (M = Cr (7), W (8)). The ^{31}P{^{1}H} spectra clearly establish these species as dppm-bridged mixed-metal complexes involving Rh, and the IR spectra show the expected four carbonyl stretches (Table I). These carbonyl stretches are similar to those of the isoelectronic [RhReH(CO)$_4$(dppm)$_2$][BF$_4$] (ν(CO) 2045, 2000, 1935, 1908 cm^{-1}),[38] except that the cationic species shows the expected shifts to higher frequency. We therefore formulate the structures of 7 and 8 as being like that determined for the above cationic RhRe species.[38] In these structures the geometries about Cr and W are presumed to be pseudooctahedral in which the Rh–H bond can be considered as occupying the sixth coordination site in each complex. The ^{1}H NMR spectra for these species strongly support these structural formulations, displaying complex multiplets at δ −14.8 (7) and −10.5 (8). The selective decoupling experiments unambiguously show that these hydride ligands bridge the metals, displaying coupling to Rh and to all phosphorus nuclei. In addition, compound 8 also displays coupling to ^{183}W ($^1J_{\text{W-H}}$ = 49 Hz).



M = Cr (7), W (8)

The chemistry described above has also been extended to include carbonylate anions that also contain the cyclopentadienyl group. Therefore, the reaction of [RhCl(dppm)$_2$] with [FeCp(CO)$_2$]$^-$ yields the compound [RhFeCp(CO)(dppm)$_2$] (9). However, as shown in Figure 3, the ^{31}P{^{1}H} spectrum suggests a structural type much different than for the previously described species. Three resonances are observed in a 1:1:2 ratio, respectively; the resonance labeled P$_A$, at δ 34.8, appears as a doublet of doublets of triplets ($^1J_{\text{Rh-P}}$ = 160 Hz, $^2J_{\text{P}_A\text{-P}_B}$ = 136 Hz, $^2J_{\text{P}_A\text{-P}_C}$ = 16 Hz), the P$_B$ resonance at δ 86.9 is a doublet with coupling only to P$_A$, and the P$_C$ resonance at δ −19.2 is a doublet of doublets ($^1J_{\text{Rh-P}_C}$ = 137 Hz). The very low carbonyl stretch (1679 cm^{-1}) indicates that this group must bridge the two metals. On the basis of these data and the structure of the closely related species [PtMoCp(CO)$_2$(dppm)$_2$]$^+$,[40] we propose the structure shown, in which one dppm group remains chelating on Rh and one bridges the two metals. This structure is in agreement with the ^{31}P{^{1}H} NMR data, which show P$_A$ and both P$_C$ nuclei bound to Rh and coupled to each other and P$_B$ only coupled to P$_A$. On the basis of an assumed piano-stool geometry at Fe, we would have expected to observe two different resonances for each end of the chelating diphosphine (P$_C$); however, even at −80 °C only one resonance is observed.



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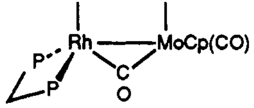

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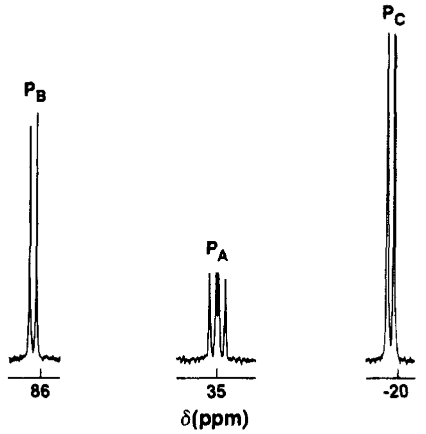

Figure 3. ^{31}P{^{1}H} NMR spectrum at 22 °C for [RhFeCp(CO)(dppm)$_2$] (9).

The Rh analogue of the above PtMo complex[40] can also be prepared by reaction of [RhCl(dppm)$_2$] with [MoCp(CO)$_3$]$^-$, yielding [RhMoCp(CO)$_2$(dppm)$_2$] (10). The carbonyl stretches for 10 (1684, 1960 cm^{-1}) are consistent with the structure shown (for the [PtMo(CO)$_2$Cp(dppm)$_2$]$^+$ cation carbonyl stretches near 1800 and 1870 cm^{-1} were reported). This RhMo species displays temperature-dependent fluxionality, as shown by the ^{31}P{^{1}H} NMR spectra, which appear as a broad (ca. 400 Hz) unresolved resonance at δ −22.1 at ambient temperature, as a doublet at δ −22.1 ($^1J_{\text{Rh-P}}$ = 108 Hz) at −40 °C, and as three broad resonances having intensity ratios of 2:1:1 at δ −28.1 (2 P), −31.2 (1 P), −34.8 (1 P), respectively at −105 °C. The low-temperature limiting spectrum that is expected, on the basis of the structure shown, was not observed, although clearly, on the basis of this structure, the two ends of the chelating phosphine must be inequivalent. Again, this proposed structure is very similar to that observed for the Pt analogue,[40] except we suggest that the carbonyl that was semibridging in the Pt complex is decidedly bridging in our Rh species; this proposal is consistent with the lower carbonyl stretch observed for the Rh species and with the greater tendency of carbonyls to bridge second-row rather than third-row metals.

Summary

The reaction of [RhCl(dppm)$_2$] with metal carbonylate anions has been shown to be a convenient and general route to a series of dppm-bridged heterobimetallic complexes containing Rh as one of the metals. In the case of anions that contain only carbonyl or carbonyl and hydride ligands, both dppm groups adopt a bridging configuration

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[40] Braunstein, P.; de Méric de Bellefon, C.; Lanfranchi, M.; Tiripicchio, A. *Organometallics* 1984, 3, 1772.

to yield complexes, all of which contain a coordinatively unsaturated square-planar Rh(I) center and coordinative saturation at the adjacent metal. It appears that these heterobimetallic complexes are best formulated as containing M→Rh dative bonds. Using the cyclopentadienyl-containing anions $[FeCp(CO)_2]^-$ and $[MoCp(CO)_3]^-$ results in only one of the dppm groups adopting a bridging configuration while the other remains chelating on Rh.

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Supplementary Material Available: Listings of additional bond lengths and angles, hydrogen atom parameters, and anisotropic thermal parameters for **5** and **6** (9 pages); listings of the observed and calculated structure factors (35 pages). Ordering information is given on any current masthead page.

Two-Dimensional ^1H NOESY of Pd(II) π-Allyl Complexes. The Concept of Reporter Ligands and the Molecular Structure of $[Pd(\eta^3\text{-}CH_2\overline{CCHCH_2CH_2CH_2})(biquinoline)]CF_3SO_3$

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A series of $[Pd(\eta^3\text{-allyl})(\text{nitrogen chelate})]CF_3SO_3$ complexes containing the coordinated β-pinene allyl or the five-membered cyclic $CH_2{\sim}\overline{C{\sim}CHCH_2CH_2CH_2}$ allyl with biquinoline and phenanthroline (among others) as nitrogen chelate have been prepared and subjected to one- and two-dimensional ^1H NMR studies. The 2-D nuclear Overhauser effect (NOE) results with phenanthroline and bipyridyl permit the determination of subtle aspects of their three-dimensional solution structure and specifically selective distortions in the hybridization of the allyl CH_2 such that the syn proton moves slightly toward the metal and the anti proton significantly away from the palladium. Interligand NOEs may also be used to assign the coordinated face of the β-pinene allyl ligand. Not all "reporter" ligands demonstrate NOE selectivity as shown by NMR as well as the molecular structure of the cyclic allyl $[Pd(\eta^3\text{-}CH_2\overline{CCHCH_2CH_2CH_2})(biquinoline)](CF_3SO_3)$, **3a**, determined via X-ray diffraction methods. Complex **3a** crystallizes in the space group $P2_1/n$ with a = 11.062 (1) Å, b = 14.595 (3) Å, c = 14.401 (1) Å, β = 94.33 (1)°, V = 2318.6 (8) Å^3, Z = 4. Relevant bond distances are as follows: Pd–N, 2.127 (2) and 2.121 (2) Å; Pd–C(11), 2.129 (3) Å; Pd–C(12), 2.131 (2) Å; Pd–C(13), 2.168 (2) Å. The reporter protons, H(8) and H(8′), of the biquinoline are both ca. 2.5 Å from their respective π-allyl counterparts. This accounts for the substantial interligand NOEs but the lack of selectivity.

Introduction

Two-dimensional NMR methods are rapidly becoming an integral part of NMR spectroscopy[1a] and are frequently associated with the simplification and assignment problems inherent in the ^1H NMR of complicated biological molecules.[1b] Of the various possible 2-D measurements, 2-D NOESY spectroscopy is somewhat more versatile in that both structural and chemical exchange information are available,[2] often simultaneously via the use of phase-sensitive ^1H 2-D NOESY.[3] Despite this useful flexibility, this NMR form has to date found only limited application in organometallic chemistry.

π-Allyl complexes of Pd(II) are well-known[4] and recognized to be catalytic precursors in a few reactions.[5] Moreover, there is a developing interest in understanding the solution structures of chiral π-allyl intermediates as

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