

The transition metal carbonyl complexes of 1,3-bis(di-R-stibino)propanes (R = Me or Ph)

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Abstract

The synthesis and characterisation of complexes of two distibinopropanes $R_2Sb(CH_2)_3SbR_2$ (R = Me or Ph) with a variety of metal carbonyls is described. These include *cis*- $[M(CO)_4\{R_2Sb(CH_2)_3SbR_2\}]$ (M = Cr, Mo or W), $\{[Fe(CO)_4]_2\{\mu-R_2Sb(CH_2)_3SbR_2\}\}$, $\{[Ni(CO)_3]_2\{\mu-R_2Sb(CH_2)_3SbR_2\}\}$, $[Co_2(CO)_6\{\mu-R_2Sb(CH_2)_3SbR_2\}]$, $[Co_2(CO)_4\{Me_2Sb(CH_2)_3SbMe_2\}]$, $[Co(CO)_4]_2$ and $[Mn_2(CO)_8\{\mu-R_2Sb(CH_2)_3SbR_2\}]$. The complexes have been characterised by analysis, mass spectrometry, IR and multinuclear NMR spectroscopy as appropriate. Comparison of the spectroscopic data on these complexes with those of other stibine complexes and with complexes of Group 16 ligands has been used to establish the relative electronic properties of the distibines.

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Keywords: Chromium; Molybdenum; Tungsten; Iron; Manganese; Nickel; Carbonyls; Stibines

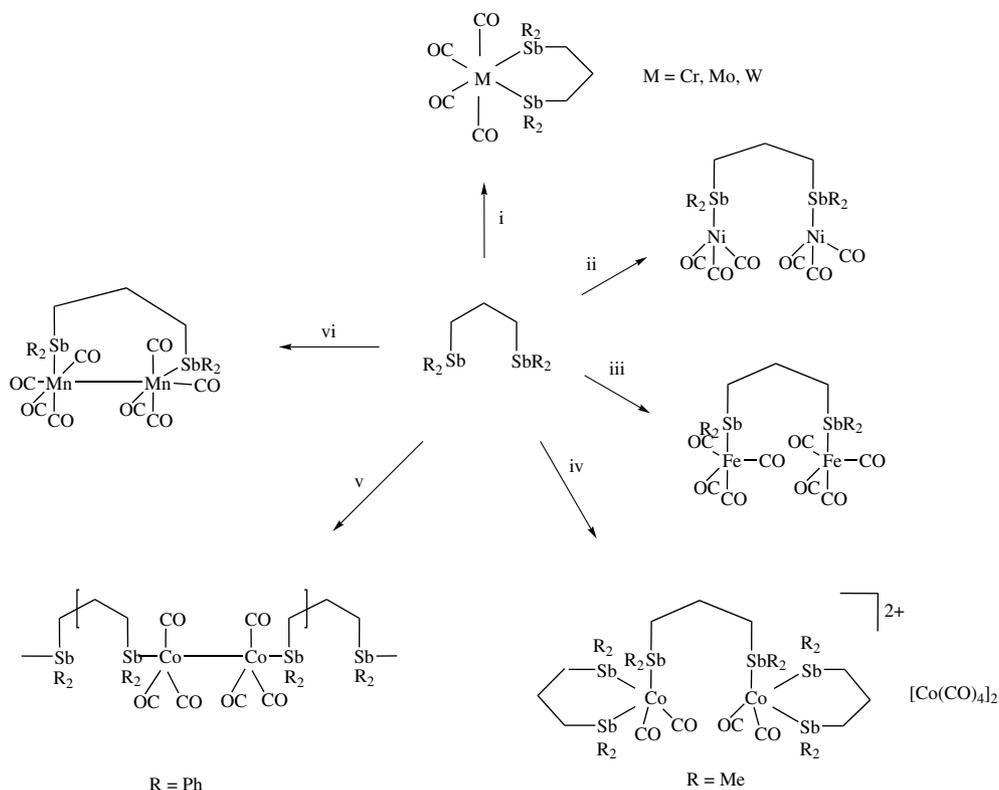
1. Introduction

Although the first examples of ligands containing two antimony donors were reported over 30 years ago [1–4] studies of their coordination chemistry remain few, a remarkable fact given the many hundreds of papers dealing with bi- and polydentate phosphorus and arsenic ligands. We have recently carried out detailed studies of the metal carbonyl chemistry of two types of distibine: the distibinomethanes ($R_2SbCH_2SbR_2$, R = Me or Ph) and three xylyl-backed ligands 1,2-, 1,3-, and 1,4-bis(dimethylstibanylmethyl)benzene (1,2-, 1,3- or 1,4- $C_6H_4(CH_2SbMe_2)_2$). The $Ph_2SbCH_2SbPh_2$ ligand exhibits a variety of coordination modes with substituted metal carbonyls – monodentate as in $[Fe(CO)_4(Ph_2SbCH_2SbPh_2)]$, bridging bidentate in $[(CO)_5W(Ph_2SbCH_2SbPh_2)W(CO)_5]$ or $[(CO)_4W(Ph_2SbCH_2SbPh_2)_2W(CO)_4]$, and bridging across M–M bonds as in $[Mn_2(CO)_6(Ph_2SbCH_2SbPh_2)_2]$ or $[Co_2-$

$(CO)_6(Ph_2Sb-CH_2SbPh_2)]$ [5–7]. The $Me_2SbCH_2SbMe_2$ is generally similar, although few η^1 -coordinated examples are known, probably due to the air sensitivity of the “free” Me_2Sb -group [5,6]. Notably, neither ligand appeared to chelate with metal carbonyl centres, although rare examples of chelation (4-membered chelate rings) were produced in ruthenium and rhodium halides [8]. The 1,3- and 1,4-bis(dimethylstibanylmethyl)benzene behave as either monodentate or bridging bidentate ligands towards tungsten, nickel or iron carbonyl moieties [9]. The 1,2-bis(dimethylstibanylmethyl)benzene gave the chelated dicarbonyl species $[Ni(CO)_2\{o-C_6H_4(CH_2SbMe_2)_2\}]$ and $[M(CO)_4\{o-C_6H_4(CH_2SbMe_2)_2\}]$ (M = Mo or W), whilst bridging bidentate behaviour was found in $\{[Fe(CO)_4]_2\{o-C_6H_4(CH_2SbMe_2)_2\}\}$ [9].

A few Group 6 metal carbonyl complexes of $o-C_6H_4(SbMe_2)_2$ [10] and $Ph_2Sb(CH_2)_3SbPh_2$ [11] were reported in the early 1970s, but with little data. We have now carried out systematic studies of the complexes of the two distibinopropanes $R_2Sb(CH_2)_3SbR_2$ (R = Me or Ph) with chromium, molybdenum, tungsten,

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Reagents: i. $[M(CO)_4(nbd)]$ in EtOH, $M = Cr, Mo$ or $[W(CO)_4(piperidine)_2]$ in EtOH; ii. $Ni(CO)_4$ in CH_2Cl_2 ; iii. $Fe_2(CO)_9$ in thf; iv. and v. $Co_2(CO)_8$ in toluene; vi. $Mn_2(CO)_{10}$ in toluene with $[CpFe(CO)_2]_2$

Scheme 1. Syntheses of the distibinopropane complexes.

manganese, iron, cobalt and nickel carbonyls, and report our results below (see Scheme 1).

2. Results and discussion

The $Ph_2Sb(CH_2)_3SbPh_2$ was obtained by the literature route [3] from $NaSbPh_2$ and $Br(CH_2)_3Br$ in liquid ammonia. The methyl analogue was made similarly from $NaSbMe_2$ [4,12], although this was generated *in situ* by a modified procedure in liquid NH_3 from the air stable Me_3SbBr_2 and 4 equivalents of Na, rather than from very reactive Me_2SbBr . $Ph_2Sb(CH_2)_3SbPh_2$ is an air-stable white solid, whereas the methyl analogue is a very air-sensitive colourless oil. The ligands were identified by comparison of their 1H NMR spectra with literature data [3,4]. The $^{13}C\{^1H\}$ NMR spectra are also characteristic, exhibiting the usual [5] low frequency resonances for C–Sb units.

2.1. Group 6 complexes

The displacement of the olefin or amine from $[M(CO)_4(norbornadiene)]$ ($M = Cr$ or Mo) or $[W(CO)_4(piperidine)_2]$ by the appropriate distibine gave $[M(CO)_4(distibine)]$ in modest yield. Direct substitution

of carbon monoxide in the $M(CO)_6$ by the distibine, catalysed by $NaBH_4$ was a less satisfactory route, although one example ($[Cr(CO)_4\{Ph_2Sb(CH_2)_3SbPh_2\}]$) made in this way is described in the Experimental Section. The solid tetracarbonyl complexes are air-stable, but the solutions in chlorocarbons are more sensitive, and should be manipulated under dinitrogen. The complexes of $Me_2Sb(CH_2)_3SbMe_2$ were poorly soluble in CH_2Cl_2 although they dissolve easily in dimethylsulfoxide, and the latter was used as a solvent for $^{13}C\{^1H\}$ NMR studies. The formulation of the complexes as *cis*- $[M(CO)_4(distibine)]$ follows from their IR spectra which show three or four carbonyl stretches (theory $2A_1 + B_1 + B_2$). The $^{13}C\{^1H\}$ NMR spectra show two $\delta(CO)$ resonances of equal intensity in each complex and, in the case of tungsten, weak satellites due to $^1J(^{183}W-^{13}C)$ couplings, the magnitude of the coupling *trans* to Sb (165 Hz) placing the stibines low in the *trans* influence series [13], reflecting the weak σ -donation by the antimony.

2.2. Iron complexes

Both ligands react with 2 equivalents of $Fe_2(CO)_9$ in thf solution to give, after removal of the solvent and the $Fe(CO)_5$ by-product, red oils identified spectroscopically

as $[(\text{CO})_4\text{Fe}(\mu\text{-distibine})\text{Fe}(\text{CO})_4]$, containing axially substituted trigonal bipyramidal iron centres [5,9,14]. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectra show single (CO) resonances attributable to fluxionality of the carbonyl groups as is usually seen [9]. For an axially substituted *tbp* geometry three IR active CO stretches are expected ($2A_1 + E$) and three were observed for $[\{\text{Fe}(\text{CO})_4\}_2\{\text{Ph}_2\text{Sb}(\text{CH}_2)_3\text{SbPh}_2\}]$ both in a Nujol mull and CH_2Cl_2 solution. However, for $[\{\text{Fe}(\text{CO})_4\}_2\{\text{Me}_2\text{Sb}(\text{CH}_2)_3\text{SbMe}_2\}]$ whilst three bands were seen in CH_2Cl_2 , in the mull spectrum a distinct shoulder was present on the lowest band, indicating some lowering of symmetry. Similar effects have been reported in some iron carbonyl diphosphine complexes [14]. The reaction of $\text{Fe}_2(\text{CO})_9$ in *thf* with $\text{Ph}_2\text{Sb}(\text{CH}_2)_3\text{SbPh}_2$ in a 1:1 mol ratio also gave a red oil in which the major species was identified as $[\{\text{Fe}(\text{CO})_4\}\{\eta^1\text{-Ph}_2\text{Sb}(\text{CH}_2)_3\text{SbPh}_2\}]$. The IR vibrations and $^{13}\text{C}\{^1\text{H}\}$ NMR of the carbonyl groups in this complex are not significantly different from those in the 2:1 complex, as expected since the trimethylene chain electronically isolates the two antimony centres. However, the formulation as $[\{\text{Fe}(\text{CO})_4\}\{\eta^1\text{-Ph}_2\text{Sb}(\text{CH}_2)_3\text{SbPh}_2\}]$ follows from the three major CH_2 resonances in the NMR spectra. Weak features in the same region are attributable to some $[\{\text{Fe}(\text{CO})_4\}_2\{\text{Ph}_2\text{Sb}(\text{CH}_2)_3\text{SbPh}_2\}]$ by comparison with the spectra of the complex discussed above. Displacement of a second carbonyl group from iron to give $[\text{Fe}(\text{CO})_3(\text{distibine})]$ is not expected under such mild conditions [14] and was not observed.

2.3. Nickel complexes

Like other nickel carbonyl distibines [5,9], the complexes formed by the distibinopropanes were unstable,

significantly decomposing in a few hours at ambient temperatures with deposition of black solids. Despite this instability the spectroscopic data required to correlate the electronic properties of these ligands with other stibines are readily extracted (Table 1). The reaction of excess $\text{Ni}(\text{CO})_4$ with $\text{Me}_2\text{Sb}(\text{CH}_2)_3\text{SbMe}_2$ in CH_2Cl_2 proceeded rapidly at room temperature with visible evolution of CO to form $[(\text{CO})_3\text{Ni}\{\mu\text{-Me}_2\text{Sb}(\text{CH}_2)_3\text{SbMe}_2\}\text{Ni}(\text{CO})_3]$ as the only product, which was isolated as a colourless wax on removal of the excess tetracarbonylnickel and the solvent *in vacuo*. The formulation as a tricarbonyl dimer follows from the characteristic $^{13}\text{C}\{^1\text{H}\}$ NMR $\delta(\text{CO})$ value and two IR active carbonyl stretches (theory $A_1 + E$). The presence of one $\delta(\text{Me})$ and two $\delta(\text{CH}_2)$ resonances in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra confirm bidentate coordination of the distibine. If the reaction is repeated using a deficit of $\text{Ni}(\text{CO})_4$, the product is a mixture of a tricarbonyl and a dicarbonyl complex (see Section 3). However, none of the frequencies of the three Me and five CH_2 resonances observed in the NMR spectra of the mixture match with those of $[(\text{CO})_3\text{Ni}\{\text{Me}_2\text{Sb}(\text{CH}_2)_3\text{SbMe}_2\}\text{Ni}(\text{CO})_3]$ or with free $\text{Me}_2\text{Sb}(\text{CH}_2)_3\text{SbMe}_2$. Hence we formulate the tricarbonyl as $[(\text{CO})_3\text{Ni}\{\eta^1\text{-Me}_2\text{Sb}(\text{CH}_2)_3\text{SbMe}_2\}]$, and the dicarbonyl as $[\text{Ni}(\text{CO})_2\{\text{Me}_2\text{Sb}(\text{CH}_2)_3\text{SbMe}_2\}]$, the latter containing chelating distibine. Several attempts to convert the products completely to the dicarbonyl either by prolonged stirring or heating of the reaction mixture failed, only decomposition occurred. In the case of $\text{Ph}_2\text{Sb}(\text{CH}_2)_3\text{SbPh}_2$ the reaction with excess $\text{Ni}(\text{CO})_4$ in CH_2Cl_2 solution was much slower, and after several hours *in situ* IR studies showed a mixture of a tricarbonyl, a dicarbonyl and unchanged tetracarbonylnickel present. The solution darkened over time indicating

Table 1
Spectroscopic data for $[\text{Ni}(\text{CO})_3(\text{ligand})]$ or $[(\text{CO})_3\text{Ni}(\text{ligand})\text{Ni}(\text{CO})_3]$

Ligand	$\nu(\text{CO})$ (cm^{-1}) ^a	^{13}C CO (ppm) ^a	References
$\text{Ph}_2\text{Sb}(\text{CH}_2)_3\text{SbPh}_2$	2071, 1996	196.8	b
$\text{Me}_2\text{Sb}(\text{CH}_2)_3\text{SbMe}_2$	2067, 1989	197.1	b
<i>m</i> - $\text{C}_6\text{H}_4(\text{CH}_2\text{SbMe}_2)_2$	2068, 1993	197.0	[9]
<i>p</i> - $\text{C}_6\text{H}_4(\text{CH}_2\text{SbMe}_2)_2$	2068, 1993	197.1	[9]
<i>m</i> - $\text{C}_6\text{H}_4(\text{SbMe}_2)_2$	2070, 1995	196.9	[9]
$\text{Me}_2\text{SbCH}_2\text{SbMe}_2$	2067, 1994	197.1	[5]
$\text{Ph}_2\text{SbCH}_2\text{SbPh}_2$	2072, 2004	196.3	[5]
SbEt_3	2067, 1996	197.9	[20,25]
SbMe_3		197.5	[20]
SbPh_3	2074, 2004	196.5	[20]
SbMe_2Ph		197.0	[20]
SbMePh_2		196.5	[20]
<i>Spectroscopic data for $[\text{Ni}(\text{CO})_2(\text{ligand})]$</i>			
$\text{Ph}_2\text{Sb}(\text{CH}_2)_3\text{SbPh}_2$	2005, 1947	201.8	b
$\text{Me}_2\text{Sb}(\text{CH}_2)_3\text{SbMe}_2$	1992, 1933	201.5	b
<i>o</i> - $\text{C}_6\text{H}_4(\text{CH}_2\text{SbMe}_2)_2$	2002, 1939	201.0	[9]
<i>m</i> - $\text{C}_6\text{H}_4(\text{SbMe}_2)_2$	2000, 1941	201.0	[9]
2SbEt_3	2004, 1949		[25]

^a Chlorocarbon solvents (CH_2Cl_2 or CDCl_3).

^b This work.

the onset of decomposition. The presence of four major CH_2 resonances in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the mixture suggest that $[\{\text{Ni}(\text{CO})_3\}_2\{\mu\text{-Ph}_2\text{Sb}(\text{CH}_2)_3\text{-SbPh}_2\}]$ and $[\text{Ni}(\text{CO})_2\{\text{Ph}_2\text{Sb}(\text{CH}_2)_3\text{SbPh}_2\}]$ are the major complexes present.

2.4. Cobalt complexes

The substitution chemistry of dicobalt octacarbonyl with bidentate Group 15 donor ligands is complicated with a variety of stoichiometries being observed with different ligands, often with several isomers identified [5,15]. For many ligands ionic $[\text{Co}(\text{CO})_3(\text{L-L})]$ - $[\text{Co}(\text{CO})_4]$ form first and these transform to neutral dimers $[\text{Co}_2(\text{CO})_6(\text{L-L})]$ on warming in solution. In other cases the $[\text{Co}_2(\text{CO})_4(\text{L-L})_3][\text{Co}(\text{CO})_4]_2$ complexes are obtained [15]. The two distibinopropane ligands gave different complexes on reaction with dicobalt octacarbonyl in toluene solution, both rather unstable, significantly decomposing in solution at room temperature in a few hours and more slowly (1–2 days) in the solid state. The complexes also contrast with the $[\text{Co}_2(\text{CO})_6(\text{R}_2\text{SbCH}_2\text{SbR}_2)]$ obtained the distibinomethanes which contain two bridging carbonyls and a bridging distibine in addition to a Co–Co bond [5]. The reaction of $[\text{Co}_2(\text{CO})_8]$ in toluene solution with $\text{Ph}_2\text{Sb}(\text{CH}_2)_3\text{SbPh}_2$ at room temperature gave a dark red-brown solution from which a brown powder separated on standing at -18°C overnight. The solid isolated had a composition corresponding to $[\text{Co}_2(\text{CO})_6\{\text{Ph}_2\text{Sb}(\text{CH}_2)_3\text{SbPh}_2\}]$ and was very poorly soluble in chlorocarbon or hydrocarbon solvents, which hindered spectroscopic studies and prevented $^{13}\text{C}\{^1\text{H}\}$ or ^{59}Co NMR spectra being obtained. The IR spectra both in the solid and in CH_2Cl_2 solution showed a very broad asymmetric band with shoulders to both high and low frequency due to terminal CO stretches and significantly no bridging carbonyls present (cf. $[\text{Co}_2(\text{CO})_6(\text{R}_2\text{SbCH}_2\text{SbR}_2)]$ [5]). Comparison of the pattern in the carbonyl region of the IR spectrum with the extensive data reported by Thornhill and Manning [15] for cobalt carbonyl diphosphine and diarsine complexes, leads to a tentative structural formulation as an oligo- (or poly-)meric $\{[\text{Co}(\text{CO})_3(\text{Ph}_2\text{Sb}(\text{CH}_2)_3\text{SbPh}_2)\text{-Co}(\text{CO})_3]_n\}$ with unbridged $\text{Co}_2(\text{CO})_6$ units linked by bridging distibine into oligomers. Stirring or heating this complex in toluene with more $\text{Ph}_2\text{Sb}(\text{CH}_2)_3\text{SbPh}_2$ resulted in decomposition with complete loss of the carbonyl groups and no other complex seemed to form. The product from the reaction of $[\text{Co}_2(\text{CO})_8]$ in toluene solution with $\text{Me}_2\text{Sb}(\text{CH}_2)_3\text{SbMe}_2$ at room temperature was also a dark brown solid, poorly soluble in most organic solvents, and even less stable. Initially the solid was poorly soluble in chlorocarbon solvents which allowed some spectroscopic studies, but after a few days the solid had darkened in colour and was completely insoluble in all solvents, and the IR spectrum of this

material showed most of the carbonyl groups had been lost. Due to this instability we have been unable to obtain satisfactory analytical data, but comparison of the spectroscopic data (reproducible from different samples) obtained immediately after isolation allowed its identification as $[\text{Co}_2(\text{CO})_4(\text{Me}_2\text{Sb}(\text{CH}_2)_3\text{SbMe}_2)_3][\text{Co}(\text{CO})_4]_2$. In particular the IR spectrum of the solid is very simple, consisting of two strong broad absorptions at 1968 and 1876 cm^{-1} . These are very similar to those reported for several diarsine complexes [15] and consistent with the formulation proposed. The band at 1878 cm^{-1} corresponds to the familiar tetracarbonylcobaltate(-1) anion, whilst the broad band in the cation is consistent with two five coordinate cobalt(I) centres “ $\text{Co}(\text{CO})_2\text{-}(\text{Me}_2\text{Sb}(\text{CH}_2)_3\text{SbMe}_2)^+$ ” bridged by the third distibine ligand [15]. The ES^- mass spectrum showed $[\text{Co}(\text{CO})_4]^-$ as the only significant feature, and the ES^+ mass spectrum a weak feature corresponding to $[\text{Co}(\text{CO})_2\text{-}(\text{Me}_2\text{Sb}(\text{CH}_2)_3\text{SbMe}_2)_2]^+$ and further ions due to sequential loss of the carbonyl groups. The ^{59}Co NMR spectrum (CH_2Cl_2 solution) (^{59}Co , $I = 7/2$, 100%) showed a very sharp resonance at $\delta -2999$ assigned to the T_d $[\text{Co}(\text{CO})_4]^-$ which compares with the literature value of $\delta -3100$ obtained [17] from $\text{Na}[\text{Co}(\text{CO})_4]$ in water, the difference attributable to solvent effects, given the very large chemical shift range observed for the cobalt nucleus. We were unable to observe a ^{59}Co NMR resonance from the cation, no doubt due to extremely large line width resulting from fast quadrupolar relaxation in the low symmetry environment. The ^1H NMR spectrum of the freshly prepared complex showed two δ (Me) resonances in approximately 1:2 ratio assignable to the bridging and chelating stibines.

2.5. Manganese complexes

Manganese carbonyl and $\text{Ph}_2\text{Sb}(\text{CH}_2)_3\text{SbPh}_2$ refluxed together in toluene in the presence of $[\{\text{CpFe}(\text{CO})_2\}_2]$ gave a single major product, which after recrystallisation from CH_2Cl_2 was identified by analysis as $[\text{Mn}_2(\text{CO})_8\{\text{Ph}_2\text{Sb}(\text{CH}_2)_3\text{SbPh}_2\}]$. Photolysis (254 nm) of $\text{Mn}_2(\text{CO})_{10}$ and $\text{Ph}_2\text{Sb}(\text{CH}_2)_3\text{SbPh}_2$ in toluene gave mainly the same product, but the photolysis route also produced some minor by-products and significant decomposition, and since purification proved difficult, the chemical route is preferred. The IR spectra in the carbonyl region in both Nujol mull and CH_2Cl_2 solution were similar, and contained six terminal CO stretches. Of the possible isomers [17,18], this rules out the diaxial (1 strong band), but is similar to the eq,eq pattern reported in $[\text{Mn}_2(\text{CO})_8(\text{distibinomethane})]$, although the longer backbone in $\text{Ph}_2\text{Sb}(\text{CH}_2)_3\text{SbPh}_2$ will probably result in further significant twisting of the Mn units away from the eclipsed geometry (I) than is observed with the smaller ring ligand [7] or in $[\text{Mn}_2(\text{CO})_8(\text{Cy}_2\text{PCH}_2\text{PCy}_2)]$ [18]. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum appears to show

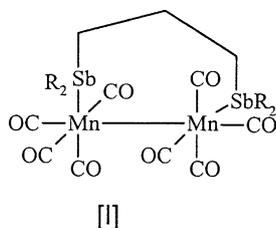


Fig. 1.

three $\delta(\text{CO})$ resonances although these partially overlap and are broadened by the ^{55}Mn quadrupole making the number of resonances uncertain, although the data are consistent with (I) (Fig. 1).

2.6. Some comparisons

These studies have provided a range of spectroscopic data on carbonyl complexes of two distibinopropanes, which when they chelate form 6-membered rings. Thus, they allow some comparisons with previous work on distibinomethanes which have so far yielded no fully characterised chelate complexes with metal carbonyl residues [1,5,6], with the isomeric *o*-, *m*- and *p*-xylyl distibines [9], and with the more restricted range of complexes reported for *o*- [10], *m*- and *p*-phenylene distibines [9], both latter types providing a range of ligand architectures. Table 1 summarises the $\nu(\text{CO})$ frequencies and ^{13}C NMR $\delta(\text{CO})$ resonances of a series of $\text{Ni}(\text{CO})_3(\text{stibine})$ units for these ligands and some related monodentates. Following Tolman's [19] classification of phosphine ligands which utilises the higher frequency (A_1) mode to rank the electronic properties of the donor group, a similar examination of the IR data

shows the σ donor properties follow from the nature of the R-group, and in this series steric effects are unimportant/absent. The ^{13}C NMR $\delta(\text{CO})$ chemical shifts provide the same ordering, the higher the frequency the more donating the stibine [20]. The second part of Table 1 shows some data on the less common $[\text{Ni}(\text{CO})_2(\text{distibine})]$ complexes where the trends are less clear, and we attribute this to the presence of a steric component due to the different ligand architectures or chelate ring sizes.

The relative bonding properties of corresponding PR_3 , AsR_3 and SbR_3 have been discussed in detail elsewhere [19,20] and clearly our distibine data are broadly in line with the accepted trends. However, we also sought to compare the distibine ligand properties with those of group 16 donor analogues (dithioether, diselenoether and ditelluroether). Since nickel carbonyl complexes of these ligands appear to be unknown, the comparison following the data in Table 1 is impossible. However, an essentially complete set of data exist for the Group 6 metal carbonyl species *cis*- $[\text{M}(\text{CO})_4(\text{ligand})]$ and these are summarised in Table 2. Since in chelate complexes the ring size is known to have a significant effect on the spectroscopic properties [21], we compare only 6-membered ring complexes. The data also reflect both σ -donor and π -acceptor properties of the neutral ligands, although the current view [22] is that π -acceptance by Group 16 donors is unimportant in low valent species and that both σ -donor and π -acceptor power decreases down Group 15 [20]. Two minor caveats need to be added: (i) that for a number of the complexes only three of the expected four bands in the IR carbonyl spectra are resolved, and (ii) for the Group 16 donor ligand complexes *meso* and DL invertomers

Table 2
Comparative spectroscopic data for some *cis*-tetracarbonyl complexes of Group 6 metals

Ligand	$[\text{Cr}(\text{CO})_4(\text{L-L})]$		$[\text{Mo}(\text{CO})_4(\text{L-L})]$		$[\text{W}(\text{CO})_4(\text{L-L})]$		References
	$\nu(\text{CO})$ (cm^{-1}) ^a	^{13}C (ppm) ^a	$\nu(\text{CO})$ (cm^{-1})	^{13}C (ppm)	$\nu(\text{CO})$ (cm^{-1})	^{13}C (ppm)	
$\text{Ph}_2\text{Sb}(\text{CH}_2)_3\text{SbPh}_2$	2004, 1911, 1895	222.8, 228.9	2021, 1927, 1912, 1892	211.0, 215.6	2015, 1916, 1902, 1882	201.4, 205.1	^b
$\text{Me}_2\text{Sb}(\text{CH}_2)_3\text{SbMe}_2$	1995, 1900, 1885, 1875	223.7, 229.9	2014, 1903, 1880	213.0, 218.4	2011, 1896, 1870	203.5, 208.2	^b
<i>o</i> - $\text{C}_6\text{H}_4(\text{CH}_2)_3\text{SbMe}_2$			2017, 1935, 1901, 1867	210.9, 215.5	2012, 1935, 1901, 1873	201.7, 206.1	[9]
$\text{MeS}(\text{CH}_2)_3\text{SMe}$	2015, 1900, 1890, 1854	217.0, 225.8	2023, 1910, 1895, 1856	207.1, 217.0	2018, 1897, 1890, 1852	202.7, 207.6	[23]
$\text{MeSe}(\text{CH}_2)_3\text{SeMe}$	2009, 1984, 1852	219.0, 227.0	2020, 1908, 1895, 1855	208.3, 216.8	2015, 1896, 1885, 1850	203, 206 ^c	[23]
$\text{MeTe}(\text{CH}_2)_3\text{TeMe}$	2000, 1887, 1858	222.9, 228.0 ^c	2015, 1908, 1862	210.6, 215.7 ^c	2010, 1894, 1859	203.5, 206.2 ^c	[23]
$\text{PhTe}(\text{CH}_2)_3\text{TePh}$	2003, 1903, 1891, 1870	222.3, 227.5 ^c	2018, 1907, 1875	210.2, 215.6 ^c	2013, 1895, 1869	203.9, 205.4 ^c	[23]

^a CH_2Cl_2 solutions except c.

^b This work.

^c Due to slow pyramidal inversion at Te in these complexes, separate resonances are observed for the DL and *meso* invertomers (in unequal abundance). These chemical shifts quoted are (unweighted) averages values for the two invertomers and as such are subject to some error.

exist [23]. The two invertomers are not distinguishable in the carbonyl IR spectra, but are potentially so in the $^{13}\text{C}\{^1\text{H}\}$ NMR data. Fast pyramidal inversion in the dithioether and diselenoether complexes at ambient temperatures for the chromium and molybdenum complexes mean the resonances of the individual invertomers are not observed, however the higher inversion barriers at Te result in separate resonances for each isomer in the telluro-ether complexes [23]. In Table 2, the ditelluroether chemical shifts have been averaged and these values (unweighted for the isomer abundance since this is not accurately known) introduce some small error. However, a comparison of the data in Table 2 shows that, in addition to the usual effects of the R-groups, the electronic properties of the distibines suggest they place more electron density on the Group 6 metal than dithioether or diselenoether analogues, and that they are closest to the ditelluroethers in properties. Previous detailed analysis of metal carbonyl complexes with Group 16 ligands [22–24] has shown that to low valent, electron rich metal centres σ -donation w.r.t. to donor centre is $\text{S} < \text{Se} \ll \text{Te}$, whereas in Group 15 it is accepted to be $\text{P} > \text{As} > \text{Sb}$ [20]. As found with telluroethers [22], it is probable that stibines would be relatively less good ligands for higher and possibly medium oxidation state centres than selenium or sulfur donors as the metal orbitals contract and the metal centre becomes harder, but insufficient spectroscopic data are available at present to explore this further.

3. Experimental

Metal carbonyls were obtained commercially (Aldrich or Strem) and used as received. All reactions were performed under dinitrogen in dried solvents. Physical measurements were made as described elsewhere [5,9].

$\text{Ph}_2\text{Sb}(\text{CH}_2)_3\text{SbPh}_2$ The ligand was made as a white air-stable powder by reaction of Ph_3Sb , Na and $\text{Br}(\text{CH}_2)_3\text{Br}$ in liquid ammonia, and recrystallised from ethanol. Yield 44% [3]. ^1H NMR (300 MHz CDCl_3) 1.8–2.0(m) [6H], 7.0–7.5(m) [20H]. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3) 25.1 CH_2Sb , 26.5 CH_2CH_2 , 128.7, 128.9, 136.0, 137.9 (aryl C).

3.1. $\text{Me}_2\text{Sb}(\text{CH}_2)_3\text{SbMe}_2$

Liquid ammonia (500 cm^3) was condensed using an acetone/ CO_2 slush, and then sodium (5.63 g, 0.24 mol) was added slowly and the solution was left to stir for 30 m. Me_3SbBr_2 (20 g, 0.06 mol) was added in portions, and then the reaction was left to stir for 90 m. NH_4Cl (3.2 g, 0.06 mol) was added to destroy the MeNa and then 1,3-dibromopropane (6.06 g, 0.03 mol) was added dropwise. The reaction was stirred overnight to evaporate the liquid ammonia. The reaction was hydrolysed

with degassed H_2O (100 cm^3) and the organic layer separated. The aqueous layer was extracted with diethyl ether (2 \times 100 cm^3), and then the combined organics were dried over anhydrous MgSO_4 for 3 h. Following filtration the solvents were distilled off and the resulting yellow oil was fractionated *in vacuo*. 65 $^\circ\text{C}/0.5$ mm (5.2 g, 50%) ^1H NMR (CDCl_3) 1.70 (q) [2H], 1.40 (t) [4H], 0.65 (s) [12H]. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): 24.45 CH_2CH_2 , 19.60 CH_2Sb , -5.00 CH_3 .

3.2. $[\text{Cr}(\text{CO})_4\{\text{Ph}_2\text{Sb}(\text{CH}_2)_3\text{SbPh}_2\}]$

Method 1. $[\text{Cr}(\text{CO})_6]$ (0.48 g, 0.22 mmol) and $\text{Ph}_2\text{Sb}(\text{CH}_2)_3\text{SbPh}_2$ (0.125 g, 0.22 mmol) were dissolved in ethanol (50 cm^3), NaBH_4 (0.1 g) added and the mixture refluxed for 2 h, during which it became yellow. The solvent was removed *in vacuo*, and the residue shaken up with water (20 cm^3) and CH_2Cl_2 (20 cm^3). The organic layer was separated, dried (MgSO_4), and evaporated to small volume to produce a yellow powder. Spectroscopic data identical to those below.

Method 2. $[\text{Cr}(\text{CO})_4(\text{C}_7\text{H}_8)]$ (0.13 g, 0.5 mmol) and $\text{Ph}_2\text{Sb}(\text{CH}_2)_3\text{SbPh}_2$ (0.297 g, 0.5 mmol) were dissolved in methylcyclohexane (50 cm^3) and stirred overnight. The reaction was heated to reflux for 2 h, cooled and reduced in volume by 50%. A pale greenish precipitate was formed, and the mixture was refrigerated overnight. The resulting pale yellow-green solid was filtered off and dried *in vacuo*. Yield: 0.094 g, 84%. Anal. Found: C, 48.7; H, 3.4. Calc. for $\text{C}_{31}\text{H}_{26}\text{CrO}_4\text{Sb}_2$: C, 49.1; H, 3.5%. ^1H NMR (CDCl_3) 2.0–2.2(m) [6H], 7.1–7.6(m) [20H]. $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{CH}_2\text{Cl}_2/\text{CDCl}_3$) 20.8 CH_2Sb , 23.5 CH_2CH_2 , 129.5, 130.2, 133.1, 134.8 aryl-C, 222.8, 228.9 CO. MS (APCI) m/z 645 $[\text{Cr}\{\text{Ph}_2\text{Sb}(\text{CH}_2)_3\text{SbPh}_2\}]^+$ IR spectrum (cm^{-1}) CH_2Cl_2 : 2004(s), 1911(sh), 1895(vs,br); Nujol: 2000(s), 1916(m), 1897(s), 1865(s).

3.3. $[\text{Mo}(\text{CO})_4\{\text{Ph}_2\text{Sb}(\text{CH}_2)_3\text{SbPh}_2\}]$

$[\text{Mo}(\text{CO})_4(\text{norbornadiene})]$ (0.15 g, 0.5 mmol) and $\text{Ph}_2\text{Sb}(\text{CH}_2)_3\text{SbPh}_2$ (0.3 g, 0.5 mmol) were dissolved in methylcyclohexane (50 cm^3) and the mixture stirred overnight. The solution was filtered, and the filtrate evaporated in vacuum to produce a pale yellow solid which was dried *in vacuo*. Yield 0.33 g, 81%. Anal. Found: C, 47.0; H, 3.1. Calc. for $\text{C}_{31}\text{H}_{26}\text{MoO}_4\text{Sb}_2$: C, 46.4; H, 3.3%. ^1H NMR (CDCl_3) 2.0–2.2(m) [6H], 7.1–7.7(m). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{CH}_2\text{Cl}_2/\text{CDCl}_3$) 20.9 CH_2Sb , 23.6 CH_2CH_2 , 129.4, 130.1, 133.1, 134.8 aryl-C, 211.0, 215.6 CO. ^{95}Mo NMR ($\text{CH}_2\text{Cl}_2/\text{CDCl}_3$) -1849 . MS (APCI) m/z 746 $[\text{Mo}(\text{CO})_2\{\text{Ph}_2\text{Sb}(\text{CH}_2)_3\text{SbPh}_2\}]^+$, 718 $[\text{Mo}(\text{CO})\{\text{Ph}_2\text{Sb}(\text{CH}_2)_3\text{SbPh}_2\}]^+$, 690 $[\text{Mo}\{\text{Ph}_2\text{Sb}(\text{CH}_2)_3\text{SbPh}_2\}]^+$. IR spectrum (cm^{-1}) CH_2Cl_2 : 2021(s), 1927(sh), 1912(vs), 1892(s); Nujol: 2015(s), 1928(m), 1906(vs), 1872(s).

3.4. $[W(CO)_4\{Ph_2Sb(CH_2)_3SbPh_2\}]$

$[W(CO)_4(\text{piperidine})_2]$ (0.23 g, 0.5 mmol) and $Ph_2Sb(CH_2)_3SbPh_2$ (0.3 g, 0.5 mmol) were refluxed gently in ethanol (30 cm³), then the mixture was cooled and filtered. The solvent was removed *in vacuo*, the residue extracted with CH_2Cl_2 , the solution filtered, and the filtrate concentrated to 10 cm³. Addition of diethyl ether (10 cm³) produced a yellow solid, which was separated and dried *in vacuo*. Yield 0.11 g, 24%. Anal. Found: C, 39.1; H, 3.0. Calc. for $C_{31}H_{26}O_4Sb_2W \cdot CH_2Cl_2$: C, 39.4; H, 3.5%. ¹H NMR ($CDCl_3$) 2.2(m) [6H], 5.4(s) CH_2Cl_2 , 7.3–7.6(m). ¹³C{¹H} NMR ($CH_2Cl_2/CDCl_3$) 20.0 CH_2Sb , 23.8 CH_2CH_2 , 129.4, 130.3, 132.1, 134.7 aryl-C, 201.4 (¹*J*_{WC} = 116 Hz) 205.1 (¹*J*_{WC} = 165 Hz) CO. MS (APCI) *m/z* 891 $[W\{Ph_2Sb(CH_2)_3SbPh_2\}(CO)_4]^+$. IR spectrum (cm⁻¹) CH_2Cl_2 : 2015(s), 1916(sh), 1902(vs), 1882(sh); Nujol: 2012(s), 1920(sh), 1900(vs), 1869(s).

3.5. $[Fe(CO)_4\{Ph_2Sb(CH_2)_3SbPh_2\}]$

$Fe_2(CO)_9$ (0.92 g, 2.6 mmol) and $Ph_2Sb(CH_2)_3SbPh_2$ (0.75 g, 1.26 mmol) were dissolved in anhydrous tetrahydrofuran (50 cm³) and the solution stirred at room temperature for 2d. Filtration and removal of all volatiles in vacuum left a viscous dark red-brown oil. Yield 1.14 g, 97%. ¹H NMR ($CDCl_3$) 2.0(m) [4H], 2.3(m) [2H], 7.3–7.6(m) [20H]. ¹³C{¹H} NMR ($CH_2Cl_2/CDCl_3$) 22.9 CH_2Sb , 25.9 CH_2CH_2 , 129.4, 129.9, 131.2, 134.7 aryl C, 213.2 (CO). MS (APCI) *m/z* 762 $[Fe(CO)_4\{Ph_2Sb(CH_2)_3SbPh_2\}]^+$, 732 $[Fe(CO)_3\{Ph_2Sb(CH_2)_3SbPh_2\}]^+$, 678 $[Fe(CO)\{Ph_2Sb(CH_2)_3SbPh_2\}]^+$, 650 $[Fe\{Ph_2Sb(CH_2)_3SbPh_2\}]^+$. IR spectrum (cm⁻¹) CH_2Cl_2 : 2044(s), 1967(m), 1934(s,br); Nujol: 2041(s), 2060(sh), 1913(vbr).

3.6. $[Fe(CO)_4\{Ph_2Sb(CH_2)_3SbPh_2\}]$

This was obtained also as a red-brown oil using a 1:1 $Fe_2(CO)_9$: $Ph_2Sb(CH_2)_3SbPh_2$ ratio. The NMR spectra show some contamination with $[Fe(CO)_4\{Ph_2Sb(CH_2)_3SbPh_2\}]$ (see text). ¹H NMR ($CDCl_3$) 1.8–2.0(m), 7.1–7.6(m). ¹³C{¹H} NMR ($CH_2Cl_2/CDCl_3$) 23.4, 24.2 CH_2Sb , 25.6 CH_2CH_2 , 128.9, 129.8, 131.0, 134.7, 136.0, 137.5 aryl C, 213.3 (CO). MS (APCI) *m/z* 763 $[Fe(CO)_4\{Ph_2Sb(CH_2)_3SbPh_2\}]^+$. IR spectrum (cm⁻¹) CH_2Cl_2 : 2044(s), 1967(m), 1934(s,br); Nujol: 2041(s), 1913(vbr).

3.7. $[Co_2(CO)_6\{Ph_2Sb(CH_2)_3SbPh_2\}]$

$[Co_2(CO)_8]$ (0.17 g, 0.5 mmol) was dissolved in dry toluene (50 cm³) and the solution was filtered. $Ph_2Sb(CH_2)_3SbPh_2$ (0.297 g, 0.5 mmol) was dissolved in dry toluene (50 cm³), and added to the toluene solu-

tion of $[Co_2(CO)_8]$. The reaction mixture was stirred for 1 h. and then filtered. The dark brown filtrate was refrigerated overnight, and the red-brown solid which deposited filtered off and dried *in vacuo*. Yield 0.13 g, 42%. The product is unstable and was stored in the freezer. It is poorly soluble in non-polar solvents. Anal. Found: C, 43.6; H, 3.4. Calc. for $C_{33}H_{26}Co_2O_6Sb_2$: C, 45.0; H, 3.0%. ¹H NMR ($CDCl_3$) 1.5–2.0(m), 7.1–7.6(m). IR spectrum (cm⁻¹) CH_2Cl_2 : 1995(m), 1969(s,br), 1934(sh); Nujol: 2004(sh), 1980(s,br), 1953(sh).

3.8. $[Mn_2(CO)_8\{Ph_2Sb(CH_2)_3SbPh_2\}]$

$[Mn_2(CO)_{10}]$ (0.45 g, 1.15 mmol), $Ph_2Sb(CH_2)_3SbPh_2$ (0.683 g, 1.15 mmol) and $[{(Cp)Fe(CO)_2}_2]$ (0.08 g, 0.23 mmol) were dissolved in toluene (50 cm³) and refluxed for 24 h. The dark brown solution was then cooled, reduced in volume to 50% and then hexane (10 cm³) was added. A waxy brown solid was collected by filtration, dissolved in the minimum volume of CH_2Cl_2 , the solution filtered, and reduced to dryness to afford a brown solid, which was dried *in vacuo*. Yield 0.32 g, 41%. Anal. Found: C, 44.6; H, 2.9. Calc. for $C_{35}H_{26}Mn_2O_8Sb_2$: C, 45.3; H, 2.8%. ¹H NMR ($CDCl_3$) 2.0–2.2 (br) [6H], 7.0–7.6(br) [20H]. ¹³C{¹H} NMR ($CH_2Cl_2/CDCl_3$) 20.6 CH_2Sb , 21.6 CH_2CH_2 , 129.3, 130.0, 134.6, 136.4 aryl C, 214.5, 217.2, 217.9 (CO). IR spectrum (cm⁻¹) CH_2Cl_2 : 2055(m), 2034(w), 1977(vbr,s), 1966(sh), 1953(s,sh), 1914(sh); Nujol: 2055(m), 2023(m), 1966(s,br), 1947(s), 1919(sh).

3.9. $[Ni(CO)_3\{Ph_2Sb(CH_2)_3SbPh_2\}]$ and $[Ni(CO)_2\{Ph_2Sb(CH_2)_3SbPh_2\}]$

CARE: $Ni(CO)_4$ is volatile and extremely toxic: All reactions were conducted in a good fume cupboard and in sealed equipment fitted with bromine water scrubbers. Spectroscopic samples were also handled in fume cupboard. Residues were destroyed with bromine-water.

Excess $Ni(CO)_4$ (ca. 1 cm³) was added to a stirred solution of the ligand (0.3 g, 0.55 mmol) in CH_2Cl_2 (20 cm³). The progress of the reaction was monitored by IR spectroscopy and when reaction had ceased, the solvent and excess tetracarbonylnickel were removed *in vacuo* leaving a yellow oil, which darkens in a few hours indicative of decomposition. It also blackened slowly in chlorocarbon solutions. Spectroscopic studies showed an inseparable mixture of the two complexes. ¹H NMR ($CDCl_3$) 2.0, 2.2(m), 7.3–7.7(m). ¹³C{¹H} NMR ($CH_2Cl_2/CDCl_3$) 20.8, 22.8, 23.5, 24.0, 129.3, 129.8, 133.0, 134.9, 196.8 ($Ni(CO)_3$), 201.8 ($Ni(CO)_2$). IR spectrum (cm⁻¹) CH_2Cl_2 : 2071(s), 1996(vs), 1947(m); thin film: 2072(s), 2005(s), 1997(s), 1957(m).

3.10. $[W(CO)_4\{Me_2Sb(CH_2)_3SbMe_2\}]$

$[W(CO)_4(\text{piperidine})_2]$ (0.26 g, 0.55 mmol) and $Me_2Sb(CH_2)_3SbMe_2$ (0.19 g, 0.55 mmol) were refluxed gently in ethanol (30 cm³), then the mixture was cooled and filtered. The solvent was removed *in vacuo*, the residue extracted with CH_2Cl_2 , the solution filtered, and the filtrate concentrated to 10 cm³. Addition of diethyl ether (10 cm³) produced a yellow solid, which was separated and dried *in vacuo*. Yield 0.13 g, 37%. ¹H NMR (CD_2Cl_2) 1.3 (s) [6H], 1.7(m) [2H], 2.1(m) [H]. ¹³C{¹H} NMR (dmsol/d⁶-dmsol) –1.9 CH₃, 16.6 CH₂Sb, 24.4 CH₂CH₂, 203.5 (¹J = 120 Hz), 208.2 (¹J = 165 Hz). MS (APCI) *m/z* 569 $[W(CO)_2\{MeSb(CH_2)_3SbMe_2\}]$, 557 $[W(CO)\{Me_2Sb(CH_2)_3SbMe_2\}]$, 543 $[W(CO)-\{MeSb(CH_2)_3SbMe_2\}]$, 528 $[W\{Me_2Sb(CH_2)_3SbMe_2\}]$. IR spectrum (cm⁻¹) CH_2Cl_2 : 2011(m), 1896(vs,br), 1870(sh); Nujol: 2009(s), 1886(vs, br), 1869(sh).

3.11. $[Mo(CO)_4\{Me_2Sb(CH_2)_3SbMe_2\}]$

$[Mo(CO)_4(C_7H_8)]$ (0.17 g, 0.55 mmol) and $Me_2Sb(CH_2)_3SbMe_2$ (0.19 g, 0.55 mmol) were dissolved in degassed EtOH (25 cm³) and the yellow solution was stirred overnight. The reaction was refluxed for 2 h, the solvent removed *in vacuo* and the residue dissolved in the minimum of CH_2Cl_2 . Hexane (10 cm³) was added to precipitate the pale brown solid which was filtered and dried *in vacuo*. Yield 0.030 g, 11%. Anal. Found: C, 23.8; H, 3.1. Calc. for C₁₁H₁₈CrO₄Sb₂: C, 23.8; H, 3.3%. ¹H NMR ($CDCl_3$) 1.05(s) [6H], 1.55(m) [2H], 1.90(m) [H]. ¹³C{¹H} NMR (dmsol/d⁶ dmsol) –1.6 CH₃, 17.8 CH₂Sb, 24.5 CH₂CH₂, 213.0, 218.4 CO. ⁹⁵Mo NMR (dmsol/d⁶-dmsol) –1843. IR spectrum (cm⁻¹) CH_2Cl_2 : 2014(m), 1903(vs,br), 1880(sh); Nujol: 2013(m), 1946(sh), 1894(vs,br), 1866(sh).

3.12. $[Cr(CO)_4\{Me_2Sb(CH_2)_3SbMe_2\}]$

Made similarly to the molybdenum complex but using $[Cr(CO)_4(C_7H_8)]$. The pale green solid was recrystallised from CH_2Cl_2 and Et₂O, and dried *in vacuo*. Yield 45%. ¹H NMR ($CDCl_3$) 1.1(s) [6H], 1.6(t) [2H], 1.9(m) [H]. ¹³C{¹H} NMR ($CH_2Cl_2/CDCl_3$) –2.1 CH₃, 17.9 CH₂Sb, 24.0 CH₂CH₂, 223.7, 229.9 CO. MS (APCI) *m/z* 509 $[Cr(CO)_4\{Me_2Sb(CH_2)_3SbMe_2\}]$, 481 $[Cr(CO)_3\{Me_2Sb(CH_2)_3SbMe_2\}]$. IR spectrum (cm⁻¹) CH_2Cl_2 : 1995(s), 1900(sh), 1885(s,vb), 1875(sh); Nujol: 1993(s), 1903(sh), 1888(vs,br), 1862(sh).

3.13. $[Fe(CO)_4\{Me_2Sb(CH_2)_3SbMe_2\}]$

$[Fe_2(CO)_9]$ (0.8 g, 2.2 mmol) was dissolved in dry degassed THF (50 cm³) and filtered. $Me_2Sb(CH_2)_3SbMe_2$ (0.38 g, 1.1 mmol) in a solution of CH_2Cl_2 (10 cm³) was added and stirred for 30 m. The reaction was re-

duced to dryness and the dark red oil was dried *in vacuo*. Yield 0.65 g, 95%. ¹H NMR ($CDCl_3$) 0.75(s) [6H], 1.4–1.8(m) [3H]. ¹³C{¹H} NMR ($CH_2Cl_2/CDCl_3$) –5.1 CH₃, 20.8 CH₂Sb, 25.6 CH₂CH₂, 213.6 CO. IR spectrum (cm⁻¹) CH_2Cl_2 : 2055(s), 1968(m), 1927(vbr,s); Nujol: 2042(m), 1965(m), 1932(s,br), 1914(sh).

3.14. $[Co_2(CO)_4\{Me_2Sb(CH_2)_3SbMe_2\}_3][Co(CO)_4]_2$

$[Co_2(CO)_8]$ (0.38 g, 1.1 mmol) was dissolved in dry degassed toluene (50 cm³) and the solution filtered. $Me_2Sb(CH_2)_3SbMe_2$ (0.39 g, 1.1 mmol) was added to the solution and the mixture stirred for 1 h. The brown precipitate produced was filtered off and dried *in vacuo*. Yield 0.15 g, 20%. ¹H NMR ($CDCl_3$) 0.6(s) [2H], 0.8(s) [4H], 1.2–1.7(m) [3H]. ⁵⁹Co NMR (CH_2Cl_2) –2999 *w*_{1/2} = 40 Hz. ES⁻ (MS) 171 Co(CO)₄, ES⁺ MS 803 Co(CO)₂{Me₂Sb(CH₂)₃SbMe₂}₂, 776 Co(CO){Me₂Sb(CH₂)₃SbMe₂}₂, 749 Co{Me₂Sb(CH₂)₃SbMe₂}₂. IR spectrum (cm⁻¹) CH_2Cl_2 : 1990(sh), 1972(s,br), 1885(s,br); Nujol: 1968(s,br), 1878(s,br).

3.15. $[Ni(CO)_3\{Me_2Sb(CH_2)_3SbMe_2\}]$

A large excess of Ni(CO)₄ (ca. 1 cm³) was added to a stirred solution of $Me_2Sb(CH_2)_3SbMe_2$ (0.19 g, 0.55 mmol) in CH_2Cl_2 (20 cm³). Carbon monoxide was rapidly evolved, and progress of the reaction was monitored by IR spectroscopy of aliquots of the solution at regular intervals. When reaction had ceased, the excess tetracarbonylnickel and the solvent was removed *in vacuo* to leave a yellowish oil. ¹H NMR ($CDCl_3$) 1.0(s) [6H], 1.6(m) [2H], 1.8(m) [H]. ¹³C{¹H} NMR ($CH_2Cl_2/CDCl_3$) –3.4 CH₃, 19.1 CH₂Sb, 24.1 CH₂CH₂, 197.1 CO. IR spectrum (cm⁻¹) CH_2Cl_2 : 2067(s), 1991(vs); thin film: 2069(s), 1996(br,s).

Reaction using a deficit of tetracarbonylnickel: ¹H NMR ($CDCl_3$) 0.68(s), 0.96(s), 0.98(s), 1.40–1.85(m). ¹³C{¹H} NMR ($CH_2Cl_2/CDCl_3$) –4.9, –3.2, –1.4 CH₃, 18.3, 19.6, 20.9, 24.1, 24.9 CH₂, 197.1, 201.5 CO. IR spectrum (cm⁻¹) CH_2Cl_2 : 2066(s), 1991(vs), 1933(m); thin film: 2069(s), 2006(sh), 1996(br,s), 1950(m).

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