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S–H Bond Activation in H_2S and Thiols by [RhMn(CO)$_4$(Ph$_2$PCH$_2$PPh$_2$)$_2$]. Compounds Containing Terminal or Bridging Sulfhydryl and Thiolato Groups

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The complex [RhMn(CO)$_4$(dppm)$_2$] (dppm = Ph$_2$PCH$_2$PPh$_2$) reacts with H_2S and thiols to yield the products [RhMn(SR)(CO)$_3$(μ-H)(dppm)$_2$] (R = H, Et, Ph), containing terminal sulfhydryl or thiolato groups bound to Rh and a bridging hydride ligand. The sulfhydryl species loses H_2 over the period of several days and scavenges CO to yield [RhMn(CO)$_4$(μ-S)(dppm)$_2$]. This sulfide-bridged product can be protonated or alkylated to give the cationic species [RhMn(CO)$_4$(μ-SR)(dppm)$_2$]$^+$ (R = H, CH$_3$, CH$_2$SiMe$_3$), containing bridging sulfhydryl or thiolato groups. The bridging sulfhydryl group in [RhMn(CO)$_4$(μ-SH)(dppm)$_2$]$^+$ undergoes a Michael-type addition to alkynes to yield [RhMn(CO)$_4$(μ-SC(R)=C(H)R')(dppm)$_2$]$^+$ (R = H, R' = C(O)Me; R = R' = CO$_2$Me) in which the unsaturated thiolato group bridges the metals. With hexafluoro-2-butyne, an analogous reaction occurs to yield the related species [RhMn(SC(CF$_3$)=C(H)CF$_3$)(CO)$_4$(dppm)$_2$]$^+$, but in this case the thiolato group is terminally bound to Rh. The structure of [RhMn(CO)$_4$(μ-S)(dppm)$_2$] has been determined by X-ray crystallography. This compound crystallizes in the monoclinic space group $P2_1/n$, with $a = 12.419(4)$ Å, $b = 25.735(2)$ Å, $c = 16.464(2)$ Å, $\beta = 97.70(2)°$, $V = 5215(3)$ Å, and $Z = 4$, and has refined to $R = 0.055$ and $R_w = 0.071$ on the basis of 5865 unique observations and 598 parameters varied. This compound shows a semibridging carbonyl group which is primarily bound to Mn (Mn–C(2) = 1.959(5) Å, Rh–C(2) = 2.214(5) Å), in line with the small Rh–C coupling of 8 Hz observed in the ^{13}C NMR for this carbonyl.

Introduction

Low-valent binuclear complexes are, in principle, well suited to "double-oxidative-addition" reactions, in which two bonds, either within a single substrate or in two separate substrates, are activated by the two adjacent metals. Not only do the two metals present more available coordination sites for the oxidative-addition fragments than does a mononuclear species, but they also minimize the oxidation-state change that is required at any one metal, and present a greater electron reservoir for reduction of the substrate or substrates.

As part of an ongoing study of binuclear oxidative-addition reactions we have been investigating the activation of X-H bonds in substrates of the type H_2X or HXR (X = SiR$_2$, SiHR, S).[1–4] Examples of both types of double-oxidative additions have been observed for these substrates in which both activated bonds are within one substrate,[1–6] or are in two separate substrates.[3,7] In addition, the potential for utilizing both metal centers is uniquely demonstrated in a dirhodium system in which double-oxidative addition of a primary silane, followed by H_2 elimination, allows the metals to add a second silyl fragment.[5]

Our interest in the chemistry of H_2S lies in its potential utilization in hydrogen recovery,[8] in the chemistry of the sulfhydryl group generated therefrom, which has applications in the synthesis of sulfur-containing organic groups,[9] and in studies of model systems for hydrodesulfurization catalysts.[10] Binuclear systems have already demonstrated their potential applicability in H_2 recovery as shown by James and coworkers[11] in studies in which dipalladium complexes stoichiometrically generated H_2 from H_2S. Related studies in our group on dirhodium,[3] diiridium,[3] and mixed systems involving Rh with either Re,[2] Ru[4] or Os[4] gave similar results. In the Rh/Re system it had been possible to characterize several key intermediates in the H-S bond-activation processes;[2] however, some presumed intermediates were not observed. It was anticipated that substitution of Re by the lighter congener, Mn, may have a significant effect on the chemistry, yielding species, the Re analogues of which were not observed. In this

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Table 1. Spectroscopic Data for the Compounds[a]

compound	IR, cm^{-1}	NMR		
		$\delta(^{31}P\{^1H\})$	$\delta(^1H)$	$\delta(^{13}C)$
[RhMn(SH)(CO)$_2$(μ-H)(dppm)$_2$] (**2**)	1940 (s),[b] 1871 (s), 1840 (sh), 1751 (m) 1938 (s),[c] 1868 (s), 1757 (m)	69.3 (m),[d] 30.9 (dm, $^1J_{\mathrm{RhP}}$ = 124 Hz)	3.39 (m, 2H),[e] 3.03 (m, 2H), –0.31 (dt, $^2J_{\mathrm{RhH}}$ = 2 Hz, $^3J_{\mathrm{P(Rh)H}}$ = 16 Hz, 1H), –14.03 (dtt, $^1J_{\mathrm{RhH}}$ = 26 Hz, $^2J_{\mathrm{P(Rh)H}}$ = $^2J_{\mathrm{P(Mn)H}}$ = 13 Hz, 1H)	260.9 (dt, $^1J_{\mathrm{RhC}}$ = 17 Hz, $^2J_{\mathrm{P(Mn)C}}$ = 17 Hz, 1C),[d] 227.2 (t, $^2J_{\mathrm{P(Mn)C}}$ = 21 Hz, 1C), 226.7 (t, $^2J_{\mathrm{P(Mn)H}}$ = 23 Hz, 1C)
[RhMn(SEt)(CO)$_2$(μ-CO)(μ-H)(dppm)$_2$] (**3**)	1935 (s),[c] 1865 (s), 1760 (m)	69.8 (m),[e] 27.6 (dm, $^1J_{\mathrm{RhP}}$ = 134 Hz)	3.44 (m, 2H),[e] 2.94 (m, 2H), –14.13 (dtt, $^1J_{\mathrm{RhH}}$ = 22 Hz, $^2J_{\mathrm{P(Rh)H}}$ = 11 Hz, $^2J_{\mathrm{P(Mn)H}}$ = 12 Hz, 1H)	260.4 (bd, $^1J_{\mathrm{RhC}}$ = 14 Hz, 1C), 227.7 (b, 2C)[e]
[RhMn(SPh)(CO)$_2$(μ-CO)(μ-H)(dppm)$_2$] (**4**)	1932 (s),[b] 1861 (s), 1764 (s) 1934 (vs),[c] 1861 (s), 1759 (m)	69.3 (m)[f] 25.8 (dm, $^1J_{\mathrm{RhP}}$ = 144 Hz)	3.32 (m, 2H)[f] 3.02 (m, 2H), –14.88 (dtt, $^1J_{\mathrm{RhH}}$ = 23 Hz, $^2J_{\mathrm{P(Rh)H}}$ = 12 Hz, $^2J_{\mathrm{P(Mn)H}}$ = 12 Hz, 1H)	259.3 (dt, $^1J_{\mathrm{RhC}}$ = 17 Hz, $^1J_{\mathrm{P(Mn)C}}$ = 23 Hz, 1C)[f] 227.4 (t, $^2J_{\mathrm{P(Mn)C}}$ = 20 Hz, 1C), 226.7 (t, $^2J_{\mathrm{P(Mn)C}}$ = 25 Hz, 1C)
[RhMn(CO)$_5$(dppm)$_2$] (**5**)		73.5 (m),[d] 29.5 (dm, $^1J_{\mathrm{RhP}}$ = 99 Hz)	4.16 (b, 4H)[d]	241.7 (b, 2C),[d] 228.4 (b, 1C), 200.3 (vb, 2C)
[RhMn(SPh)(CO)$_4$(μ-H)(dppm)$_2$] (**6**)		61.0 (m)[f] 30.3 (dm, $^1J_{\mathrm{RhP}}$ = 107 Hz)	4.71 (m, 2H)[f] 3.81 (m, 2H), –12.20 (td, $^2J_{\mathrm{P(Mn)H}}$ = 20 Hz, $^1J_{\mathrm{RhH}}$ = 5 Hz, 1H)	229.0 (b, 1C),[d] 222.3 (b, 1C), 219.8 (t, $^2J_{\mathrm{P(Mn)C}}$ = 21 Hz, 1C), 200.9 (dt, $^1J_{\mathrm{RhC}}$ = 78 Hz, $^2J_{\mathrm{P(Rh)C}}$ = 15 Hz, 1C)
[RhMn(CO)$_4$(μ-S)(dppm)$_2$] (**7**)	1984 (m),[b] 1962 (s), 1866 (s), 1796 (m) 1980 (sh),[c] 1955 (vs), 1876 (s), 1799 (m)	57.4 (m)[f] 25.6 (dm, $^1J_{\mathrm{RhP}}$ = 136 Hz)	4.60 (m, 2H)[f] 2.48 (m, 2H)	239.1 (dt, $^1J_{\mathrm{RhC}}$ = 8 Hz, $^2J_{\mathrm{P(Mn)C}}$ = 14 Hz, 1C),[g] 225.3 (t, $^2J_{\mathrm{P(Mn)C}}$ = 20 Hz, 1C), 222.2 (t, $^2J_{\mathrm{P(Mn)C}}$ = 18 Hz, 1C), 192.8 (dt, $^1J_{\mathrm{RhC}}$ = 69 Hz, $^2J_{\mathrm{P(Rh)C}}$ = 19 Hz, 1C)
[RhMn(CO)$_4$(μ-SH)(dppm)$_2$][BF$_4$] (**8a**)	2004 (w),[b] 1987 (vs), 1934 (s), 1858 (m) 2021 (sh),[c] 1990 (vs), 1932 (s), 1845 (w)	55.2 (m, 1P),[d] 51.2 (m, 1P) ($^2J_{\mathrm{P(Mn)P}}$ = 38 Hz), 28.0 (dm, 1P, $^1J_{\mathrm{RhP}}$ = 115 Hz), 18.8 (dm, 1P, $^1J_{\mathrm{RhP}}$ = 112 Hz) ($^2J_{\mathrm{P(Rh)P}}$= 302 Hz)	3.82 (m, 2H),[d] 3.69 (m, 1H), 3.23 (m, 1H), –2.67 (tt, 1H, $^3J_{\mathrm{P(Mn)H}}$ = 11 Hz, $^3J_{\mathrm{P(Rh)H}}$ = 13 Hz) 3.92 (b, 2H),[e] 3.52 (b, 2H), –2.50 (tt, 1H)	224.4 (b, 1C),[c] 219.3 (b, 1C), 216.2 (b, 1C), 190.4 (dt, 1C, $^1J_{\mathrm{RhC}}$ = 74 Hz, $^2J_{\mathrm{P(Rh)C}}$ = 13 Hz)
[RhMn(CO)$_4$(μ-SH)(dppm)$_2$][SO$_3$CF$_3$] (**8b**)	2008 (w),[b] 1986 (vs), 1936 (s), 1864 (m) 2020 (sh),[c] 1992 (vs), 1933 (s), 1845 (w)	55.2 (m, 1P),[d] 51.2 (m, 1P), 28.1 (dm, 1P, $^1J_{\mathrm{RhP}}$ = 115 Hz), 18.7 (dm, 1P, $^1J_{\mathrm{RhP}}$ = 112 Hz)	3.81 (m, 2H),[d] 3.68 (m, 1H), 3.23 (m, 1H), –2.66 (tt, 1H) ($^3J_{\mathrm{P(Mn)H}}$ = 11 Hz, $^3J_{\mathrm{P(Mn)H}}$ = 13 Hz)	
[RhMn(CO)$_4$(μ-SMe)(dppm)$_2$][SO$_3$CF$_3$] (**9**)	2003 (w),[b] 1974 (vs), 1917 (s), 1826 (m) 2020 (sh),[c] 1991 (vs), 1914 (s), 1837 (w)	56.8 (m),[e] 26.8 (dm, $^1J_{\mathrm{RhP}}$ = 116 Hz) 61.6 (m, 1P),[d] 53.4 (m, 1P) ($^2J_{\mathrm{P(Mn)P}}$ = 43 Hz), 33.1 (dm, 1P, $^1J_{\mathrm{RhP}}$ = 119 Hz), 23.8 (dm, 1P, $^1J_{\mathrm{RhP}}$ = 113 Hz) ($^2J_{\mathrm{P(Rh)P}}$ = 296 Hz)	3.68 (m, 2H),[e] 3.25 (m, 2H), 1.68 (b, 3H) 3.87 (m, 1H),[d] 3.55 (m, 1H), 3.12 (m, 1H), 2.78 (m, 1H), 1.68 (s, 3H)	226.9 (b),[e] 224.0 (b), 216.7 (b), 189.8 (dt, $^1J_{\mathrm{RhC}}$ = 71 Hz, $^2J_{\mathrm{P(Rh)C}}$ = 16 Hz) 227.6 (t, 1C, $^2J_{\mathrm{P(Mn)C}}$ = 18 Hz),[d] 223.2 (t, 1C, $^2J_{\mathrm{P(Mn)C}}$ = 18 Hz), 216.5 (b, 1C), 189.2 (dt, 1C) $^1J_{\mathrm{RhC}}$ = 71 Hz, $^2J_{\mathrm{(Rh)C}}$ = 16 Hz)
[RhMn(CO)$_4$(μ-SCH$_2$SiMe$_3$)(dppm)$_2$][SO$_3$CF$_3$] (**10**)	2021 (m),[b] 1997 (vs), 1917 (s), 1830 (m) 2025 (sh),[c] 1995 (vs), 1920 (s), 1843 (w)	63.0 (m, 1P),[d] 52.2 (m, 1P) ($^2J_{\mathrm{P(Mn)P}}$ = 42 Hz), 36.8 (dm, 1P, $^1J_{\mathrm{RhP}}$ = 119 Hz), 20.2 (dm, 1P, $^1J_{\mathrm{RhP}}$ = 113 Hz) ($^2J_{\mathrm{P(Rh)P}}$ = 298 Hz)	4.11 (m, 1H),[d] 3.47 (m, 1H), 3.24 (m, 1H), 2.77 (m, 1H), 0.98 (d, $^2J_{\mathrm{HCH}}$ = 12 Hz, 1H), 0.67 (d, 1H), –0.43 (s, 9H)	229.3 (b, 1C),[d] 223.7 (b, 1C), 217.1 (b, 1C), 189.0 (dt, 1C, $^1J_{\mathrm{RhC}}$ = 71 Hz, $^2J_{\mathrm{P(Rh)C}}$ = 16 Hz)
[RhMn(CO)$_4$(μ-SC(R)=CHR)(dppm)$_2$][SO$_3$CF$_3$] (**11**) (R = COOMe)	2010 (sh),[b] 2000 (vs), 1917 (s),1837 (w) 2030 (sh),[c] 2004 (vs), 1930 (s), 1852 (w)	49.0 (m),[e] 21.4 (dm, $^1J_{\mathrm{RhP}}$ = 115 Hz) 48.9(m, 1P),[d] 47.2 (m, 1P), 23.5 (m, 1P), 38.5 (m, 1P)	5.78 (s, 1H),[e] 3.94 (m, 2H), 3.68 (m, 2H), 3.49 (s, 3H), 3.28 (s, 3H) 4.04 (b, 1H),[d] 3.92 (b, 1H), 3.73 (b, 1H), 3.52 (b, 1H), 3.14 (b, 3H), 3.10 (b, 3H)	222.9 (b, 1C),[e] 220.1 (b, 1C), 214.5 (b, 1C), 190.3 (dt, $^1J_{\mathrm{RhC}}$ = 74 Hz, $^2J_{\mathrm{P(Rh)C}}$ = 15 Hz, 1C)
[RhMn(CO)$_4$(μ-SC(H)=CHCOMe)(dppm)$_2$][SO$_3$CF$_3$] (**12**)	1991 (vs),[b] 1914 (s), 1810 (w) 2020 (sh),[c] 2004 (vs), 1924 (s), 1804 (w)	54.5 (m),[e] 25.0 (dm, $^1J_{\mathrm{RhP}}$ = 116 Hz) 57.4 (m, 1P),[d] 53.3 (m, 1P), 28.8 (m, 1P), 24.0 (m, 1P)	6.94 (d, $^3J_{\mathrm{HH}}$ = 15.2 Hz, 1H),[e] 5.99 (d, $^3J_{\mathrm{HH}}$ = 15.2 Hz, 1H), 3.71 (m, 2H), 3.37 (m, 2H), 1.93 (s, 3H)	224.3 (b, 1C),[e] 223.6 (b, 1C), 215.7 (b, 1C), 189.7 (dt, $^1J_{\mathrm{RhC}}$ = 74 Hz, $^2J_{\mathrm{P(Rh)C}}$ = 16 Hz, 1C)
[RhMn(SC(R)=CHR)(CO)$_4$(dppm)$_2$][SO$_3$CF$_3$] (**13**) (R = CF$_3$)	2032 (s),[b] 1990 (vs), 1924 (m), 1824 (s) 2037 (s),[c] 2000 (s), 1929 (m), 1821 (s)	56.8 (m),[e] 19.3 (dm, $^1J_{\mathrm{RhP}}$ = 107 Hz) 55.4 (m),[d] 18.4 (dm)	5.14 (1H, q, $^4J_{\mathrm{HF}}$ = 9 Hz),[e] 3.17 (4H, m) 4.96 (1H, b),[d] 3.07 (4H, b)	238.1 (b, 2C),[e] 216.6 (b, 2C) 237.8 (m, 1C),[d] 236.5 (m, 1C), 218.1 (m, 1C), 212.8 (m, 1C)
[RhMn(CO)$_4$(μ-H)(dppm)$_2$][BF$_4$] (**14**)	2020 (w),[b] 1991 (s), 1922 (s), 1880 (sh) 2030 (w),[c] 2000 (s), 1941 (s), 1900 (sh)	61.7 (m),[e] 25.6 (dm, $^1J_{\mathrm{RhP}}$ = 110 Hz) 61.7 (m),[d] 25.3 (dm, $^1J_{\mathrm{RhP}}$ = 111 Hz)	3.63 (m, 4H),[e] –15.32 (dtt, $^1J_{\mathrm{RhH}}$ = 18 Hz, $^2J_{\mathrm{P(Rh)H}}$ = 15 Hz, $^2J_{\mathrm{P(Mn)H}}$ = 15 Hz) 3.67 (b, 2H),[i] 3.48 (b, 2H), –15.36 (b)	224.6 (b, 1C),[h] 219.7 (b, 1C), 219.0 (b, 1C), 179.1 (bd, 1C, $^1J_{\mathrm{RhC}}$ = 74 Hz)

Table 1 (Continued)

compound	IR, cm^{-1}	NMR		
		δ($^{31}P\{^1H\}$)	δ(^1H)	δ(^{13}C)
$[RhMn(SEt)(CO)_4(dppm)_2]$-$[BF_4]$ (**15**)		49.6 (m),[e] 22.4 (dm, $^1J_{RhP}$ = 110 Hz) 49.4 (m),[d] 22.1 (dm, $^1J_{RhP}$ = 111 Hz)	4.03 (b, 2H),[e] 3.47 (b, 2H) 3.94 (b, 2H),[d] 3.37 (b, 2H),[j]	222.6 (b, 1C),[e] 221.3 (b, 1C), 214.2 (b, 1C), 188.2 (dt, 1C, $^1J_{RhC}$ = 83 Hz, $^2J_{P(Rh)C}$ = 13 Hz)
$[RhMn(CO)_4(\mu\text{-}SEt)(dppm)_2]$-$[BF_4]$ (**16**)		56.7 (m),[e] 26.5 (dm, $^1J_{RhP}$ = 116 Hz) 60.2 (m, 1P),[d] 54.1 (m, 1P), 30.0 (dm, 1P, $^1J_{RhP}$ = 115 Hz), 25.9 (dm, 1P, $^1J_{RhP}$ = 114 Hz)	3.62 (b, 2H),[e] 3.25 (b, 2H), 2.02 (q, 2H, $^3J_{HH}$ = 7 Hz), 0.92 (t, 3H)	226.4 (t, 1C, $^2J_{P(Mn)C}$ = 16 Hz),[e] 223.8 (t, 1C, $^2J_{P(Mn)C}$ = 19 Hz), 216.7 (t, 1C, $^2J_{P(Mn)C}$ = 12 Hz), 190.1 (dt, 1C, $^1J_{RhC}$ = 72 Hz, $^2J_{P(Rh)C}$ = 16 Hz)

[a] $^{31}P\{^1H\}$ chemical shifts are referenced vs external 85% H_3PO_4 while ^1H and $^{13}C\{^1H\}$ shifts are referenced vs external TMS. Chemical shifts for the phenyl hydrogens are not given in ^1H NMR data. IR abbreviations: s = strong, sh = shoulder, m = medium, vs = very strong, w = weak. NMR abbreviations: m = multiplet, dm = doublet of multiplets, t = triplet, dt = doublet of triplets, dtt = doublet of triplet of triplets, bd = broad doublet, b = broad, q = quartet. [b] Nujol mull. [c] CH_2Cl_2 solution. [d] −80 °C. [e] 22 °C. [f] −40 °C. [g] −60 °C. [h] −90 °C. [i] −100 °C. [j] The ethyl protons in the intermediate species **15** are masked by those of EtSH, which is present in vast excess.

paper we present our results on the oxidative addition of H_2S and thiols to $[RhMn(CO)_4(dppm)_2]$ (dppm = $Ph_2PCH_2PPh_2$).

Experimental Section

General Procedures. Purified argon and carbon monoxide were obtained from Linde, and hydrogen sulfide was purchased from Matheson. The 99% carbon-13-enriched carbon monoxide was purchased from Isotec Inc. All gases were used as received. Diethyl ether and hexane were dried over sodium benzophenone ketyl whereas CH_2Cl_2 was dried by P_2O_5; all solvents were distilled under argon before use. The perdeuterated methylene chloride was dried over molecular sieves and deoxygenated by repeated freeze–pump–thaw cycles. The compounds ethanethiol, benzenethiol, tetrafluoroboric acid–diethyl ether, triflic acid, methyl triflate, (trimethylsilyl)methyl triflate, dimethyl acetylenedicarboxylate, and 3-butyn-2-one were used as received from Aldrich; elemental sulfur was purchased from Sargent-Welch and hexafluoro-2-butyne from PCR Inc. Reactions were routinely conducted under Schlenk conditions. Hydrated rhodium trichloride was purchased from Johnson Matthey and $Mn_2(CO)_{10}$ from Strem Chemicals Inc. Compound **1**, $[RhMn(CO)_4(dppm)_2]$ (dppm = $Ph_2PCH_2PPh_2$), was prepared as previously reported.[12]

All routine NMR experiments were conducted on a Bruker AM-400 spectrometer, whereas the $^{13}C\{^{31}P\}$ NMR experiments were conducted on a Bruker AM-200 spectrometer. For all NMR experiments CD_2Cl_2 was used as solvent. The PANIC program, supplied by Bruker, was used to simulate the $^{31}P\{^1H\}$ NMR spectra of selected compounds. IR spectra were recorded either on a Nicolet 7199 Fourier transform interferometer or on a Perkin-Elmer 883 spectrophotometer as solids (Nujol mull or CH_2Cl_2 cast) or CH_2Cl_2 solutions. Elemental analyses were performed by the microanalytical service within our department. The spectral data for all compounds are given in Table 1. All compounds were moderately air sensitive in solution and so were routinely handled using Schlenk techniques. Compounds isolated as solids were not air sensitive over short periods of time and could be handled in air; however they were routinely stored under nitrogen.

Preparation of Compounds. (a) $[RhMn(SH)(CO)_3(\mu\text{-}H)(dppm)_2]$ (2). Compound **1** (50 mg, 48.1 μmol) was dissolved in 10 mL of CH_2Cl_2; then 10 mL of H_2S (*ca.* 400 μmol) was added via a gastight syringe. Over a 2-h period, the stirred solution gradually changed from light yellow to orange. After this time, the solvent was removed under vacuum and the residue was recrystallized from CH_2Cl_2/Et_2O to generate a red powder (yield 64%). Anal. Calcd for $C_{53}H_{46}O_3P_4MnRhS$: C, 60.46; H, 4.32. Found: C, 60.20; H, 4.37.

(b) $[RhMn(SEt)(CO)_3(\mu\text{-}H)(dppm)_2]$ (3). Compound **1** (5 mg, 4.8 μmol) was dissolved in 0.5 mL of CD_2Cl_2, and the solution was transferred to a 5-mm NMR tube to which 50 μL of EtSH (675 μmol) was added. The color changed to orange from yellow within 5 min. After 1 h, the NMR spectra were recorded and compound **3** was observed in *ca.* 5–10% yield by $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and ^1H NMR and IR spectra. Compound **3** was only observed spectrally and was not isolated; only decomposition products were obtained in attempts to isolate **3**.

(c) $[RhMn(SPh)(CO)_3(\mu\text{-}H)(dppm)_2]$ (4). Compound **1** (50 mg, 48.1 μmol) was dissolved in 10 mL of CH_2Cl_2 and 100 μL of PhSH (973 μmol) was added. After *ca.* 4 h, the solution had turned red and the reaction was judged to be complete, as shown by IR spectra. Removal of the solvent under vacuum and recrystallization from CH_2Cl_2/hexane yielded an orange-brown solid (yield 85%). Anal. Calcd for $C_{59}H_{50}O_3P_4MnRhS$: C, 62.73; H, 4.39. Found: C, 62.73; H, 4.68.

(d) $[RhMn(CO)_5(dppm)_2]$ (5). Compound **1** (5 mg, 4.8 μmol) was dissolved in 0.5 mL of CD_2Cl_2; the mixture was transferred to a 5-mm NMR tube, freeze-thaw-degassed, and then exposed to ^{13}CO at −78 °C, resulting in a red solution. Compound **10** was identified in solution at low temperature by ^1H, ^{13}C, and ^{31}P NMR experiments.

(e) $[RhMn(SPh)(CO)_4(H)(dppm)_2]$ (6). Compound **1** (5 mg, 4.8 μmol), dissolved in 0.5 mL of CD_2Cl_2, was transferred to a 5-mm NMR tube; then 50 μL of PhSH (487 μmol) was added. The color changed to orange within 10 min. After the sample had stood at room temperature for 2 h, the NMR experiments ($^{31}P\{^1H\}$, $^{13}C\{^1H\}$, ^1H) were conducted at temperatures between −40 and −80 °C, showing the presence of compound **6**. This species disappeared upon raising the temperature.

(f) $[RhMn(CO)_4(\mu\text{-}S)(dppm)_2]$ (7). Method i. Compound **1** (50 mg, 48.1 μmol) was dissolved in 10 mL of CH_2Cl_2; then 1.54 mg of sulfur (48.1 μmol), suspended in 1.0 mL of CH_2Cl_2, was added, causing the solution to turn deep orange instantly. The solvent was removed under vacuum and recrystallized from CH_2Cl_2/Et_2O, yielding a yellow powder (yield 75%).

Method ii. Compound **1** (50 mg, 48.1 μmol) was dissolved in 10 mL of CH_2Cl_2; then 10 mL of H_2S (g) (about 400 μmol, excess) was added via a gastight syringe. After 48 h, the reaction was complete, as shown by IR spectra, leaving a deep orange solution. Removal of the solvent under vacuum and recrystallization from CH_2Cl_2/Et_2O yielded a yellow solid (yield 60%). Anal. Calcd for $C_{54}H_{44}O_4P_4MnRhS{\cdot}CH_2Cl_2$: C, 57.16; H, 4.01; S, 2.77. Found: C, 57.07; H, 4.14; S, 3.30.

(g) $[RhMn(CO)_4(\mu\text{-}SH)(dppm)_2][BF_4]$ (8a). Compound **7** (50 mg, 46.7 μmol) was dissolved in 10 mL of CH_2Cl_2; then 6.7 μL of $HBF_4{\cdot}Et_2O$ (47 μmol) was added, causing an immediate color change to yellow from orange. Removal of the solvent and recrystallization of the residue from CH_2Cl_2/Et_2O gave a yellow powder (yield 83%). Anal. Calcd for $C_{54}H_{45}O_4P_4MnRhSBF_4{\cdot}0.84CH_2Cl_2$: C, 53.55; H, 3.83; Cl, 4.85. Found: C, 53.29; H, 3.86; Cl, 4.85. The presence of CH_2Cl_2 in the solid was confirmed by ^1H NMR spectra with $CDCl_3$ as solvent.

(h) $[RhMn(CO)_4(\mu\text{-}SH)(dppm)_2][SO_3CF_3]$ (8b). Compound **7** (50 mg, 46.7 μmol) was dissolved in 10 mL of CH_2Cl_2; then 4.1 μL of CF_3SO_3H (47 μmol) was added *via* syringe. The color changed immediately from orange to yellow. Removal of the solvent and recrystallization of the residue from CH_2Cl_2/Et_2O gave a yellow powder (yield 85%). Spectroscopically compound **8b** was essentially identical to **8a** apart from differences due to the anions.

(i) $[RhMn(CO)_4(\mu\text{-}SCH_3)(dppm)_2][SO_3CF_3]$ (9). Compound **7** (50 mg, 46.7 μmol) was dissolved in 10 mL of CH_2Cl_2; then 5.4 μL of $CF_3SO_3CH_3$ (47 μmol) was added, causing an immediate change in color to light orange. After 0.5 h, removal of the solvent under vacuum and recrystallization from CH_2Cl_2/Et_2O gave a yellow-orange powder (yield 84%). Anal. Calcd for $C_{56}H_{47}O_7P_4MnRhF_3S_2$: C, 54.47; H, 3.84. Found: C, 54.39; H, 4.05.

(j) $[RhMn(CO)_4(\mu\text{-}SCH_2SiMe_3)(dppm)_2][SO_3CF_3]$ (10). Compound **7** (50 mg, 46.7 μmol) was dissolved in 10 μL of CH_2Cl_2; then 9.4 μL of $CF_3SO_3CH_2SiMe_3$ (47 μmol) was added. The color changed to yellow from orange immediately, but the sample was stirred for an additional 0.5 h. Removal of the solvent under vacuum and recrystallization from

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

CH_2Cl_2/Et_2O gave a yellow powder (yield 80%). Anal. Calcd for $C_{59}H_{55}O_7P_4MnRhF_3SiS_2$: C, 54.22; H, 4.21. Found: C, 54.43; H, 4.55.

(k) [RhMn(CO)$_4$(μ-SC(CO$_2$Me)=C(H)CO$_2$Me)(dppm)$_2$][SO$_3$CF$_3$] (11). Compound **8b** (50 mg, 41.0 μmol) was dissolved in 10 mL of CH_2Cl_2; then 100 μL of $MeO_2CC{\equiv}CCO_2Me$ (810 μmol) was added. The solution was stirred for 24 h, resulting in a change in color from yellow to deep orange. Removal of the solvent and recrystallization of the residue from CH_2Cl_2/Et_2O gave a yellow solid (yield 84%). Anal. Calcd for $RhMnC_{61}H_{51}S_2P_4O_{11}F_3$: C, 53.76; H, 3.77. Found: C, 53.33; H, 4.00.

(l) [RhMn(CO)$_4$(μ-SC(H)=C(H)COMe)(dppm)$_2$][SO$_3$CF$_3$] (12). Compound **8b** (50 mg, 41.0 μmol) was dissolved in 10 mL of CH_2Cl_2; then 10 μL of 3-butyn-2-one (128 μmol) was added. The solution was stirred for 24 h, during which time it turned orange. The solvent was removed *in vacuo*, and the residue was recrystallized from CH_2Cl_2/Et_2O, yielding a yellow powder in 78% yield. Anal. Calcd for $RhMnS_2P_4O_8F_3C_{59}H_{49}$: C, 54.97; H, 3.80. Found: C, 54.06; H, 4.02.

(m) [RhMn(CO)$_4$(SC(CF$_3$)=C(H)CF$_3$)(dppm)$_2$][SO$_3$CF$_3$] (13). Compound **8b** (50 mg, 41.0 μmol) was dissolved in 10 mL of CH_2Cl_2. The nitrogen atmosphere above the solution was replaced by hexafluoro-2-butyne; then the sample was stirred for 5 days, resulting in a color change to deep orange. Removal of the solvent and recrystallization of the residue from CH_2Cl_2/hexane gave a red solid (yield 70%). Anal. Calcd for $RhMnC_{59}H_{45}P_4S_2O_7F_9$: C, 51.23; H, 3.26. Found: C, 50.97; H, 3.23.

(n) [RhMn(CO)$_4$(μ-H)(dppm)$_2$][BF$_4$] (14). Compound **1** (50 mg, 48.1 μmol) was dissolved in 10 mL of CH_2Cl_2; then 8.2 μL of $HBF_4{\cdot}Et_2O$ (48 μmol) was added. Instantly the color changed to deep red. Monitoring the solution by IR spectroscopy indicated that the reaction was complete. Removal of the solvent and recrystallization from CH_2Cl_2/Et_2O gave a red solid (yield 90%). Anal. Calcd for $C_{54}H_{45}O_4P_4MnRhBF_4$: C, 57.58; H, 4.03. Found: C, 57.12; H, 4.43.

(o) [RhMn(SEt)(CO)$_4$(dppm)$_2$][BF$_4$] (15). Compound **1** (5 mg, 4.8 μmol) was dissolved in 0.5 mL of CD_2Cl_2, and the solution was transferred to a 5-mm NMR tube to which 50 μL of EtSH (675 μmol) was added. After 1 day, 10 μL of $HBF_4{\cdot}Et_2O$ (68 μmol) was added to the solution. After 4 days, the $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and ^1H NMR spectra showed the formation of compound **15**. Compounds **15** and **16** were identified on the basis of their spectroscopic properties and were not isolated.

(p) [RhMn(CO)$_4$(μ-SEt)(dppm)$_2$][BF$_4$] (16). Compound **14** (5 mg, 4.4 μmol), dissolved in 0.5 mL of CD_2Cl_2, was transferred to a 5-mm NMR tube; then 50 μL of EtSH (675 μmol) was added. After 1 week, the $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and ^1H NMR spectra showed the formation of compound **16**.

Reaction of Compound 2 with CO. A 50-mg sample of compound **2** was dissolved in 5 mL of CH_2Cl_2, and the solution was purged with a slow stream of CO for 24 h. Recrystallization from CH_2Cl_2/Et_2O gave a mixture of compounds **1** (*ca.* 70%) and **7** (*ca.* 30%).

Reaction of Compound 3 with CO. To a CD_2Cl_2 solution of compound **1** (10 mg, 9.6 μmol in 0.5 mL) in an NMR tube was added 50 μL of EtSH (675 μmol). After 1 h, the ^{31}P NMR spectrum showed the formation of compound **3** (*ca.* 10%). The solution was put under CO at −78 °C for 10 min and then warmed to room temperature. This resulted in a color change from orange to yellow, and the subsequent ^{31}P NMR spectrum showed the presence of only compound **1**.

Reaction of Compound 4 with CO. A CH_2Cl_2 solution of compound **4** (50 mg in 5 mL) was placed under an atmosphere of CO and stirred for 0.5 h. Complete conversion to compound **1** was observed, as shown by the IR spectrum.

Deprotonation of Compound 8. To a CD_2Cl_2 solution of compound **8a** (10 mg, 9 μmol in 0.5 mL) in a 5-mm NMR tube was added 2 μL of piperidine (20 μmol). After 4 h, the ^{31}P NMR spectrum showed the presence of only compound **7**.

X-ray Data Collection. Deep red-orange crystals of [RhMn(CO)$_4$(μ-S)(dppm)$_2$]·CH_2Cl_2 (**7**) were grown by diffusion of hexanes into a concentrated CH_2Cl_2 solution of the compound. Several of these were mounted and flame-sealed in glass capillaries under an atmosphere of N_2 and solvent vapor to minimize decomposition and/or solvent loss. Data were collected on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation. Unit-cell parameters were obtained from a least-squares refinement of the setting angles of 25 reflections in the range $20.0° \leq 2\theta \leq 24.0°$. The monoclinic diffraction symmetry and the systematic absences ($h0l$, $h + l \neq 2n$; $0k0$, $k \neq 2n$) defined the space group as $P2_1/n$ (a nonstandard setting of $P2_1/c$ [No. 14]).

Table 2. Crystallographic Data for [RhMn(CO)$_4$(μ-S)(dppm)$_2$]·CH_2Cl_2 (**7**)

formula	$C_{55}H_{46}Cl_2MnO_4P_4RhS$	fw	1155.69
a	12.419(4) Å	space group	$P2_1/n$ (a nonstandard setting of $P2_1/c$ [No. 14])
b	25.735(2) Å		
c	16.464(2) Å		
β	97.70(2)°	T	22 °C
V	5215(3) Å^3	λ	0.710 69 Å (Mo Kα)
Z	4	μ	8.502 cm^{-1}
ρ_{calcd}	1.472 g cm^{-3}	$R(F_o)^a$	0.055
		$R_w(F_o)^b$	0.071

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/wF_o^2]^{1/2}$, where $w = 4F_o^2/\sigma^2(F_o^2)$.

Intensity data were collected at 22 °C by using the $\theta/2\theta$ scan technique, covering reflections having indices of the form $+h,+k,\pm l$ to a maximum $2\theta = 50.0°$. Of the data collected, 9352 reflections were unique after merging. Backgrounds were scanned for 25% of the scan width on either side of the scan region. Three reflections were chosen as intensity standards, being remeasured after every 120 min of X-ray exposure time. The intensities of these standards remained approximately constant over the duration of data collection so no decomposition correction was deemed necessary. The data were processed in the usual way, with a value of 0.04 for p employed to downweight intense reflections;[13] 5865 reflections were considered observed ($F_o^2 \geq 3\sigma(F_o^2)$) and were used in subsequent calculations.[14] Absorption corrections were applied to the data according to the method of Walker and Stuart.[15] See Table 2 for crystal data and more information on the X-ray data collection.

Structure Solution and Refinement. The structure of [RhMn(CO)$_4$(μ-S)(dppm)$_2$]·CH_2Cl_2 was solved in the space group $P2_1/n$ using standard Patterson and Fourier techniques. Full-matrix least-squares refinements proceeded so as to minimize the function $\sum w(|F_o| - |F_c|)^2$, where the weighting factor $w = 4F_o^2/\sigma^2(F_o)^2$. Atomic scattering factors[16,17] and anomalous dispersion terms[18] 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. All hydrogen atoms were then included in the calculations with fixed, isotropic Gaussian parameters 20% greater than those of the attached atoms and were constrained to "ride" on the attached atoms. There was no evidence for secondary extinction; therefore no correction was applied.

The final model for [RhMn(CO)$_4$(μ-S)(dppm)$_2$]·CH_2Cl_2, with 598 parameters varied, converged to values of $R = 0.055$ and $R_w = 0.071$. In the final difference Fourier map, the 10 highest residuals (1.5–0.6 e/Å^3) were found in the vicinity of the CH_2Cl_2 solvent molecule and the Rh atom (a typical carbon atom in an earlier synthesis had an intensity of 5.0 e/Å^3). The atomic coordinates and thermal parameters for selected atoms of [RhMn(CO)$_4$(μ-S)(dppm)$_2$]·CH_2Cl_2 are given in Table 3, and selected bond lengths and angles are given in Tables 4 and 5, respectively.

Results and Discussion

At ambient temperature [RhMn(CO)$_4$(dppm)$_2$] (**1**) (dppm = $Ph_2PCH_2PPh_2$) reacts with H_2S, EtSH and PhSH generating compounds **2**–**4**, respectively, as shown in Scheme 1. For these species the $^{31}P\{^1H\}$ NMR spectra display resonances typical of an AA′BB′X spin system, in which the Mn-bound phosphorus nuclei resonate near δ 70 and the Rh-bound phosphorus nuclei appear at *ca.* δ 30. The ^1H NMR spectra show two signals for the dppm methylene protons, consistent with the structure shown in which the environment on one side of the $RhMnP_4$ plane differs from that on the other side. The hydride resonances for the three compounds are found at typically high field (δ −14.03 to −14.88) and display coupling to Rh between 22 and 26 Hz and almost equal coupling ($^2J_{PH} \simeq 12$ Hz) to both sets of phosphorus nuclei

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(14) Programs used were those of the Enraf-Nonius Structure Determination Package by B. A. Frenz, in addition to local programs by R. G. Ball.

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Table 3. Atomic Coordinates and Thermal Parameters for Selected Atoms of $[RhMn(CO)_4(\mu\text{-}S)(dppm)_2]\cdot CH_2Cl_2$ (7)[a]

atom	x	y	z	B_{eq}, Å^2
Rh	0.19364(4)	0.12378(2)	–0.10942(3)	1.90(1)
Mn	0.37000(8)	0.14463(4)	–0.21062(6)	1.86(2)
S	0.1725(1)	0.15200(7)	–0.2458(1)	2.43(4)
P(1)	0.1498(1)	0.04560(7)	–0.1715(1)	2.01(4)
P(2)	0.3454(1)	0.06444(7)	–0.2711(1)	2.15(4)
P(3)	0.1771(1)	0.21013(7)	–0.0727(1)	2.12(4)
P(4)	0.3783(1)	0.22715(7)	–0.1564(1)	2.13(4)
O(1)	0.1723(4)	0.0837(2)	0.0587(3)	4.0(1)
O(2)	0.4181(4)	0.0898(2)	–0.0468(3)	3.4(1)
O(3)	0.6075(4)	0.1413(2)	–0.1976(4)	4.1(2)
O(4)	0.3743(6)	0.1926(2)	–0.3737(3)	5.1(2)
C(1)	0.1815(6)	0.0996(3)	–0.0044(4)	2.5(2)
C(2)	0.3710(5)	0.1115(3)	–0.1034(4)	2.3(2)
C(3)	0.5124(6)	0.1413(3)	–0.2015(4)	2.4(2)
C(4)	0.3709(6)	0.1741(3)	–0.3115(4)	3.0(2)
C(5)	0.2171(5)	0.0306(3)	–0.2604(4)	2.3(2)
C(6)	0.2473(5)	0.2531(3)	–0.1365(4)	2.2(2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits in this and all subsequent tables. All atoms above were refined anisotropically. Thermal parameters for the anisotropically refined atoms are given in the form of the equivalent isotropic Gaussian diplacement parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ac(\cos \beta)\beta_{13}]$.

Table 4. Selected Distances (Å) in $[RhMn(CO)_4(\mu\text{-}S)(dppm)_2]\cdot CH_2Cl_2$ (7)

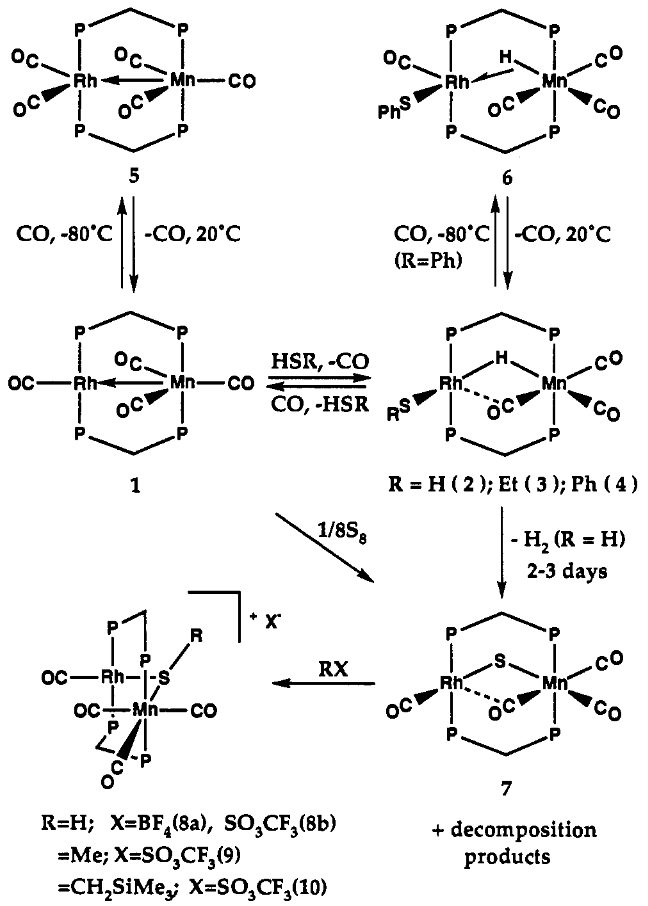
Rh–S	2.341(1)	Mn–C(4)	1.828(6)
Rh–P(1)	2.289(1)	P(1)–C(5)	1.821(5)
Rh–P(3)	2.319(1)	P(2)–C(5)	1.845(5)
Rh–C(1)	1.863(5)	P(3)–C(6)	1.825(5)
Rh–C(2)	2.214(5)	P(4)–C(6)	1.828(5)
Mn–S	2.450(2)	O(1)–C(1)	1.137(6)
Mn–P(2)	2.294(2)	O(2)–C(2)	1.173(6)
Mn–P(4)	2.300(2)	O(3)–C(3)	1.173(6)
Mn–C(2)	1.959(5)	O(4)–C(4)	1.135(6)
Mn–C(3)	1.757(5)		

Table 5. Selected Angles (deg) in $[RhMn(CO)_4(\mu\text{-}S)(dppm)_2]\cdot CH_2Cl_2$ (7)

S–Rh–P(1)	81.66(5)	P(4)–Mn–C(2)	93.3(2)
S–Rh–P(3)	87.16(5)	P(4)–Mn–C(3)	91.1(2)
S–Rh–C(1)	169.0(2)	P(4)–Mn–C(4)	87.9(2)
S–Ph–C(2)	94.0(1)	C(2)–Mn–C(3)	91.0(2)
P(1)–Rh–P(3)	159.16(5)	C(2)–Mn–C(4)	178.6(2)
P(1)–Rh–C(1)	94.4(2)	C(3)–Mn–C(4)	88.2(2)
P(1)–Rh–C(2)	94.0(1)	Rh–S–Mn	76.66(4)
P(3)–Rh–C(1)	93.2(2)	Rh–P(1)–C(5)	116.0(2)
P(3)–Rh–C(2)	104.3(1)	Mn–P(2)–C(5)	116.7(2)
C(1)–Rh–C(2)	96.6(2)	Rh–P(3)–C(6)	111.4(2)
S–Mn–P(2)	84.04(5)	Mn–P(4)–C(6)	114.3(2)
S–Mn–P(4)	90.66(5)	Rh–C(1)–O(1)	177.9(5)
S–Mn–C(2)	97.6(1)	Rh–C(2)–Mn	90.6(2)
S–Mn–C(3)	171.1(2)	Rh–C(2)–O(2)	119.4(4)
S–Mn–C(4)	83.1(2)	Mn–C(2)–O(2)	149.9(4)
P(2)–Mn–P(4)	174.44(6)	Mn–C(3)–O(3)	176.8(5)
P(2)–Mn–C(2)	89.1(2)	Mn–C(4)–O(4)	178.2(5)
P(2)–Mn–C(3)	93.9(2)	P(1)–C(5)–P(2)	118.1(3)
P(2)–Mn–C(4)	89.8(2)	P(3)–C(6)–P(4)	112.7(3)

(on Rh or Mn), establishing that the hydride ligands bridge the metals. In compound **2** the sulfhydryl proton resonates at δ –0.31, displaying coupling to Rh and to the phosphorus nuclei on Rh, as demonstrated by selective ^{31}P decoupling experiments. The absence of coupling of this sulfhydryl proton to the Mn-bound phosphorus nuclei is consistent with the terminal, Rh-bound sulfhydryl formulation shown but does not unequivocally establish this. In the $^{13}C\{^1H\}$ NMR spectra three equal-intensity carbonyl resonances are observed for each of the three products. In each case two resonances (at *ca.* δ 227) display coupling of *ca.* 20 Hz to only the Mn-bound phosphorus nuclei, establishing that these carbonyls are terminally bound to Mn. The remaining resonance (at *ca.* δ 260) displays coupling to the Mn-bound phosphorus atoms ($^2J_{PC} \sim$ 20Hz) in addition to Rh coupling of *ca.* 17 Hz; no coupling of this carbonyl to the Rh-bound phosphines is observed. These data indicate that this low-field resonance corresponds to a semibridging carbonyl which is σ bound to Mn while interacting weakly with Rh. By comparison, terminal carbonyls on Rh typically display Rh–C coupling of about 60–70 Hz, whereas symmetrically bridged carbonyls display Rh–C coupling of about 30 Hz.[19] With the bridging sites on both sides of the $RhMnP_4$ plane occupied by the hydride and the semibridging carbonyl group and with the absence of any other terminally bound ligand on Rh, the sulfhydryl or thiolato ligands in **2**–**4** are by necessity terminally bound to Rh as shown in the scheme.

Scheme 1



Although examples of terminally bound SR groups are well-known,[3,8a,20] there is a strong tendency for these ligands to bridge two metals.[2,4,7,8a,21] The isolation of the stable complexes **2** and **4** (compound **3** was not isolated), containing terminal sulfhydryl or thiolato groups, was of some surprise to us, since all related chemistry with Rh/Re,[2] Rh/Ru,[4] and Rh/Os[4] complexes had yielded products in which the thiolato groups bridged the metals; terminal SR groups had only been observed in this chemistry as labile low-temperature intermediates, rearranging to give SR-bridged complexes at ambient temperature. However, stable

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(19) See for example: Jenkins, J. A.; Cowie, M. *Organometallics* **1992**, *11*, 2767.

(20) See for example: (a) Gaffney, T. R.; Ibers, J. A. *Inorg. Chem.* **1982**, *21*, 2854. (b) Piers, W. E.; Koch, L.; Ridge, D. S.; MacGillivray, L. R.; Zaworotko, M. *Organometallics* **1992**, *11*, 3148. (c) Carlton, L.; Bulbulia, Z. *J. Organomet. Chem.* **1990**, *389*, 139. (d) Di Vaira, M.; Peruzzini, M.; Stoppioni, P. *Inorg. Chem.* **1991**, *30*, 1001. (e) Amarasekera, J.; Rauchfuss, T. B. *Inorg. Chem.* **1989**, *28*, 3875. (f) Osakada, K.; Yamamoto, T.; Yamamoto, A. *Inorg. Chim. Acta* **1985**, *105*, L9. (g) Klein, D. P.; Kloster, G. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 2022.

(21) See for example: (a) Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M. *Inorg. Chem.* **1986**, *25*, 4617. (b) Neher, A.; Lorenz, I.-P. *Angew. Chem., Int. Ed. Engl.* **1989**, 1342. (c) Stephan, D. W. *Inorg. Chem.* **1992**, *31*, 4218 and references therein.

complexes with terminally bound thiolato groups *had* been obtained in a related diiridium system.[3] It is also notable that compounds **2**–**4** are tricarbonyl species whereas the labile thiolato intermediates, observed in the Rh/Re system,[2] were all tetracarbonyl species. Carbonyl loss *was* observed for the ethane- and benzenethiolato Rh/Re complexes, but this was accompanied by movement of the thiolato group to a bridging position. Compound **1** and its Rh/Re analogue also show significant differences in their rates of reaction with H_2S and thiols. In all cases, reactions with $[RhRe(CO)_4(dppm)_2]$, carried out at −80 °C, showed complete consumption of the complex within minutes.[2] By contrast, compound **1** is unreactive with these substrates at temperatures below 0 °C and reacts slowly with large excesses (>8 times) even at ambient temperature. We were also unable to observe the presumed initial H_2S and HSR adducts of compound **1**, analogous to the Rh/Re compounds, $[RhRe(HSR)(CO)_4(dppm)_2]$ (R = H, Et, Ph), which were observed at temperatures below −50 °C in our previous study.[2]

Although compounds **2** and **4** can be isolated as the sole products in their respective reactions, compound **3** is only ever observed spectroscopically in low yield (*ca.* 5–10%) in reaction mixtures. The only other species observed are unidentified decomposition products in which the RhMn framework is apparently no longer intact.

The reactivity of **1** with H_2S parallels that observed with another isoelectronic heterobinuclear complex, $[RhIr(CO)_3(dppm)_2]$,[3] but is in contrast to that observed in the analogous Rh/Re system,[2] in $[RhOs(CO)_4(dppm)_2]^+$,[4] and in the homobinuclear complexes $[Pd_2Cl_2(dppm)_2]$,[8f] $[Rh_2(CO)_3(dppm)_2]$,[3] and $[Ir_2(CO)_3(dppm)_2]$.[3] Only the present Rh/Mn complex and that involving Rh/Ir stopped at activation of one S–H bond; all others resulted in facile cleavage of both S–H bonds, yielding sulfido-bridged products. For the diiridium complex,[3] the dihydride species formed were inert, undergoing H_2 loss only after days at room temperature, whereas for the others, the presumed dihydride intermediates were never observed, with H_2 loss occurring instantly. The reluctance of the Rh/Mn complex to activate the second S–H bond is understandable in terms of a double oxidative addition involving both S–H bonds, since only the unsaturated Rh center is susceptible to oxidative addition (although as noted later, slow loss of H_2 does occur from **2** to yield a sulfide-bridged product). In this respect the difference between Re and Mn is interesting given that activation of *both* S–H bonds in H_2S occurred readily with the Rh/Re complex.[2]

In all cases the S–H activation step in the reaction of **1** with H_2S, HSEt, and HSPh is reversible, so reaction of compounds **2**–**4** with CO regenerates **1** and the respective thiols.

One consequence of carbonyl loss upon reaction of **1** with HSR is the observation of the labile carbonyl adduct $[RhMn(CO)_5(dppm)_2]$ (**5**), as shown in Scheme 1. This species was observed only upon cooling the reaction mixture to −80 °C and results from reaction of **1** with liberated CO; predictably it can also be prepared directly by the addition of CO to **1** at −80 °C. The $^{13}C\{^1H\}$ NMR of **5** at −80 °C shows three carbonyl resonances at δ 241.7, 228.4, and 200.3 in a 2:1:2 intensity ratio, respectively. No coupling to either Rh or P is obvious although the high-field signal is extremely broad, presumably masking the expected 60–80 Hz coupling to Rh. The broadness of this signal is probably due to the facile, reversible loss of CO which undoubtedly is occurring at Rh. Raising the temperature results in the disappearance of **5**, leaving only **1**.

When a mixture of **1** and HSPh is cooled to −40 °C, an additional species, $[RhMn(SPh)(CO)_4(\mu\text{-}H)(dppm)_2]$ (**6**), is observed. The ^1H NMR spectrum displays a high-field signal at δ −12.20 and selective, and broad-band ^{31}P decoupling experiments establish that this hydride is coupled strongly to the Mn-bound phosphorus nuclei ($^2J_{PH}$ = 20 Hz) and weakly coupled to Rh ($^1J_{RhH}$ = 5 Hz). The magnitudes of these couplings and the absence of coupling to the Rh-bound phosphorus nuclei suggest a structure in which the hydride ligand is primarily bound to Mn yet interacting weakly with Rh; this can be viewed as a weak agostic interaction between Rh and the Mn–H bond. In the $^{13}C\{^1H\}$ NMR four equal-intensity resonances appear for the carbonyls, with the high-field signal at δ 200.9 showing strong coupling to Rh ($^1J_{RhC}$ = 78 Hz) and to the two adjacent phosphorus nuclei ($^2J_{PC}$ = 15 Hz). This species is a labile CO adduct of **4** and disappears with time or upon warming. The structure shown for **6** in Scheme 1 is based on the assumption that CO attack will occur at the vacant site opposite the semibridging CO in **4**. This CO adduct would not necessarily be an intermediate in the displacement of HSPh from **4** by CO but may instead be an isomer, since the H and SPh fragments are not adjacent, as expected for their subsequent reductive elimination. (It should be noted, however, that movement of a bridged hydride between the metals is known to be facile,[12,22,23] and this would bring the hydrido and thiolato ligands into a position to undergo reductive elimination.)

Attempts to obtain single crystals of the sulfhydryl species **2** have resulted instead in the isolation of the sulfide-bridged tetracarbonyl complex $[RhMn(CO)_4(\mu\text{-}S)(dppm)_2]$ (**7**) in *ca.* 66% yield. This transformation occurs slowly over the period of 2–3 days, during which time no intermediate can be detected. In particular, no dihydride intermediate of the type observed in the analogous Ir_2 system[3] was ever observed. The additional carbonyl ligand, required in the transformation of the tricarbonyl species **2** to the tetracarbonyl **7**, is presumably scavenged from the unidentified decomposition products which appear as a number of low-intensity resonances in the $^{31}P\{^1H\}$ NMR spectrum. Compound **7** can also be prepared quantitatively from **1** via reaction with elemental sulfur. This species shows one low-frequency carbonyl stretch at 1796 cm^{-1} in the IR spectrum and a corresponding resonance at δ 239.1 in the $^{13}C\{^1H\}$ NMR spectrum. This carbonyl is identified as a semibridging group which is primarily bound to Mn while interacting weakly with Rh, on the basis of the rather small magnitude of the Rh–C coupling of 8 Hz. By comparison, the carbonyl which is terminally bound to Rh (δ 192.8) shows Rh–C coupling of 69 Hz, and those terminally bound to Mn show no Rh coupling. This semibridging carbonyl displays no coupling to the Rh-bound P nuclei but does show coupling to the Mn-bound phosphines of 14 Hz, which is slightly less than the 18–20 Hz couplings displayed by the terminal carbonyls coupled to the appropriate adjacent P nuclei.

The X-ray structure of **7** confirms this formulation and clearly shows the semibridging interaction with one carbonyl. An ORTEP diagram of this compound is shown in Figure 1. The geometry at Mn is as expected for an octahedral Mn(1+) compound, having an almost undistorted geometry. At Rh the geometry is distorted from that of a square plane, having Rh lying 0.282 Å out of the P(1), P(3), S, C(1) plane in the direction of C(2).[24] As such, the geometry at Rh can be described as a tetragonal pyramid having C(2) at the apical site.

The sulfido ligand bridges the metals in a slightly asymmetric manner. Surprisingly, the Mn–S distance is longer than that of Rh–S (2.450(2) *vs* 2.341(1) Å), the reverse of what is expected on the basis of the covalent radii of the metals.[25] The Rh–S

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(23) Puddephatt, R. J.; Azam, K. A.; Hill, R. H.; Brown, M. P.; Nelson, C. D.; Moulding, R. P.; Seddon, K. R.; Grossel, M. C. *J. Am. Chem. Soc.* **1983**, *105*, 5642.

(24) Atoms defining the weighted least-squares plane (deviations (in Å) from that plane): S (0.085), P(1) (−0.089), P(3) (−0.084), C(1) (0.088). Equation of the plane: $12.3493x - 1.5543y - 0.7819z - 2.0020 = 0$. The weights are derived from the positional esd's using the method described in: Hamilton, W. C. *Acta Crystallogr.* **1961**, *14*, 185.

(25) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1960.

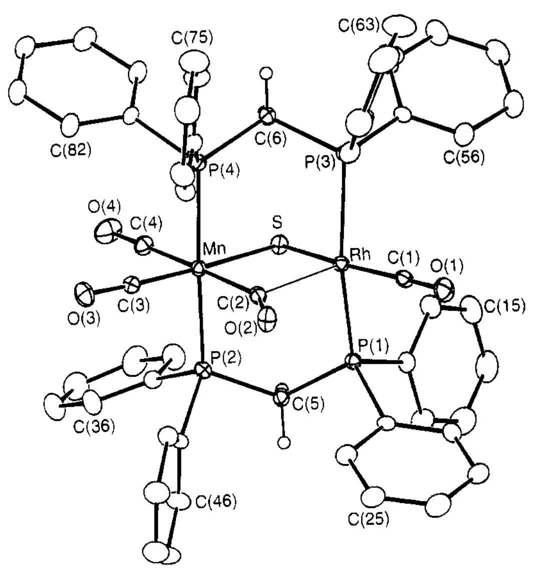
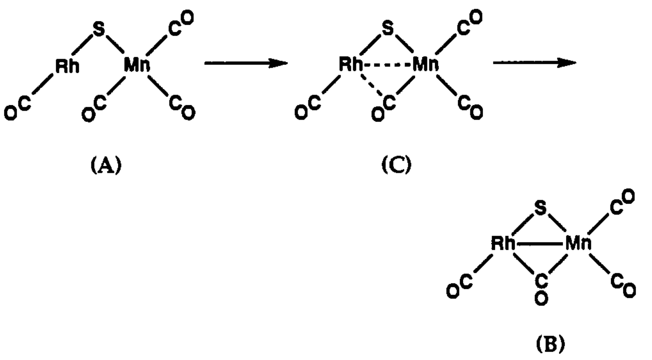


Figure 1. Perspective view of $[RhMn(CO)_4(\mu\text{-}S)(dppm)_2]$ (**7**) showing the numbering scheme. Thermal ellipsoids are drawn at the 20% level, except for methylene hydrogens which are shown arbitrarily small and phenyl hydrogens which are omitted.

distance is comparable to that observed in $[Rh_2(CO)_2(\mu\text{-}S)(dppm)_2]$ (2.367(3) Å)[26] and does not appear to be unusual. It may be that the Mn–S distance is longer because of increased steric crowding at the more crowded octahedral Mn center. However, another explanation is that the shorter Rh–S distance results from π donation from sulfur to the unsaturated Rh, as has previously been proposed.[27] The angle at sulfur (76.66(4)°) is more acute than that observed (83.5(1)°) in $[Rh_2(CO)_2(\mu\text{-}S)(dppm)_2]$ because of the shorter metal–metal separation (2.972(7) *vs* 3.154(2) Å) in the present compound. This separation is longer than expected for a Rh–Mn single bond (compare, for example, that observed (2.8428(8) Å) in the precursor (**1**))[12] but is not long enough to clearly indicate the absence of such bonding. One explanation is that there is no formal Rh–Mn bond; instead the short separation results from interaction of Rh with the semibridging carbonyl (C(2)O(2)). Not only is the Mn–C(2) distance (1.959(5) Å) substantially shorter than Rh–C(2) (2.214(5) Å), but more significantly this carbonyl is more linear with respect to Mn than to Rh (Mn–C(2)–O(2) = 149.9(4)°, Rh–C(2)–O(2) = 119.4(4)°). A comparison of the structural parameters of the carbonyls shows some interesting features. Not surprisingly, the semibridging carbonyl has the longest metal–carbon distances. By contrast Mn–C(3) is the shortest separation (1.757(5) Å), presumably because it is opposite the π-donor sulfide ligand; this is consistent with the correspondingly long C(3)–O(3) distance (1.173(6) Å), which is the same as that of the semibridging group, which interacts with both metals.

Although, as noted above, there is no need to formulate a formal Rh–Mn bond in **7**, we propose that the interaction of Rh with the semibridging carbonyl results in some metal–metal bonding interaction. A structure containing a semibridging carbonyl can be viewed as an intermediate in the transformation of a terminal carbonyl (**A**) to a bridging one (**B**) (diphosphine ligands, which are perpendicular to this plane are not shown). In order to maintain the compound's diamagnetism and an 18-e count at Mn, this transformation of a single carbonyl from terminal to bridged must be accompanied by a change in metal–metal bond order, as shown below. On this basis, the intermediate (**C**), representing compound **7**, would be expected to show the onset of a metal–metal interaction.



Compound **7** is one of a series of sulfido-bridged, A-frame complexes involving the late transition metals.[2,11,26,28] In previous studies[11b,29] some of these, and related sulfido-bridged species, had been readily oxidized to give complexes containing bridging sulfoxide or sulfur dioxide complexes. However, attempts to oxidize the sulfide bridge in **7** failed, as this compound was found to be unreactive with molecular oxygen, *m*-chloroperbenzoic acid, hydrogen peroxide, *tert*-butyl peroxide, or sodium periodate. Similarly, attempts to at least partially reverse the reaction in which $[RhMn(CO)_4(\mu\text{-}S)(dppm)_2]$ (**7**) was obtained from $[RhMn(CO)_4(dppm)_2]$ and H_2S by reaction of **7** with H_2 also failed. No evidence of metal hydride or sulfhydryl resonances was observed in the ^1H NMR spectrum; only starting material was observed. This duplicated our earlier findings for $[Rh_2(CO)_2(\mu\text{-}S)(dppm)_2]$,[30] which also proved to be unreactive with H_2, but was in contrast to findings for $[Ir_2(CO)_2(\mu\text{-}S)(dppm)_2]$[31] and $[RhIr(CO)_2(\mu\text{-}S)(dppm)_2]$,[30] both of which yielded hydrido complexes upon reaction with H_2. Apparently the third-row metal is necessary in these systems to give a sufficiently strong metal–hydride bond.

As expected, the bridging sulfide moiety in **7** is susceptible to attack by electrophiles. So although sulfhydryl- and thiolato-bridged species were not observed in the S–H bond-activation reactions described in this RhMn system, such species could be prepared via protonation or alkylation of the sulfide bridge in compound **7**. Therefore reaction of **7** with $HBF_4{\cdot}Et_2O$, HSO_3CF_3, $MeSO_3CF_3$, and $Me_3SiCH_2SO_3CF_3$, shown in Scheme 1, yields products **8**–**10**, respectively, having the appropriate counterion (BF_4^- or $SO_3CF_3^-$). At ambient temperature the $^{31}P\{^1H\}$ NMR spectra of **8** and **10** are broad and unresolved, whereas that of **9** appears as that of a well-resolved AA'BB'X spin system. When the samples are cooled to −80 °C, however, all species give $^{31}P\{^1H\}$ spectra characteristic of ABCDX spin systems in which all four phosphorus nuclei within the complex are chemically inequivalent, as shown for compound **9** in Figure 2. The coalescence temperature (from $^{31}P\{^1H\}$NMR) for **9** is −30 ± 5 °C whereas for **8** and **10** coalescence had not occurred by 22 °C, so these temperatures were not obtained. The top–bottom asymmetry that renders the two phosphorus atoms on a given metal inequivalent is probably due to the orientation of the thiolate substituent (R = H, CH_3, CH_2SiMe_3) as diagramed in Scheme 1. The fluxionality at ambient temperature, which equilibrates the phosphorus nuclei on either of the metals, would then result from inversion at sulfur. Another ground-state structure that

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(26) Kubiak, C. P.; Eisenberg, R. *Inorg. Chem.* **1980**, *19*, 2726.

(27) Cotton, F. A.; Lahuerta, P.; Latorre, J.; Sanaú, M.; Solana, I.; Schwotzer, W. *Inorg. Chem.* **1988**, *27*, 2131.

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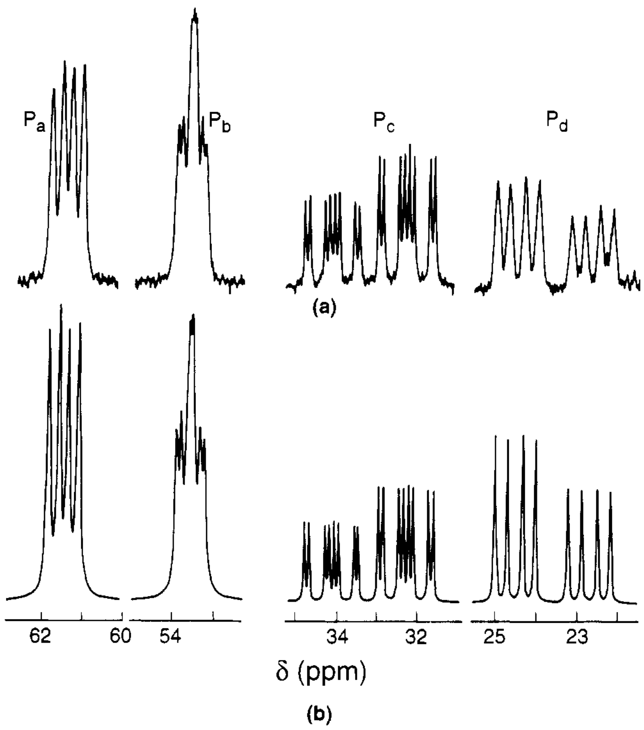
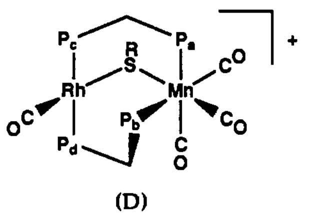


Figure 2. (a) Observed and (b) calculated $^{31}P\{^1H\}$ NMR spectra for $[RhMn(CO)_4(\mu\text{-}SMe)(dppm)_2][SO_3CF_3]$ (**9**) at –80 °C. Simulated parameters: $^2J_{P_aP_b}$ = 43 Hz, $^2J_{P_cP_d}$ = 296 Hz, $^2J_{P_aP_c}$ = 81 Hz, $^2J_{P_bP_d}$ = 52 Hz, $^4J_{P_bP_c}$ = 17 Hz, $^1J_{RhP_c}$ = 119 Hz, $^1J_{RhP_d}$ = 113 Hz.

would render all phosphorus nuclei inequivalent is that in which the phosphines are trans at one metal but cis at another (structure **D**), a structural type that is not uncommon in such compounds.[32–35]



(**D**)

Fluxionality of such a species would then result from pivoting about the Mn–S bond bringing P_a out of and P_b into the $RhMnP_cP_d$ plane, accompanied by inversion at sulfur. This latter possibility can be ruled out with reasonable confidence on the basis of the NMR studies. The simulation of the NMR spectrum of **9** yields a coupling of 296 Hz between the two Rh-bound phosphorus nuclei, consistent with a trans arrangement of phosphines at this metal and can be compared to the values of 321–337 Hz reported for *trans*-$[RhX(CO)(PH^tBu_2)_2]$.[36] The coupling between the Mn-bound phosphorus nuclei is much smaller (43 Hz) but is still believed to result from a trans, or almost-trans, diphosphine arrangement at this metal. By comparison, the $^2J_{PP}$ values for trans phosphine arrangements in *trans*-$[PhC(O)Mn(CO)_3P_2]$ and *trans*-$[PhMn(CO)_3P_2]$ (P = $P(OCH_2)_3CEt$) are 70 and 110 Hz, respectively, whereas the cis phosphines in *cis*-$[PhC(O)Mn(CO)_3P_2]$ display P–P coupling of only 5 Hz.[37] Although the P–Mn–P coupling in **9** is significantly smaller than the trans coupling noted above for these mononuclear Mn complexes, larger coupling is expected when more electronegative phosphite substituents are involved.[38] In addition, a *cis*-diphosphine arrangement at Mn (**D**) in compounds **8–10** can be ruled out since it would require the Mn-bound ends of the phosphines to be opposite carbonyl ligands, and no P–C coupling consistent with such an arrangement is observed. The $^{13}C\{^1H\}$ NMR spectra of the three compounds show one Rh-bound carbonyl at *ca.* δ 190 ($^1J_{RhC} \simeq 72$ Hz, $^2J_{PC} \simeq 14$ Hz) and three Mn-bound carbonyls between δ 216 and 230 with $^2J_{PC}$ values about 18 Hz, consistent with an arrangement in which the carbonyls are cis to the phosphines. The IR spectra of compounds **8–10** are also more consistent with a *trans*-diphosphine arrangement, since their low-frequency carbonyl stretch (at *ca.* 1850 cm^{-1}) is probably due to the carbonyl on Mn which is directed toward Rh, giving a weak semibridging interaction; this interaction would occur readily for the *trans*-diphosphine arrangement but would be less likely in structure **D**. Also consistent with the proposed inversion at sulfur, the $^{13}C\{^1H\}$ NMR spectra do not change substantially upon cooling. A structural rearrangement involving a *cis*-diphosphine geometry at Mn would require carbonyl scrambling, which would presumably be evident in the ^{13}C NMR spectra.

The fluxionality of compounds **8** and **9** is also evident in the ^1H NMR spectra, which display four resonances for the four chemically distinct dppm methylene protons at –80 °C but only two resonances at ambient temperature. For compound **10** the four dppm methylene resonances do not coalesce into two at ambient temperature but appear as four broad unresolved resonances. In addition, the two diastereotopic protons of the bridging SCH_2SiMe_3 group appear as an AB quartet at –80 °C and as two broad unresolved resonances at ambient temperature. Although inversion at sulfur, which would exchange dppm methylene protons pairwise and would also exchange the two thiolato methylene protons on **10**, was not obvious in the variable-temperature ^1H NMR spectra, it was clearly established at –60 °C by spin-saturation-transfer experiments. These showed exchange of the dppm methylene protons at δ 4.11 and 2.77 and at δ 3.47 and 3.24 and exchange of the thiolato methylene protons at δ 0.98 and 0.67.

The sulfhydryl proton of **8** appears in the ^1H NMR spectrum at δ –2.67, over the temperature range noted, and displays coupling to all phosphorus nuclei, confirming the bridging arrangement of the SH group.

It was of interest to establish the relative acidities of the terminal and bridging sulfhydryl ligands in these compounds. Although we have not investigated this in depth, we have carried out the deprotonations using piperidine in CH_2Cl_2. As expected, the cationic, sulfhydryl-bridged complex **8** is readily deprotonated by piperidine, reacting instantly to regenerate **7**. By contrast, the neutral species, $[RhMn(SH)(CO)_3(\mu\text{-}H)(dppm)_2]$ (**2**), reacts only slowly in the presence of a 100-fold excess of the base, yielding comparable amounts of the starting material (**2**) and compound **7** after 16 h (again the scavenging of CO to give **7** has yielded minor amounts of decomposition products). We had considered that loss of H_2 from **2** may proceed by deprotonation of the sulfhydryl group and subsequent reaction with the metal hydride to give H_2, as has been proposed[11b] (instead of oxidative addition of the second S–H bond and subsequent reductive elimination of H_2 as noted earlier); however, we detect no significant rate difference in the transformation of **2** to **7** in the presence or absence of base.

A characteristic reaction of mercaptans is their Michael addition to α,β-unsaturated substrates,[39] a reactivity that has also been demonstrated for metal complexes containing sulfhydryl

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[32] Woodcock, C.; Eisenberg, R. *Inorg. Chem.* **1985**, *24*, 1285.

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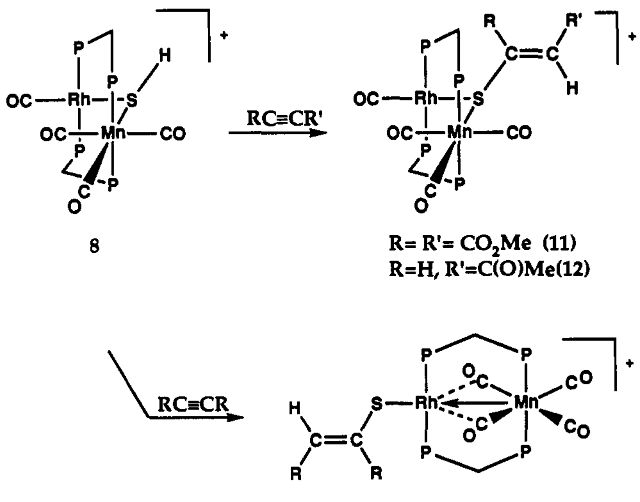
Scheme 2



groups.[10,40] We find that the terminal-sulfhydryl complex $[RhMn(SH)(CO)_3(\mu\text{-}H)(dppm)_2]$ (**2**) does not react with unsaturated substrates such as dimethyl acetylenedicarboxylate (DMAD), even in the presence of added base, but instead, as noted above, shows only the formation the sulfide-bridged species **7**. However the cationic sulfhydryl-bridged species $[RhMn(CO)_4(\mu\text{-}SH)(dppm)_2]^+$ (**8**) does yield the alkyne-insertion products, $[RhMn(CO)_4(\mu\text{-}SC(R){=}C(H)R')(dppm)_2][SO_3CF_3]$, **11** and **12** upon reaction with DMAD and 3-butyn-2-one, respectively, as shown in Scheme 2. These Michael-type addition products are proposed, on the basis of their spectroscopic similarities to compounds **8**–**10**, to be the thiolato-bridged complexes shown. In particular, the $^{13}C\{^1H\}$ NMR spectra show one high-field carbonyl resonance with 74-Hz coupling to Rh, indicating a terminal Rh-bound CO, and three low-field resonances for the Mn-bound carbonyls. Although none of the Mn-bound carbonyls show resolvable coupling to Rh, the low-frequency stretch in the IR (*ca.* 1800–1850 cm^{-1}) suggests that one of these carbonyls has a weak semibridging interaction with Rh. The configuration of the olefinic moiety in compound **12**, in which the original alkyne substituents (H and C(O)Me) are now mutually cis, is established from the ^1H NMR, in which the resonances at δ 6.94 and 5.99 display a trans coupling of 15.2 Hz. Although the olefin stereochemistry of **11** could not be unambiguously determined, it is also assigned as having cis CO_2Me groups, on the basis of analogies with **12**.

Hexafluoro-2-butyne also reacts with **8** to give the 1,2-addition product resulting from alkyne insertion into the S–H bond, namely $[RhMn(SC(CF_3){=}C(H)CF_3)(CO)_4(dppm)_2][SO_3CF_3]$ (**13**). Although not technically a Michael-addition reaction, it no doubt proceeds in a similar manner. Interestingly, compound **13** has a terminal rather than a bridging thiolato group and consequently has spectral parameters different from those of compounds **8**–**12**. Whereas the $^{31}P\{^1H\}$ NMR spectra of the thiolato-bridged species (**8**–**12**) display a temperature dependence (*vide supra*), none was observed for **13**. Moreover, the $^{13}C\{^1H\}$ NMR spectrum at ambient temperature shows only two equal-intensity low-field carbonyl resonances (δ 237.8, 236.5) with no resolvable Rh coupling, ruling out a terminally bound CO on Rh. The low-frequency CO stretch in the IR spectrum is again suggestive of a semibridging CO binding mode, leading to the formulation shown above. A dative Mn→Rh bond is proposed, in order to give Rh a 16-e configuration. At –80 °C the two carbonyl resonances resolve into four, presumably because restricted rotation about the Rh–S or S–C bonds can lead to differentiation of the "back" and "front" of the complex, on either side of the $RhMnP_4$ plane. The geometry at the olefin is established on the basis of ^1H and ^{19}F NMR spectra. In the ^{19}F NMR the two olefin-bound CF_3 groups appear at δ –55.81 and –58.93, displaying mutual coupling ($^5J_{FF}$) of 10 Hz. The low-field resonance also displays geminal coupling to the olefinic proton of 9 Hz, which is verified in the ^1H NMR by the quartet at δ 5.14. These results dictate a cis arrangement of CF_3 groups, on the basis of previous studies[41] which showed that $^5J_{FF}$ for a trans arrangement was only 2–2.5 Hz compared to 12–14 Hz for cis.

We propose that the destabilization of a bridging thiolato arrangement for **13** results from the effect of the more electronegative CF_3 groups (compared to CO_2Me).[42] These groups would destabilize the bridging arrangement, which has a formal positive charge on sulfur, by virtue of the dative sulfur-to-metal bond. Although we have no direct evidence, we suggest that the olefinic moiety in compounds **11**–**13** is not coordinated to either metal, since its arrangement does not appear suitable for interaction with the metals in either the bridging (**11**, **12**) or terminal (**13**) modes. Such an assignment is consistent with previous studies on analogous species.[10,36]

Sulfhydryl- or thiolato-bridged species have also been obtained by other routes. Therefore the sulfhydryl-bridged complex **8a** can also be obtained by protonation of $[RhMn(SH)(CO)_3(\mu\text{-}H)(dppm)_2]$ (**2**) with $HBF_4{\cdot}Et_2O$ via reductive elimination of H_2. Also obtained in this reaction are the hydride-bridged species $[RhMn(CO)_4(\mu\text{-}H)(dppm)_2][BF_4]$ (**14**), from the elimination of H_2S, together with decomposition products that were presumably the source of the additional carbonyl in each of these products. Compound **14** could also be prepared directly by protonation of **1**. The hydride resonance of **14** displays coupling to rhodium and to all phosphorus nuclei, indicating that it is bridging, and the $^{13}C\{^1H\}$ NMR at –90 °C shows four unique resonances for the terminal carbonyls. Unlike the case of **7**, no evidence for a semibridging carbonyl interaction is found. Presumably, the positive charge on the complex and the absence of the π-donor sulfide group render the rhodium too electron deficient to favor substantial π back-donation to one of the Mn-bound carbonyls. The structure of **14** is proposed to be exactly analogous to that determined for the "RhRe" analogue.[22] The reaction of this hydride-bridged species (**14**) with ethanethiol yields two species. The first product, $[RhMn(SEt)(CO)_4(dppm)_2][BF_4]$ (**15**), is proposed to have a terminal thiolate group, primarily on the basis of spectroscopic data and, in particular, its $^{31}P\{^1H\}$ NMR spectrum, which is temperature invarient, unlike those of all characterized thiolato-bridged species (*vide supra*). Furthermore, compound **15** transforms with time into an isomeric species **16** which is almost identical in its spectroscopic parameters to the methanethiolato-bridged species **9** and so is assigned an analogous structure. Presumably, **16** could also have been generated by attack of the $C_2H_5^+$ electrophile on **7**, as were the analogous species; however this reaction was not attempted. It is particularly noteworthy that the AA'BB'X pattern in the $^{31}P\{^1H\}$ NMR spectrum of **16** at ambient temperature transforms to an ABCDX pattern at –80 °C, exactly as for **9**. Compound **15** is subtly different from **13**, which has an analogous stoichiometry, having a terminal thiolato group and four carbonyls. Whereas **13** has all carbonyls bound to Mn, one carbonyl in **15** is terminally bound to Rh, as shown by the large ^{103}Rh–^{13}C coupling (83 Hz) involving

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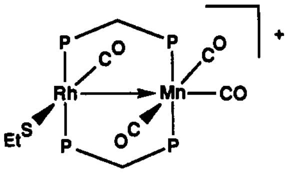
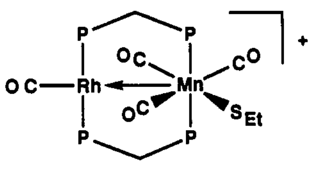
this group. Unfortunately, we have not been able to completely characterize **15**, since it is only observed as an intermediate in the presence of vast excesses of EtSH. Whether the thiolato group is terminally bound to Rh (E) or to Mn (F) could not be established; however, we tend to support structure **F** on the grounds that conversion of **15** to **16** is slow. We would expect that if the thiolato group occupied a site adjacent to the Rh–Mn bond, as in **E**, conversion to **16** would be facile (this also rules out the structure having the thiolato group terminally bound to Mn but cis to the Mn–Rh bond). Assuming the metals in both formulations are in the +1 oxidation state, these formulations differ in the direction of the metal–metal dative bond that is required to give Mn an 18-e configuration in **E** or Rh a 16-e configuration in **F**. Compounds **15** and **16** were also obtained by protonation of [RhMn(SEt)(CO)$_3$(μ-H)(dppm)$_2$] (**3**) with HBF$_4$·Et$_2$O, although this route yields many other unidentified products since, as noted earlier, **3** is only obtained in *ca.* 10% yield together with other products. Presumably, the additional CO in the transformation of **3** to **15** and **16** originates either from CO liberated in the preparation of **3** from **1** or from decomposition products.



(E)



(F)

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Supplementary Material Available: Tables of crystallographic data, parameters for the dppm phenyl carbons and solvent atoms, anisotropic thermal parameters, bond lengths and angles involving the phenyl groups, and hydrogen atom parameters (11 pages). Ordering information is given on any current masthead page.