Complexes of Distibinomethane Ligands. 1. Iron, Cobalt, Nickel, and Manganese Carbonyl Complexes

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The reaction of $Fe_2(CO)_9$ in thf with $Ph_2SbCH_2SbPh_2$ (dpsm) or $Me_2SbCH_2SbMe_2$ (dmsm) produced $[Fe(CO)_4(\eta^1\text{-dpsm})]$ and $[Fe(CO)_4(\mu\text{-dmsm})Fe(CO)_4]$, and $Co_2(CO)_8$ reacted with either distibine ligand (L-L) to give $[Co_2(CO)_4(\mu\text{-}CO)_2(\mu\text{-L-L})]$. $Ni(CO)_4$ and dpsm gave $[Ni(CO)_3(\eta^1\text{-dpsm})]$ and $[Ni(CO)_3(\mu\text{-dpsm})Ni(CO)_3]$, while with dmsm only $[Ni(CO)_3(\mu\text{-dmsm})Ni(CO)_3]$ was isolated. $Mn_2(CO)_{10}$ reacted slowly with dpsm or dmsm in the presence of a $[\{(Cp)Fe(CO)_2\}_2]$ catalyst to give $[Mn_2(CO)_8(\text{L-L})]$, but no reaction occurred with $Re_2(CO)_{10}$ under similar conditions. *cis*-$[Mn(CO)_4X(\text{dpsm})]$ (X = Cl, Br, or I) and $[Mn_2(CO)_8Br_2(\mu\text{-dmsm})]$ were also prepared from the appropriate $[Mn(CO)_5X]$, but iron carbonyl halide derivatives were too unstable to isolate in the pure state. The complexes have been characterized by elemental analysis, IR and multinuclear NMR (^1H, $^{13}C\{^1H\}$, ^{55}Mn, or ^{59}Co) spectroscopy, and FAB mass spectrometry. The X-ray structures of dpsm, $[Fe(CO)_4(\eta^1\text{-dpsm})]$, and $[Co_2(CO)_4(\mu\text{-}CO)_2(\mu\text{-dmsm})]$ have been determined. No evidence for chelation by dmsm or dpsm was found, and Sb−C fission does not occur to significant extents in the reactions studied.

Introduction

The coordination chemistry of bis(diphenylphosphino)methane (dppm), $Ph_2PCH_2PPh_2$, has been intensively investigated.[1,2] In contrast to diphosphines with two or three carbon backbones which usually chelate to metal centers, the presence of a single methylene linkage in dppm sufficiently disfavors chelation through the strain in the four-membered ring that monodentate or bridging bidentate coordination are often preferred. Ligands with similar architecture such as $Me_2PCH_2PMe_2$ (dmpm), $Ph_2AsCH_2AsPh_2$, 2-$Ph_2PC_5H_4N$, or $Ph_2PCH_2PPhCH_2PPh_2$ have been used to assemble bi- or polymetallic complexes.[2,3] Bis(di-*R*-stibino)methanes, $Ph_2SbCH_2SbPh_2$ (dpsm), and $Me_2SbCH_2SbMe_2$ (dmsm) were reported[4] in the 1970s and a small number of complexes with limited characterization have been prepared.[5−13] The only structurally characterized complex of these ligands is[14] $[Pd_2(\mu\text{-}Ph_2SbCH_2SbPh_2)_2(\sigma\text{-}Ph)_2Cl_2]$, which is a face-to-face dimer obtained by photolysis of *cis*-$[Pd(Ph_2SbCH_2SbPh_2)_2Cl_2]$, the σ-Ph groups being derived from degradation of $Ph_2SbCH_2SbPh_2$. We report here the synthesis of new complexes and a reinvestigation of some reported complexes[15] of dpsm and dmsm with a variety of metal carbonyls and their detailed characterizations. Where appropriate comparisons are drawn with the analogous diphosphinomethane ligands.

Results and Discussion

Bis(diphenylstibino)methane was made by reaction of $NaSbPh_2$ and CH_2Cl_2 in liquid ammonia.[4] It is an air-stable white solid, readily soluble in chlorocarbons, less soluble in cold alcohols. The $\delta(CH_2)$ resonance ($CDCl_3$ solution) lies at 2.1 ppm in the ^1H NMR and at 4.5 ppm in the $^{13}C\{^1H\}$ spectra, both shifting in characteristic ways on coordination. Bis(dimethylstibino)methane was made in poor yield from $NaSbMe_2$ and CH_2Cl_2 in liquid ammonia[16] or more conveniently from $Cl_2SbCH_2SbCl_2$[17] and MeMgI in diethyl ether, the yield being improved by using $MeMgI/Me_2NCH_2CH_2NMe_2$. The reaction of MeLi with $Cl_2SbCH_2SbCl_2$ also affords the ligand in poor yield. The ligand is a pyrophoric oil which must be handled with rigorous exclusion of oxygen. The ^1H NMR spectrum ($CDCl_3$ solution) has $\delta(CH_2)$ at 1.1 ppm and $\delta(Me)$ at 0.8 ppm, with corresponding resonances at −4.3 and −1.6 ppm in the $^{13}C\{^1H\}$ NMR spectrum. The low-frequency $^{13}C\{^1H\}$ Me and CH_2 NMR resonances are typical of these groups bonded to heavy atoms such as I or Te.[18] The crystal structure of $Ph_2SbCH_2SbPh_2$ is shown in Figure 1, and selected bond

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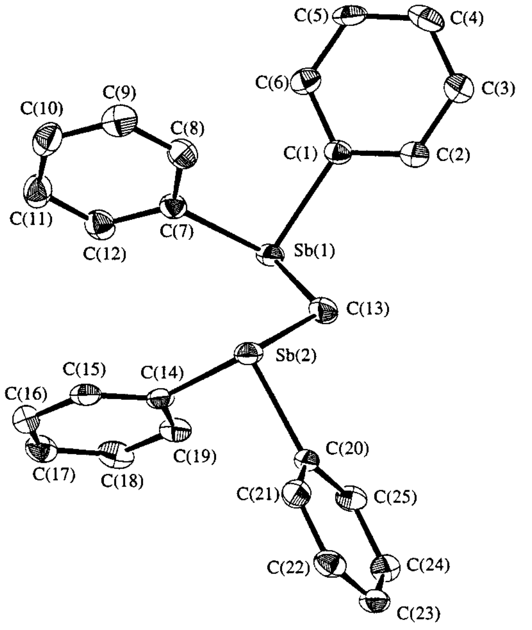

Figure 1. Molecular structure of $Ph_2SbCH_2SbPh_2$ showing the atom labeling scheme. H atoms have not been drawn for clarity, and the thermal ellipsoids are drawn at the 50% probability level.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $Ph_2SbCH_2SbPh_2$

Sb(1)−C(1)	2.157(3)	Sb(2)−C(13)	2.155(4)
Sb(1)−C(7)	2.144(4)	Sb(2)−C(14)	2.157(4)
Sb(1)−C(13)	2.169(4)	Sb(2)−C(20)	2.161(3)
Sb(1)···Sb(2)	3.692(1)	C−C	1.369(6)−1.416(5)

Sb(1)−C(13)−Sb(2)	117.3(2)
C−Sb−C	94.4(1)−98.7(1)
Sb−C−C	116.4(3)−125.0(3)
C−C−C	118.1(3)−121.6(3)

lengths and angles are in Table 1. The Sb−C distances do not vary markedly (2.144(4)−2.169(4) Å), and there is no evidence that Sb−C(H_2) is different from the rest. The key points are the Sb(1)···Sb(2) distance (3.692(1) Å), the angle at the methylene group (117.3(2)°), and the C−Sb−C angles (94.4(1)−98.7(1), 96.7° average). The structures of the phosphorus[19] and arsenic[20] ligands have been reported, the latter in $\{(C_6F_5)_2Hg\}_2 \cdot Ph_2AsCH_2AsPh_2$ where there is a weak association between Hg and As. The P−C−P and As−C−As angles are 106.2(3)° and 113(3)°, respectively.

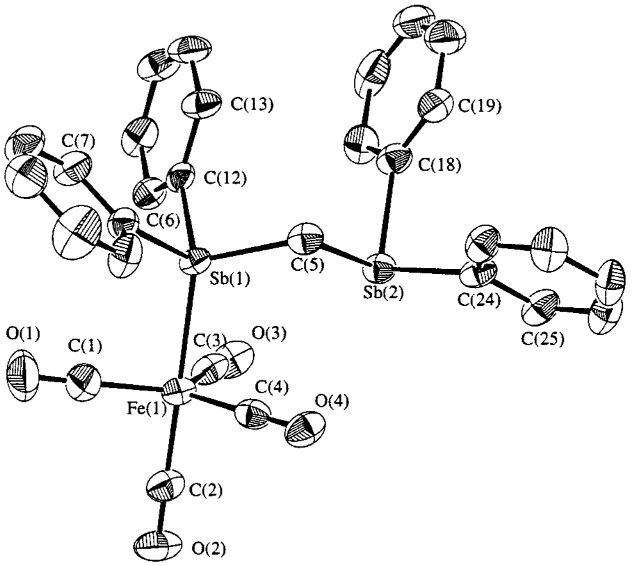

Figure 2. Molecular structure of $[Fe(CO)_4(Ph_2SbCH_2SbPh_2)]$ showing the atom labeling scheme. H atoms have not been drawn for clarity, and the thermal ellipsoids are drawn at the 50% probability level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[Fe(CO)_4(Ph_2SbCH_2SbPh_2)]$

Sb(1)−Fe(1)	2.491(2)	Sb(1)···Sb(2)	3.4806(9)
Sb(1)−C(5)	2.144(9)	Sb(2)−C(5)	2.160(8)
Sb(1)−C(6)	2.132(8)	Sb(2)−C(18)	2.156(8)
Sb(1)−C(12)	2.119(8)	Sb(2)−C(24)	2.150(9)
Fe(1)−C	1.773(9)−1.79(1)	C−O	1.13(1)−1.17(1)
C−C	1.36(1)−1.41(1)		

Sb(1)−Fe(1)−C(1)	87.6(3)	Sb(1)−Fe(1)−C(3)	91.2(3)
Sb(1)−Fe(1)−C(2)	176.9(3)	Sb(1)−Fe(1)−C(4)	87.0(3)
Sb(1)−C(5)−Sb(2)	107.9(3)		

Fe(1)−C−O	175.2(7)−179.4(9)	C−Sb(2)−C	96.5(3)−97.7(3)
Fe(1)−Sb(1)−C	112.5(2)−117.6(2)	Sb−C−C	116.4(6)−124.3(6)
C−Sb(1)−C	100.8(3)−106.8(3)	C−C−C	118.4(9)−121.1(9)

Iron Complexes. $[Fe(CO)_4(dpsm)]$ was originally prepared[7] directly from $Fe(CO)_5$ and dpsm in refluxing *n*-heptane; in our hands, the yield was *ca.* 5%. Better yields (*ca.* 10%) were obtained using catalysts such as $NaBH_4/EtOH$[21] or $[\{(Cp)Fe(CO)_2\}_2]$,[22] but the complex is best made (40%) from $Fe_2(CO)_9$ in tetrahydrofuran (thf)[23] in a 1:1 $Fe_2(CO)_9$:dpsm ratio (half the contained iron is lost as $Fe(CO)_5$). The orange solid is very soluble in organic solvents and in CH_2Cl_2 solution, and it exhibited three IR-active ν(CO) bands at 2042 (m), 1970 (w), and 1932 (s) cm^{-1} consistent with an axially substituted tbp (theory $2A_1 + E$) (Cf $[Fe(CO)_4(Ph_3Sb)]$[24]) and, hence, η^1-coordinated dpsm. In a Nujol mull, four ν(CO) bands are present at 2043 (m), 1970 (w), 1940 (s), and 1920 (m) cm^{-1}, an effect observed in several $[Fe(CO)_4(\eta^1\text{-diphosphine})]$ complexes[25] due to the bulky ligand reducing the symmetry at the metal center. The single δ(CO) $^{13}C\{^1H\}$ NMR resonance at 213.3 ppm indicates fluxionality of the carbonyl groups. The structure was confirmed by an X-ray study which showed the η^1 coordination (see Figure 2 and Table 2). Sb(1) occupies an axial site of the tbp surrounding the iron, and there is no difference between the Fe−C axial/equatorial values, unlike the $[Fe(CO)_4(SbPh_3)]$ complex[26] where there is a slightly shorter axial Fe−C distance. The Sb−Fe distance (2.491(2) Å) is comparable to the value in the $SbPh_3$ complex (2.472(1) Å). The complex illustrates the changes that occur to the C−Sb−C angles on coordination, where the bonded Sb(1) has *larger* angles than Sb(2). Values for the uncoordinated antimony (Sb(2)) are comparable with the free ligand (see Tables 1 and 2). The Sb···Sb distance *shortens* (by 0.211 Å) on complex formation, and the related Sb−C−Sb angle becomes smaller. The corresponding diphosphine

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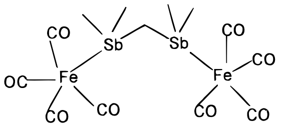
complex structure has been determined[27] and is isomorphous with the Sb compound, but here the P−C−P angle (112.6(4)°) is *larger* than that in the free ligand[19] (106.2(3)°).

Prolonged reflux of [Fe(CO)$_4$(dpsm)] with a large excess of Fe(CO)$_5$ in toluene, even in the presence of catalysts, resulted mainly in recovery of the starting materials. On a few occasions the ^{1}H and ^{13}C{^{1}H} NMR spectra of the crude products showed that a second species was present with δ(CH$_2$) at 2.5 in the ^{1}H NMR spectrum and at 5.9 ppm in the ^{13}C{^{1}H} NMR spectrum, with δ(CO) at 213.5 ppm. The reaction of dpsm with Fe$_2$(CO)$_9$ (1:2) in thf formed a brown solid containing larger amounts of the second product mixed with [Fe(CO)$_4$(dpsm)]. The FAB mass spectrum of this material showed very weak features at *m/z* 903 and 874 and a strong feature at *m/z ca.* 790 with the appropriate isotope patterns for [Fe$_2$(dpsm)(CO)$_8$]$^+$, [Fe$_2$(dpsm)(CO)$_7$]$^+$, and [Fe$_2$(dpsm)(CO)$_4$]$^+$, respectively. Attempts to drive this reaction to completion failed, and in solution the material decomposed quite rapidly to [Fe(CO)$_4$(dpsm)], preventing chromatographic separation. The second complex is clearly [Fe(CO)$_4$(μ-dpsm)Fe(CO)$_4$], and the very similar IR spectrum to that of [Fe(CO)$_4$(dpsm)] confirms the structure as ligand-bridged with two isolated axially substituted tbp tetracarbonyliron groups (I). Similar complexes are known with Ph$_2$P(CH$_2$)$_n$PPh$_2$ ($n \geq 2$),[25] but with Ph$_2$PCH$_2$PPh$_2$ the dinuclear complex [Fe$_2$(CO)$_7$(Ph$_2$PCH$_2$PPh$_2$)], which contains an Fe−Fe bond and a bridging CO ligand, is formed.[23]



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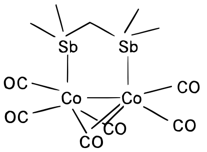

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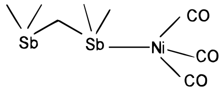

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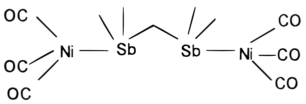

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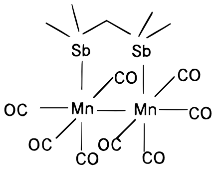

(V)

In contrast to the reaction with dpsm, the reaction of dmsm with Fe(CO)$_5$ or Fe$_2$(CO)$_9$ gave only yellow-brown [Fe$_2$(CO)$_8$(μ-dmsm)]. The carbonyl region of the IR spectrum shows three ν(CO) stretches consistent with axially substituted tbp iron centers, and the single resonances for the Me and CH$_2$ groups in the ^{1}H NMR and ^{13}C{^{1}H} spectra show that dmsm is symmetrically bridging (structure I). The ^{13}C{^{1}H} NMR spectrum has a single δ(CO) resonance, again showing fluxional carbonyl groups. Structures analogous to I are formed by several diphosphines[25] [Fe$_2$(CO)$_8${Ph$_2$P(CH$_2$)$_n$PPh$_2$}] (n = 2−4), but in contrast dmpm produces [Fe$_2$(CO)$_7$(dmpm)] and [Fe$_2$(CO)$_5$(dmpm)$_2$] which have Fe−Fe bonds and bridging dmpm.[28] Unlike the dpsm analogue, [Fe$_2$(CO)$_8$(dmsm)] does not decompose to the 1:1 complex in solution.

Cobalt Complexes. The reaction of dpsm or dmsm with Co$_2$(CO)$_8$ in benzene gave [Co$_2$(CO)$_6$(L-L)] (L-L = dpsm or dmsm).[10] The red-brown solids are easily soluble in organic solvents, although the dpsm complex decomposes slowly in solution. The [Co$_2$(CO)$_6$(dpsm)] complex exhibits three terminal and two bridging CO vibrations in the IR spectra in both the solid and CH$_2$Cl$_2$ solution, consistent with a [(CO)$_2$Co(μ-CO)$_2$(μ-R$_2$SbCH$_2$SbR$_2$)Co(CO)$_2$] structure (II).[29] The IR spectrum of [Co$_2$(CO)$_6$(dmsm)] in CH$_2$Cl$_2$ was similar, but in a Nujol mull or KBr disc this complex exhibited five terminal and three bridging CO vibrations. No evidence of a second complex was found in the NMR spectra. The X-ray structure of this complex reveals molecules with structure II, and thus the extra IR bands are tentatively attributed to a second conformer (as seen in complexes with longer backbones[29]). The δ(CH$_2$) resonances in both the ^{1}H and ^{13}C{^{1}H} NMR spectra of [Co$_2$(CO)$_6$(L-L)] show low-frequency coordination shifts which may correlate with a sharper Sb−C−Sb angle. In both complexes, a single δ(CO) resonance shows the carbonyl groups to be fluxional. The ^{59}Co NMR spectra show very broad resonances ($w_{1/2}$ *ca.* 12000−14000 Hz) at δ −1820 (dpsm) and −1710 (dmsm), which may be compared with −2100 in [Co$_2$(CO)$_8$].[30] Although [Co$_2$(CO)$_4$(L-L)$_2$] complexes are known with some diphosphines,[29] attempts to substitute more carbonyl groups with distibinomethanes failed. A solution of [Co$_2$(CO)$_6$(dpsm)] in benzene containing excess dpsm was monitored by solution IR spectroscopy over 24 h; the ν(CO) frequencies of the starting material were slowly lost, but with no new ν(CO) appearing, indicating decomposition to carbonyl-free products. The crystal structure of [Co$_2$(CO)$_6$(dmsm)] is shown in Figure 3, and selected bond lengths and angles in Table 3. The structure shows the expected bridging Sb ligand and two bridging carbonyl groups. The Co−Co distance (2.472(3) Å) is very similar to that found[31] in [Co$_2$(CO)$_6${Me$_2$AsC=C(AsMe$_2$)CF$_2$CF$_2$}] (2.483(4) Å). There is no crystallographic symmetry, but the molecule approximates to C_S with the mirror plane passing through C(3), C(4), and C(9). Sb(1), Sb(2), Co(1), and Co(2) are nearly coplanar, with C(3) and C(9) forming a “shallow boat” conformation.

Nickel Complexes. The reaction of Ni(CO)$_4$ with dpsm in a 1:1 ratio in CHCl$_3$ at ambient temperatures produced white [Ni(CO)$_3$(dpsm)], which has two ν(CO) in the IR spectrum, consistent (theory A$_1$ + E) with the expected structure III.[32] In solution, the complex partially decomposes into Ni(CO)$_4$ and free ligand, the

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(30) ^{59}Co 100%, I = $^7/_2$, Ξ = 23.73 MHz, $D_c = 1.56 \times 10^3$, $Q = 0.42 \times 10^{-28}$ m^2; *Multinuclear NMR*; Mason, J., Ed.; Plenum: New York, 1987.

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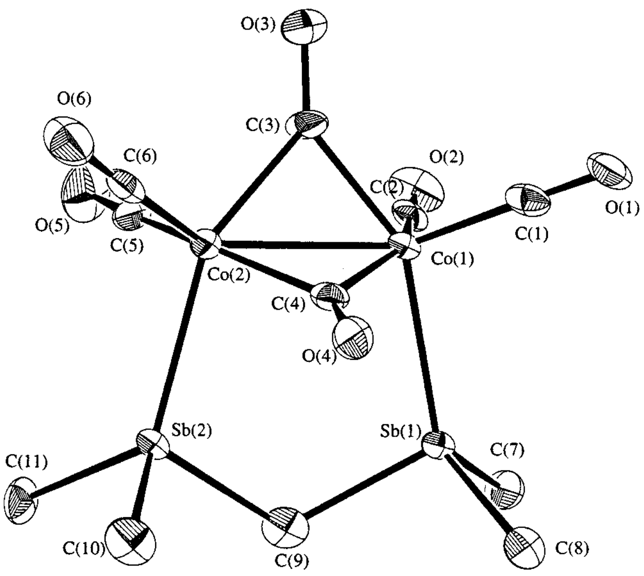

Figure 3. Molecular structure of [$Co_2(CO)_6(Me_2SbCH_2SbMe_2)$] showing the atom labeling scheme. H atoms have not been drawn for clarity, and the thermal ellipsoids are drawn at the 50% probability level.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for [$Co_2(CO)_6(Me_2SbCH_2SbMe_2)$]

Sb(1)–Co(1)	2.508(2)	Sb(2)–Co(2)	2.529(2)
Sb(1)···Sb(2)	3.572(2)	Co(1)–Co(2)	2.472(3)
Sb(1)–C(7)	2.08(2)	Sb(2)–C(9)	2.15(2)
Sb(1)–C(8)	2.12(2)	Sb(2)–C(10)	2.09(2)
Sb(1)–C(9)	2.10(2)	Sb(2)–C(11)	2.11(2)
Co(1)–C(1)	1.77(2)	Co(2)–C(3)	1.93(2)
Co(1)–C(2)	1.82(2)	Co(2)–C(4)	1.91(2)
Co(1)–C(3)	1.90(2)	Co(2)–C(5)	1.82(2)
Co(1)–C(4)	1.92(2)	Co(2)–C(6)	1.75(2)
Sb(1)–C(9)–Sb(2)	114.5(7)		
Sb(1)–Co(1)–C(1)	104.5(5)	Sb(2)–Co(2)–C(3)	151.0(5)
Sb(1)–Co(1)–C(2)	89.6(5)	Sb(2)–Co(2)–C(4)	85.0(5)
Sb(1)–Co(1)–C(3)	151.1(6)	Sb(2)–Co(2)–C(5)	90.1(5)
Sb(1)–Co(1)–C(4)	86.1(4)	Sb(2)–Co(2)–C(6)	107.0(5)
Co(1)–C(3)–O(3)	141(1)	Co(1)–C(4)–O(4)	139(1)
Co(2)–C(3)–O(3)	139(1)	Co(2)–C(4)–O(4)	141(1)
Co–Sb–C(9)	109.0(4), 107.2(4)	C–Sb(2)–C	99.0(7)–102.3(6)
Co–Sb–C(n[a])	119.7(5)–123.4(5)	Co–C–O (term)	174(1)–178(1)
C–Sb(1)–C	100.0(6)–102.4(7)		

[a] $n = 7, 8, 10$, or 11.

tetracarbonyl being identified by a $\delta(^{13}C\{^{1}H\})$ resonance at 192.0 and the T_{1u} mode at 2043 cm^{-1} in the IR spectrum.[33–35]

The reaction of dpsm with excess $Ni(CO)_4$ produced a colorless waxy solid identified as [$Ni_2(CO)_6(dpsm)$]. The IR spectrum of this complex in both Nujol mulls or CH_2Cl_2 solution was very similar to that of the 1:1 complex, as expected for structure IV. An analogue [$Ni_2(CO)_6(Ph_2PPPh_2)$] has been characterized by an X-ray study.[36] On standing in CH_2Cl_2 solution, the complex partially decomposes into [$Ni(CO)_3(dpsm)$] and $Ni(CO)_4$.[35]

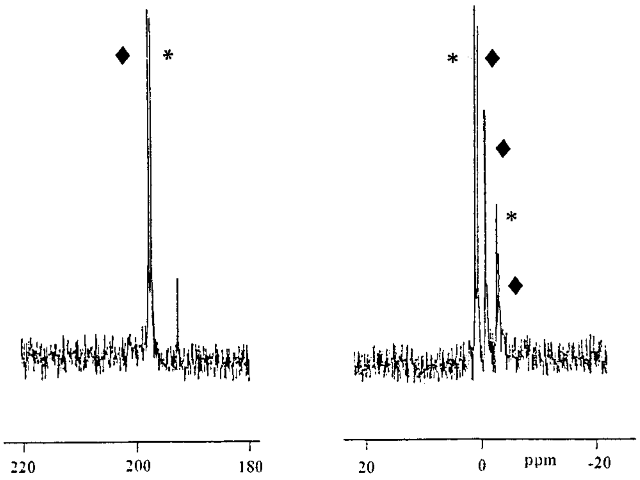

Figure 4. $^{13}C\{^{1}H\}$ NMR spectrum of [$Ni_2(CO)_6(dmsm)$] in $CHCl_3$: (*) resonances attributed to [$Ni_2(CO)_6(dmsm)$], (♦) resonances attributed to [$Ni(CO)_3(\eta^1$-dmsm)].

If the reaction mixture of excess $Ni(CO)_4$ with dmsm in $CHCl_3$ was worked up immmediately after evolution of CO had stopped, a clear viscous oil identified by analysis and mass spectrometry as [$Ni_2(CO)_6(dmsm)$] was obtained. Once isolated, the oil appears to be stable under nitrogen at −20 °C for some weeks but the initial reaction mixture turns black in a few hours. The IR spectrum of the oil, both in a mull and in solution, shows two ν(CO) bands, as expected for structure IV. On standing, the solution decomposes; the ^{1}H NMR spectrum in $CDCl_3$ shows five singlets at δ 0.8♦, 0.9♦, 1.1*, 1.45♦, and 1.6* and singlets in the $^{13}C\{^{1}H\}$ NMR spectrum at δ 197.1♦, 196.6*, 192.0 ($Ni(CO)_4$), 0.4*, −0.1♦, −1.45♦, −3.37*, and −3.81♦ (Figure 4). From the relative intensities and shift patterns we assign the resonances marked by an asterisk (*) to [$Ni_2(CO)_6(dmsm)$] and a solid diamond (♦) to [$Ni(CO)_3(\eta^1$-dmsm)], the latter having structure III. Unfortunately, the reaction does not go to completion and a pure sample of the 1:1 complex has not been isolated. The reaction of $Me_2PCH_2PMe_2$ with $Ni(CO)_4$ produces the chelate [$Ni(CO)_2(Me_2PCH_2PMe_2)$][28] as a white powder sublimable in vacuum, but when [$Ni_2(CO)_6(dmsm)$] was heated *in vacuo* (100 °C/10^{-3} mmHg), it pyrolyzed to a black carbonyl-free solid.

Manganese Complexes. Initial attempts to react $Mn_2(CO)_{10}$ and dpsm either photochemically in *n*-hexane or thf or thermally in *n*-hexane or ethanol failed. The thermal reaction in toluene using [$\{(Cp)Fe(CO)_2\}_2$][22] as a catalyst produced moderate yields of orange [$Mn_2(CO)_8(dpsm)$], which was separated from unreacted starting materials by crystallization from CH_2Cl_2-*n*-hexane. There was no evidence for other products, although with diphosphines (L-L),[37] [$Mn_2(CO)_8$(L-L)], [$Mn_2(CO)_6$(L-L)$_2$], [$Mn_2(CO)_5(dppm)_2$], and mononuclear products form. The IR spectrum of the complex as a Nujol mull shows five terminal and no bridging carbonyl stretches, and the structure is identified as V. Consistent with this structure, the $^{13}C\{^{1}H\}$ NMR spectrum shows three carbonyl resonances in the approximate ratio 1:1:2. The $\delta(CH_2)$ at 3.3 (^{1}H) and 21.1 ($^{13}C\{^{1}H\}$) have shifted considerably to high frequency compared with other complexes, and presumably this reflects the effect of the five-membered metallocyclic ring. Unfortunately, we have been unable to grow crystals of this

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[33] Bodner, G. M.; May, M. P.; McKinney, L. E. *Inorg. Chem.* **1980**, *19*, 1951.

[34] Noak, K. *Helv. Chim. Acta* **1962**, *45*, 1847.

[35] Mass balance requires that other product(s) form, but none were identified, although a grey precipitate was sometimes seen in the NMR tubes.

[36] Mais, R. H. B.; Owston, P. G.; Thompson, D. T.; Wood, A. M. *J. Chem. Soc. A* **1967**, 1744.

[37] (a) Colton, R.; Commons, C. J. *Aust. J. Chem.* **1975**, *28*, 1673. (b) Reimann, R. H.; Singleton, E. *J. Organomet. Chem.* **1972**, *38*, 113.

complex for an X-ray study which would reveal the detailed conformation. Literature examples[38] with this structure are $[Mn_2(CO)_8\{Me_2As\overline{C{=}C(AsMe_2)CF_2C}F_2\}]$ and $[Mn_2(CO)_8(Ph_2AsCH_2AsPh_2)]$. $[Mn_2(CO)_8(dmsm)]$ was made by an analogous route in higher yield and is spectroscopically very similar. Both complexes exhibited very broad ^{55}Mn NMR resonances[39] at δ −2195 (dpsm) and −2317 (dmsm), which may be compared with that in $[Mn_2(CO)_{10}]$ (δ −2353).[39]

When $Re_2(CO)_{10}$ and dpsm were heated together in toluene in the presence of $[\{(Cp)Fe(CO)_2\}_2]$, no reaction was observed after 96 h.

Carbonyl Halides. The reaction of $[FeCl_2(CO)_4]$ with dpsm in CH_2Cl_2 at room temperature produced an unstable orange solid which had ν(CO) at 2018 and 1969 cm^{-1} in a Nujol mull and at 2027 and 1980 cm^{-1} in CH_2Cl_2 solution. The complex decomposed with complete loss of the carbonyl groups in a few hours in CH_2Cl_2 solution and over a period of days in the solid state. From the very similar IR spectrum to that[40] of $[FeBr_2(CO)_2(SbPh_3)_2]$ it seems probable that the complex is $[FeCl_2(CO)_2(\eta^1\text{-dpsm})_2]$, but due to the solution instability we have been unable to obtain an analytically pure sample. No complex was obtained from the corresponding reaction with $[FeI_2(CO)_4]$.

In contrast, stirring $[Mn(CO)_5X]$ (X = Cl, Br, or I) with dpsm in CH_2Cl_2 at room temperature produced orange-red powders *cis*-$[Mn(CO)_4X(dpsm)]$ in good yield. For a *cis* tetracarbonyl arrangement,[41] four IR-active ν(CO) vibrations are expected (theory $2A_1 + B_1 + B_2$) and in practice three or four were observed (Experimental Section). The NMR spectra are consistent with η^1-dpsm, and the ^{55}Mn NMR show a single broad resonance for each complex, shifted to low frequency from those[42] of the parent $[Mn(CO)_5X]$ compound. A similar reaction between $[Mn(CO)_5Br]$ and dmsm in a 2:1 molar ratio gave red $[Mn_2(CO)_8Br_2(dmsm)]$, which has very similar spectroscopic properties and is assigned a related structure with dmsm bridging two *cis*-$Mn(CO)_4Br$ units.

Conclusions

Three coordination modes of the distibinomethanes have been established, viz, monodentate to a single metal center, bridging bidentate between two otherwise unconnected metal centers, and bridging a M−M-bonded system, but no examples of chelation. The diphosphine analogues, $R_2PCH_2PR_2$, exhibit all four bonding modes in appropriate systems.[1,2] The results are consistent with increased strain in the four-membered ring as the donor atom size increases, exacerbated by the weaker bonds being less able to overcome this strain. In the majority of cases, the stibine only substitutes a single carbonyl group per metal center whereas the phosphine analogues often replace more than one. Moreover, the reactions involving the stibines are relatively slow and give poor to moderate yields, suggestive of the weak donor power of the antimony. For isostructural complexes, the ν(CO) frequencies are slightly lower in the stibine complexes compared to the phosphines. The familiar synergic bonding model for the M−CO linkage would attribute lower ν(CO) frequencies to better σ-donation or poorer π-acceptance by the coligands, leading to increased π-acceptance by the CO groups. The poor reactivity of the stibines do not provide support for good σ-donor power, and weaker π-acceptance by the stibine is the most likely effect, as concluded by others in tertiary stibine systems.[15,33]

It should be noted that the low yields do not reflect side reactions; in the majority of cases, monitoring the reactions over time via IR spectroscopy in the carbonyl region and/or NMR spectroscopy of the crude products revealed that only the products described and unreacted reagents were present in significant amounts. C−Sb bond fission was not observed in the reactions described, which was unexpected given the ease with which such fission occurs for Ph_3Sb on reaction with platinum metal halides[14,43] and in some carbonyl systems including $Fe(CO)_5$.[44]

Experimental Section

Physical Measurements. ^1H NMR spectra (300 MHz) were recorded on a Bruker AC300 in $CDCl_3$ solutions and were referenced to the residual ^1H solvent resonance. $^{13}C\{^1H\}$ NMR spectra (90.6 MHz) were obtained on a Bruker AM360 from $CHCl_3/CDCl_3$ or $CH_2Cl_2/CDCl_3$ solutions using a 2 s pulse delay, with added $Cr(acac)_3$ as a relaxation agent, and referenced to $CDCl_3$. ^{55}Mn (89.4 MHz) and ^{59}Co (68.7 MHz) were obtained on a Bruker AM360 from $CHCl_3/CDCl_3$ solutions and referenced to external aqueous $KMnO_4$ and $K_3[Co(CN)_6]$, respectively. IR spectra were obtained as Nujol mulls between NaCl plates for solid samples and from CH_2Cl_2 solutions in 1 mm NaCl solution cells on a Perkin Elmer Paragon 1000. FAB mass spectra were obtained on a VG Analytical 70-250-SE double-focusing mass spectrometer using 3-NOBA as the matrix. Analyses were by the microanalytical service of Imperial College, London.

$Ph_2SbCH_2SbPh_2$ was made as previously described[4] (62%) as white air-stable crystals. ^1H NMR ($CDCl_3$): 2.5 (s, 2H), 7.2−7.6 (m, 20H). $^{13}C\{^1H\}$ NMR ($CHCl_3$): 4.5, 129.0, 136.0, 139.0. EI MS: *m/z* 566, 198, 154. Calcd for $C_{25}H_{22}{}^{121}Sb_2$ 564, $C_6H_5{}^{121}Sb$ 198, $C_{12}H_{10}$ 154.

$Me_2SbCH_2SbMe_2$ was made from $NaSbMe_2$ and CH_2Cl_2 in liquid ammonia as previously described[4] (21%). An alternative route based upon that of Matsumura and Okawara[17] was more convenient. dpsm (20.0 g, 35.5 mmol) was dissolved in dry $CHCl_3$ (100 cm^3) and saturated with dry hydrogen chloride at 0 °C. The white precipitate ($Cl_2SbCH_2SbCl_2$) was isolated by Schlenk filtration and dried *in vacuo* (13.0 g, 93%). To the Grignard reagent prepared from magnesium (3.12 g, 0.13 mol) and iodomethane (18.5 g, 0.13 mol) in diethyl ether (200 cm^3) and dry *N,N,N′,N′*-tetramethylethylenediamine (15.1 g, 0.13 mol) was added dropwise a solution of $Cl_2SbCH_2SbCl_2$ (13.0 g, 0.033 mol) in diethyl ether (200 cm^3), and the yellowish-green solution stirred at room temperature for 4 h and then heated to reflux for 15 min. The mixture was cooled and

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[39] ^{55}Mn 100% I = $^5/_2$, Ξ = 24.8 MHz, $D_c = 1 \times 10^3$, $Q = 0.55 \times 10^{-28}$ m^2; Pregosin, P. S. *Transition Metal Nuclear Magnetic Resonance*; Elsevier: Amsterdam, 1991.

[40] Hieber, W.; Thalhofer, A. *Angew. Chem.* **1956**, *68*, 679. Cohen, I. A.; Basolo, F. *J. Inorg. Nucl. Chem.* **1966**, *28*, 511.

[41] (a) Angelici, R. J.; Basolo, F. *J. Am. Chem. Soc.* **1962**, *84*, 2495. (b) Smith, F. E.; Butler, I. S. *Can. J. Chem.* **1969**, *47*, 1311.

[42] Calderazzo, F.; Lucken, E. A. C.; Williams, D. F. *J. Chem. Soc. A* **1967**, 154. $[Mn(CO)_5Cl]$ δ = −1005, $[Mn(CO)_5Br]$ δ = −1160, $[Mn(CO)_5I]$ δ = −1485.

[43] (a) Chini, R.; Giorgi, G.; Perriccioli, L. *Inorg. Chim. Acta* **1992**, *196*, 7. (b) Mentes, A.; Kemmitt, R. D. W.; Fawcett, J.; Russell, D. R. *J. Organomet. Chem.* **1997**, *528*, 59.

[44] Cane, D. J.; Forbes, E. J.; Silver, J. *J. Organomet. Chem.* **1977**, *129*, 181.

hydrolyzed with deoxygenated saturated ammonium chloride solution (200 cm^3). The organic layer was separated and dried ($MgSO_4$), and the solvent was removed by distillation under nitrogen. The residue was fractionated *in vacuo* at 40 °C/0.2 torr to yield $Me_2SbCH_2SbMe_2$ (2.5 g, 24%) as a colorless, pyrophoric oil. ^{1}H NMR ($CDCl_3$): 1.1 (s, 2H), 0.8 (s, 12H). ^{13}C{^{1}H} NMR ($CHCl_3$): −1.6, −4.3. EI MS: *m/z* 318, 303. Calcd for $C_5H_{14}{}^{121}Sb_2$ 316, $C_4H_{11}{}^{121}Sb_2$ 301. The ligand was also made in poor yield (*ca.* 15%) from $Cl_2SbCH_2SbCl_2$ and MeLi in diethyl ether.

All complex preparations were carried out under a nitrogen atmosphere.

[Fe(CO)$_4$(dpsm)]. $Fe_2(CO)_9$ (0.46 g, 1.3 mmol) and dpsm (0.72 g, 1.26 mmol) were stirred in thf (50 cm^3) at room temperature for 18 h. The mixture was filtered, and the filtrate was evaporated *in vacuo*. The residue was dissolved in a minimum amount of CH_2Cl_2, and pentane was added to produce an orange precipitate (0.41 g, 44%). Anal. Calcd for $C_{29}H_{22}FeO_4Sb_2$: C, 47.4; H, 3.0. Found: C, 47.6; H, 3.1. ^{1}H NMR ($CDCl_3$): 2.45, 7.4−7.8. ^{13}C{^{1}H} NMR ($CDCl_3$): 5.4, 126−140, 213.3. FAB MS (3-NOBA): *m/z* 734, 706. Calcd for [$^{56}Fe(Ph_2{}^{121}SbCH_2{}^{121}SbPh_2)(CO)_4$] 732, [P − CO] 704. IR (ν(CO)): Nujol mull 2043 (m), 1970 (w), 1940 (s), 1920 (m) cm^{-1}; CH_2Cl_2 2042 (m), 1970 (m), 1932 (vs) cm^{-1}.

[Fe$_2$(CO)$_8$(dmsm)] was prepared similarly from $Fe_2(CO)_9$ (3.3 mmol) and dmsm (1.15 mmol). After evaporation of the solvent, the residue was dried *in vacuo*. It was redissolved in CH_2Cl_2 and precipitated with pentane to afford a pale orange solid, which was dried *in vacuo* (39%). Anal. Calcd for $C_{13}H_{14}Fe_2O_8Sb_2$: C, 23.9; H, 1.8. Found: C, 23.8; H, 2.1. ^{1}H NMR ($CDCl_3$): 1.45, 2.2. ^{13}C{^{1}H} NMR ($CHCl_3$): 1.3, 1.6, 213.6. FAB MS (3-NOBA): *m/z* 598, 461. Calcd for [$^{56}Fe_2(Me_2{}^{121}SbCH_2{}^{121}SbMe_2)(CO)_6$] 598, [P − 7CO] 458. IR (ν(CO)): Nujol mull 2038 (s), 1961 (s), 1928 (s); CH_2Cl_2 2040 (s), 1963 (m), 1931 (vs) cm^{-1}.

[Co$_2$(CO)$_6$(dpsm)]. [$Co_2(CO)_8$] (0.73 g, 2.14 mmol) and dpsm (1.21 g, 2.14 mmol) were stirred in benzene (80 cm^3) at room temperature until evolution of CO ceased (*ca.* 2 h). The solvent was removed *in vacuo*, and the red residue was dissolved in CH_2Cl_2 and filtered. The filtrate was concentrated to 10 cm^3, and *n*-hexane was added dropwise. The red precipitate was isolated by filtration and dried *in vacuo* (1.4 g, 77%). Anal. Calcd for $C_{31}H_{22}Co_2O_6Sb_2$: C, 43.7; H, 2.6. Found: C, 43.8; H, 2.3. ^{1}H NMR ($CDCl_3$): 1.9, 7.4−7.8. ^{13}C{^{1}H} NMR (CH_2Cl_2): −2.2, 127−139, 216.5. ^{59}Co NMR (CH_2Cl_2): −1820 ($w_{1/2}$ = 14 000 Hz). FAB MS (3-NOBA): *m/z* 768, 740, 712. Calcd for [$Co_2(Ph_2{}^{121}SbCH_2{}^{121}SbPh_2)(CO)_3$] 766. IR ($\nu$(CO)): Nujol mull 2043 (s), 2006 (s),1967 (s), 1832 (s), 1773 (s) cm^{-1}; CH_2Cl_2 2044 (s), 2111 (s), 1987 (s), 1825 (m), 1772 (m) cm^{-1}.

[Co$_2$(CO)$_6$(dmsm)] was prepared similarly from [$Co_2(CO)_8$] (0.32 g, 0.93 mmol) and dmsm (0.30 g, 0.93 mmol) in benzene as dark red crystals (0.34 g, 61%). Anal. Calcd for $C_{11}H_{14}Co_2O_6Sb_2$: C, 21.9; H, 2.3. Found: C, 22.1; H, 2.3. ^{1}H NMR ($CDCl_3$): 1.42 (2H), 1.36 (12H). ^{13}C{^{1}H} NMR (CH_2Cl_2): −7.4, −1.3, 217.5. ^{59}Co NMR (CH_2Cl_2): −1710 ($w_{1/2}$ = 12 000 Hz). FAB MS (3-NOBA): *m/z* 604, 576, 548, 520, 492, 464, 436. Calcd for [$Co_2(CO)_6(Me_2{}^{121}SbCH_2{}^{121}SbMe_2)$] 602, other peaks are due to sequential loss of CO's. IR (ν(CO)): Nujol mull 2031 (s), 1998 (s), 1987 (m), 1969 (s), 1947 (m), 1805 (s), 1772 (sh), 1764 (s) cm^{-1}; CH_2Cl_2 2037 (s), 2003 (s), 1977 (s), 1815 (m), 1764 (m) cm^{-1}.

[Ni(CO)$_3$(dpsm)]. (CARE: $Ni(CO)_4$ is volatile and very toxic. All reactions were performed in sealed vessels in a good hood, and residues were destroyed with bromine.) dpsm (0.57 g, 1.0 mmol) was dissolved in $CHCl_3$ (5 cm^3), and $Ni(CO)_4$ (0.17 g, 1.0 mmol) was added. The mixture was stirred at room temperature for 3 h, and the solvent was removed *in vacuo*. The white oily residue was stirred with diethyl ether (20 cm^3) producing a white powder, which was separated by filtration and dried *in vacuo* (0.54 g, 76%). Anal. Calcd for $C_{28}H_{22}NiO_3Sb_2$: C, 47.4; H, 3.1. Found: C, 47.5; H, 3.0. ^{1}H NMR ($CDCl_3$): 2.3 (2H), 7.2−7.6 (20H). ^{13}C{^{1}H} NMR ($CHCl_3$): 1.3, 128−139, 196.8. IR (ν(CO)): Nujol mull 2072 (m), 1999 (s) cm^{-1}; CH_2Cl_2 2072 (m), 2004 (s) cm^{-1}.

[Ni$_2$(CO)$_6$(dpsm)]. dpsm (0.566 g, 1.0 mmol) was dissolved in $CHCl_3$ (5 cm^3), and $Ni(CO)_4$ (0.34 g, 2.0 mmol) was added. The mixture was stirred at room temperature for 3 h, and then the solvent was removed *in vacuo*. The product was a white waxy solid (0.68 g, 80%). Anal. Calcd for $C_{31}H_{22}Ni_2O_6Sb_2$: C, 43.7; H, 2.6. Found: C, 43.3; H, 3.0. ^{1}H NMR ($CDCl_3$): 2.5 (2H), 7.2−7.6 (20H). ^{13}C{^{1}H} NMR ($CHCl_3$): 2.9, 129−138, 196.3. FAB MS: *m/z* 738, 707, 679. Calcd for [$^{58}Ni_2(Ph_2{}^{121}SbCH_2{}^{121}SbPh_2)(CO)_2$] 736, [$^{58}Ni(Ph_2{}^{121}SbCH_2{}^{121}SbPh_2)(CO)_3$] 706, [$^{58}Ni(Ph_2{}^{121}SbCH_2{}^{121}SbPh_2)(CO)_2$] 678. IR ($\nu$(CO)): Nujol mull 2070 (m), 2000 (s) cm^{-1}; CH_2Cl_2 2072 (m), 1998 (s) cm^{-1}.

[Ni$_2$(CO)$_6$(dmsm)]. A solution of dmsm (0.44 g, 1.4 mmol) in $CHCl_3$ (15 cm^3) was treated with an excess of $Ni(CO)_4$ (0.59 g, 3.5 mmol), and the mixture was stirred until evolution of CO ceased (*ca.* 1 h). The excess $Ni(CO)_4$ and the solvent were removed *in vacuo*, and the residue was pumped at 10^{-2} mmHg for 3 h. The product was a colorless, viscous oil which did not solidify on cooling for some days at −20 °C (0.69 g, 82%). Anal. Calcd for $C_{11}H_{14}Ni_2O_6Sb_2$: C, 21.9; H, 2.3. Found: C, 21.6; H, 2.5. ^{1}H NMR ($CDCl_3$): 1.1 (12H), 1.6 (2H). ^{13}C{^{1}H} NMR ($CHCl_3$): see text and Figure 4. FAB MS *m/z* 602. Calcd for [$^{58}Ni_2(Me_2{}^{121}SbCH_2{}^{121}SbMe_2)(CO)_6$] 600. IR($\nu$(CO)): Nujol mull 2067 (m), 1994 (s); CH_2Cl_2 2067 (m), 1994 (s) cm^{-1}.

[Mn$_2$(CO)$_8$(dpsm)]. $Mn_2(CO)_{10}$ (0.25 g, 0.65 mmol), dpsm (0.64 g, 1.1 mmol), and [{(Cp)Fe(CO)$_2$}$_2$] (0.15 mmol) were dissolved in degassed toluene (10 cm^3). The mixture was refluxed for 24 h, and then the toluene was removed *in vacuo*. The residue was dissolved in a minimum amount of CH_2Cl_2, *n*-hexane was added dropwise, and an orange solid precipitated, which was isolated by filtration and dried *in vacuo* (0.12 g, 21%). Anal. Calcd for $C_{33}H_{22}Mn_2O_8Sb_2$: C, 44.0; H, 2.4. Found: C, 44.1; H, 2.1. ^{1}H NMR ($CDCl_3$): 3.3 (2H), 7.4−7.8 (20H). ^{13}C{^{1}H} NMR (CH_2Cl_2): 21.1, 128−135, 221.0, 224.0, 225.9. ^{55}Mn NMR (CH_2Cl_2): −2195 ($w_{1/2}$ 20 000 Hz). FAB MS (3-NOBA): *m/z* 816, 788, 760, 732, 704, 676. Calcd for [$Mn_2(Ph_2{}^{121}SbCH_2{}^{121}SbPh_2)(CO)_5$] 814, remainder are due to successive loss of CO groups. IR(ν(CO)): Nujol mull 2051 (m), 1985 (m), 1964 (s), 1910 (sh), 1902 (s) cm^{-1}; CH_2Cl_2 2020 (w), 1975 (sh), 1965 (m), 1913 (s) cm^{-1}.

[Mn$_2$(CO)$_8$(dmsm)]. $Mn_2(CO)_{10}$ (0.45 g, 1.15 mmol), dmsm (0.36 g, 1.15 mmol), and [{(Cp)Fe(CO)$_2$}$_2$] (0.08 g, 0.23 mmol) were dissolved in degassed toluene (30 cm^3) and refluxed for 28 h. The mixture was filtered, and the filtrate was taken to dryness *in vacuo*. Recrystallization of the residue from CH_2Cl_2−*n*-hexane (1:10 v/v) gave a rust-colored solid (0.26 g, 35%). Anal. Calcd for $C_{13}H_{14}Mn_2O_8Sb_2$: C, 23.9; H, 2.2. Found: C, 24.1; H, 2.2. ^{1}H NMR ($CDCl_3$): 2.15 (2H), 1.3 (12H). ^{13}C{^{1}H} NMR (CH_2Cl_2): −0.5, 16.0, 221.2, 224.2, 227.0. ^{55}Mn NMR (CH_2Cl_2): −2317 ($w_{1/2}$ = 4000 Hz). FAB MS (3-NOBA): *m/z* 652, 624. Calcd for [$Mn_2(CO)_8(Me_2{}^{121}SbCH_2{}^{121}SbMe_2)$] 650, [$Mn_2(CO)_7(Me_2{}^{121}SbCH_2{}^{121}SbMe_2)$] 622. IR($\nu$(CO)): Nujol mull 2042 (m), 2002 (sh), 1988 (sh), 1942 (s), 1899 (m) cm^{-1}; CH_2Cl_2 2047 (s), 1983 (s), 1961 (s), 1931 (m), 1912 (m) cm^{-1}.

[Mn(CO)$_4$Cl(dpsm)]. [$Mn(CO)_5Cl$] (0.17 g, 0.74 mmol) was dissolved in $CHCl_3$ (8 cm^3), and dpsm (0.42 g, 0.74 mmol) was added. The mixture was stirred for 24 h at room temperature, and then the chloroform was evaporated in a stream of nitrogen. The resulting oil was dried *in vacuo* and then washed with *n*-pentane (3 × 10 cm^3) producing an orange powder, which was separated and dried *in vacuo* (0.41 g, 72%). Anal. Calcd for $C_{29}H_{22}ClMnO_4Sb_2$: C, 45.3; H, 2.9. Found: C, 45.8; H, 2.8. ^{1}H NMR ($CDCl_3$): 2.45 (2H), 7.4−7.8 (20H). ^{13}C{^{1}H} NMR (CH_2Cl_2): 2.2, 128−139, 212.3, 215.1, 219.0. ^{55}Mn NMR (CH_2Cl_2): −1277 ($w_{1/2}$ = 5000 Hz). FAB MS (3-NOBA): *m/z* 654. Calcd for [$Mn(Ph_2{}^{121}SbCH_2{}^{121}SbPh_2){}^{35}Cl$] 654. IR($\nu$(CO)): Nujol mull 2084 (m), 2021 (m), 2000 (s), 1932 (m) cm^{-1}; CH_2Cl_2 2088 (m), 2010 (s), 1954 (m) cm^{-1}.

[Mn(CO)$_4$Br(dpsm)] was prepared similarly from [$Mn(CO)_5Br$], although a 48 h reaction time was used (76%). Anal.

Table 4. Crystal Data for $Ph_2SbCH_2SbPh_2$, $[Fe(CO)_4(Ph_2SbCH_2SbPh_2)]$, and $[Co_2(CO)_6(Me_2SbCH_2SbMe_2)]$

compound	$Ph_2SbCH_2SbPh_2$	$[Fe(CO)_4(Ph_2SbCH_2SbPh_2)]$	$[Co_2(CO)_6(Me_2SbCH_2SbMe_2)]$
formula	$C_{25}H_{22}Sb_2$	$C_{29}H_{22}FeO_4Sb_2$	$C_{11}H_{14}Co_2O_6Sb_2$
fw	565.95	733.84	603.59
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a/Å	10.674(5)	8.766(9)	9.050(4)
b/Å	11.864(6)	27.820(47)	15.244(5)
c/Å	9.368(5)	11.316(8)	12.727(5)
α/deg	108.17(4)	90.0	90.0
β/deg	90.18(4)	96.11(7)	98.82(3)
γ/deg	108.31(3)	90.0	90.0
volume/Å^3	1063.5(1.0)	2744(6)	1735.2(1.1)
2θ range for cell/deg	49.8−51.1	45.1−49.7	19.0−23.0
T/K	150	150	150
D_c (calcd), g cm^{-3}	1.767	1.776	2.310
Z	2	4	4
$F(000)$/e	548	1424	1136
cryst size/mm	0.6 × 0.6 × 0.3	0.65 × 0.60 × 0.20	0.62 × 0.1 × 0.03
scan mode	$\omega-2\theta$	ω	$\omega-2\theta$
total no. of obsns	3945	5293	3395
no. of unique obsns	3725 ($R_{int} = 0.014$)	4959 ($R_{int} = 0.032$)	3186 ($R_{int} = 0.126$)
hkl range	0−12, −14 to 13, −11 to 11	0−10, 0−33, −13 to 13	0−10, 0−18, −15 to 14
abs corr	ψ-scan (3 refs)	ψ-scan (3 refs)	ψ-scan (3 refs)
min, max transmission	0.69, 1.00	0.510, 1.000	0.762, 1.000
no. of data in refinement	3487 ($I > 3\sigma(I)$)	4146 ($I > 2.5\sigma(I)$)	1987 ($I > 3\sigma(I)$)
no. of params	245	325	190
weighting scheme (w^{-1})	$\sigma^2(F_o)$	$\sigma^2(F_o)$	$\sigma^2(F_o)$
λ/Å (Mo Kα)	0.710 69	0.710 69	0.710 69
μ/cm^{-1}	25.43	25.05	49.74
max 2θ/deg	50.0	50.0	50.0
S	3.4	3.00	2.22
max shift/esd	0.02	0.01	0.01
resid electron density/e Å^{-3}	0.66 to −0.66	1.20 to −2.57	1.90 to −2.12
R, wR^a	0.023, 0.037	0.049, 0.080	0.050, 0.063

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$; w$R = [\sum w(F_o - F_c)^2/\sum wF_o{}^2]^{1/2}$.

Calcd for $C_{29}H_{22}BrMnO_4Sb_2$: C, 42.8; H, 2.7. Found: C, 42.6; H, 3.0. ^{1}H NMR ($CDCl_3$): 2.55 (2H), 7.2−7.6 (20H). $^{13}C\{^1H\}$ NMR (CH_2Cl_2): 3.7, 129−139, 210.5, 212 (sh), 215.8. ^{55}Mn NMR (CH_2Cl_2): −1410 ($w_{1/2}$ = 10 000 Hz). FAB MS (3-NOBA): *m/z* 698, 619. Calcd for $[Mn(Ph_2{}^{121}SbCH_2{}^{121}SbPh_2)-{}^{79}Br]$ 698. IR(ν(CO)): Nujol mull 2079 (s), 2015 (s), 1991 (s), 1956 (s) cm^{-1}; CH_2Cl_2 2084 (m), 2006 (s), 1955 (m) cm^{-1}.

$[Mn(CO)_4I(dpsm)]$. $[Mn(CO)_5I]$ (0.323 g, 1.0 mmol) was dissolved in $CHCl_3$ (30 cm^3), and dpsm (0.57 g, 1.0 mmol) was added. The mixture was heated to 50 °C and stirred for 24 h at this temperature. The chloroform was evaporated in a stream of nitrogen, and the resulting red oil was dried *in vacuo*. It was washed with *n*-pentane (3 × 10 cm^3) producing an orange powder, which was separated and dried *in vacuo* (0.57 g, 66%). Anal. Calcd for $C_{29}H_{22}IMnO_4Sb_2$: C, 40.4 ; H, 2.5. Found: C, 40.1; H, 2.1. ^{1}H NMR ($CDCl_3$): 2.85 (2H), 7.3−7.9 (20H). $^{13}C\{^1H\}$ NMR (CH_2Cl_2): 5.9, 129−139, 211.7, 212.8, 218.0. ^{55}Mn NMR (CH_2Cl_2): −1732 ($w_{1/2}$ = 12 000 Hz). IR (ν(CO)): Nujol mull 2077 (m), 2011 (sh), 2001 (s), 1955 (m) cm^{-1}; CH_2Cl_2 2077 (m), 2010 (sh), 2000 (s), 1958 (m) cm^{-1}.

$[Mn_2(CO)_8Br_2(dmsm)]$. $[MnBr(CO)_5]$ (0.83 g, 3.0 mmol) was dissolved in $CHCl_3$ (8 cm^3), and dmsm (0.48 g, 1.5 mmol) was added. The mixture was stirred at room temperature for 48 h, and then the chloroform was evaporated in a stream of nitrogen. The resulting oil was dried *in vacuo*, then washed with *n*-pentane (3 × 10 cm^3), and an orange powder formed (0.41 g, 34%). Anal. Calcd for $C_{13}H_{14}Br_2Mn_2O_8Sb_2$: C, 19.3; H, 1.7. Found: C, 19.0; H, 2.0. ^{1}H NMR ($CDCl_3$): 1.5 (12H), 2.2 (2H). $^{13}C\{^1H\}$ NMR ($CHCl_3$): 220.5, 216.8, 212.3, −0.2, −5.9. ^{55}Mn NMR (CH_2Cl_2): −1465 ($w_{1/2}$ = 8700 Hz). FAB MS (3-NOBA): *m/z* 540, 484, 453. Calcd for $[Mn_2(Me_2{}^{121}SbCH_2{}^{121}SbMe_2)(CO)_4]$ 538, $[Mn_2(Me_2{}^{121}SbCH_2{}^{121}SbMe_2)(CO)_2]$ 482, $[Mn^{79}Br(Me_2{}^{121}SbCH_2{}^{121}SbMe_2)]$ 450. IR(ν(CO)): Nujol mull 2079 (m), 2000 (s), 1940 (s), 1903 (m); CH_2Cl_2 2084 (m), 2004 (s), 1966 (m), 1916 (w) cm^{-1}.

X-ray Structure of $Ph_2SbCH_2SbPh_2$, $[Fe(CO)_4(Ph_2SbCH_2SbPh_2)]$, and $[Co_2(CO)_6(Me_2SbCH_2SbMe_2)]$. Suitable crystals of the free ligand were grown during attempts to grow crystals of the $[W(CO)_5(dpsm)]$ complex from CH_2Cl_2/EtOH, the iron complex from a CH_2Cl_2 solution of the complex on cooling, and the cobalt complex from a solution in CH_2Cl_2/toluene/ether in the dark. Data were collected using a Rigaku AFC7S diffractometer fitted with Mo Kα radiation, a graphite monochromator, and Oxford Cryosystems low-temperature device running at 150 K, and crystal data are given in Table 4. The structures were solved using the direct methods in SHELXS-86[45] to locate the heavy atoms, and a number of light atoms and all remaining non-H atoms were found by structure-factor and electron-density calculations. Hydrogen atoms were positioned geometrically (d(C−H) = 0.95 Å) for the Fe and Co complex but located in later electron-density maps for the free ligand, where they were added to the model but not refined. Full-matrix least-squares refinement on F with anisotropic non-H atoms was carried out using the teXsan package.[46]

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Supporting Information Available: Tables of crystal data, atomic coordinates, anisotropic displacement parameters, and bond lengths and angles (20 pages). Ordering information is given on any current masthead page.

OM9706121

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(46) *teXsan, crystal structure analysis package* (version 1.7-1); Molecular Structure Corp.: The Woodlands, TX, 1995.