View Article Online / Journal Homepage / Table of Contents for this issue
Dynamic Article Links

Dalton Transactions

Cite this: *Dalton Trans.*, 2011, **40**, 6565

www.rsc.org/dalton

PAPER

Hybrid dibismuthines and distibines as ligands towards transition metal carbonyls†

Sophie L. Benjamin, William Levason,* Gillian Reid and Michael C. Rogers

Received 16th March 2011, Accepted 12th April 2011
DOI: 10.1039/c1dt10447k

The hybrid dibismuthines $O(CH_2CH_2BiPh_2)_2$ and $MeN(CH_2\text{-}2\text{-}C_6H_4BiPh_2)_2$ react with $[M(CO)_5(thf)]$ (M = Cr or W) to form $[\{M(CO)_5\}_2\{O(CH_2CH_2BiPh_2)_2\}]$ and $[\{Cr(CO)_5\}_2\{MeN(CH_2\text{-}2\text{-}C_6H_4BiPh_2)_2\}]$ containing bridging bidentate (Bi_2) coordination. The unsymmetrical tertiary bismuthine complexes $[M(CO)_5\{BiPh_2(\textit{o}\text{-}C_6H_4OMe)\}]$ are also described. Depending upon the molar ratio, the hybrid distibines $O(CH_2CH_2SbMe_2)_2$ and $MeN(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2$ react with $[M(CO)_5(thf)]$ to give the pentacarbonyl complexes $[\{M(CO)_5\}_2\{O(CH_2CH_2SbMe_2)_2\}]$ and $[\{Cr(CO)_5\}_2\{MeN(CH_2\text{-}2\text{-}C_6H_4\text{-}SbMe_2)_2\}]$ or tetracarbonyls *cis*-$[M(CO)_4\{O(CH_2CH_2SbMe_2)_2\}]$ and *cis*-$[M(CO)_4\{MeN(CH_2\text{-}2\text{-}C_6H_4\text{-}SbMe_2)_2\}]$. The latter can also be obtained from $[Cr(CO)_4(nbd)]$ or $[W(CO)_4(pip)_2]$, and contain chelating bidentates (Sb_2-coordinated) as determined crystallographically. $S(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2$ coordinates as a tridentate (SSb_2) in *fac*-$[M(CO)_3\{S(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2\}]$ (M = Cr or Mo) and *fac*-$[Mn(CO)_3\{S(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2\}][CF_3SO_3]$. *Fac*-$[Mn(CO)_3\{MeN(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2\}][CF_3SO_3]$ contains NSb_2-coordinated ligand in the solid state, but in solution a second species, Sb_2-coordinated and with a κ^1-CF_3SO_3 replacing the coordinated amine is also evident. X-ray crystal structures were also determined for *fac*-$[Cr(CO)_3\{S(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2\}]$, *fac*-$[Mn(CO)_3\{S(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2\}][CF_3\text{-}SO_3]$ and *fac*-$[Mn(CO)_3\{MeN(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2\}]$ $[CF_3SO_3]$. Hypervalent $N\cdots Sb$ interactions are present in *cis*-$[M(CO)_4\{MeN(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2\}]$ (M = Mo or W), but absent for M = Cr.

Introduction

Detailed studies of the antimony donor ligands (stibines) carried out in the last 25 years or so, have shown a significantly different chemistry to that of their lighter analogues, phosphines and arsines.[1] This is clearly demonstrated by the key work of Werner[2] who prepared the first examples of bridging ER_3 (E = P, As, Sb) ligands with Sb^iPr_3, and showed that metathesis with PR_3 or AsR_3 led to examples of these as bridging ligands, although the latter complexes cannot be obtained directly.[2] It is also clear that the organometallic chemistry supported by tertiary stibines is significantly different to that of the lighter analogues.[1] Although there is an extensive organic chemistry of bismuth,[3] bismuthine ligands have been very little studied, partly due to their weak σ-donor power and to the reactive C–Bi bonds which are prone to fission in the presence of some metals.[1] The majority of bismuthine complexes are with metal carbonyls and contain only symmetrical monodentate BiR_3 ligands;[1,4,5] only one dibismuthine, *p*-$Ph_2BiC_6H_4BiPh_2$, has been complexed (with Cr and W carbonyls),[6] and there are a few hybrid ligands containing one bismuthine function in combination with O, N, P *etc.* donor atoms,[1,7] although characterisation of complexes of the last group are poor by current standards. The only complexes of a tridentate stibine are with the tripodal $MeC(CH_2SbPh_2)_3$.[8]

We have recently reported the synthesis of a series of new ligands (L) containing two bismuthine or stibine groups in combination with a single O, N or S donor atom, *viz* $O(CH_2CH_2ER_2)_2$ (E = Sb or Bi, R = Ph; E = Sb, R = Me), $MeN(CH_2\text{-}2\text{-}C_6H_4ER_2)_2$ and $S(CH_2\text{-}2\text{-}C_6H_4ER_2)_2$ (E = Sb or Bi, R = Me or Ph).[9–11] Complexation of these ligands with the $[(\eta^5\text{-}Cp)Fe(CO)_2]^+$ acceptor unit showed coordination only *via* one Bi or Sb to each iron centre, to give bridging bidentate coordination, although hypervalent $N(O)\cdots Bi(Sb)$ interactions were present in some, but not all examples.[11] Hypervalency involving the heavier group 15 atoms is currently a very active research topic.[12] In this companion paper we report complexes of these ligands with chromium, tungsten and manganese carbonyl moieties which illustrate the ligands functioning in bridging bidentate, chelating bidentate or chelating tridentate modes. In contrast to the reactions with $[(\eta^5\text{-}Cp)Fe(CO)_2]^+$, for which only one coordination mode was identified across all the ligand types (although the bismuthine complexes were less stable than the stibines), the present study has established markedly different behaviour by ligands involving Sb or Bi donor groups, and provided examples where the lighter heteroatom also coordinates.

School of Chemistry, University of Southampton, Southampton, UK, SO17 1BJ. E-mail: wxl@soton.ac.uk

† CCDC reference numbers 817769–817775. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt10447k

Results and discussion

The aim of this study was to elucidate the range of structural types formed by metal carbonyl complexes of the hybrid ligands, and therefore the different metal carbonyl fragments are discussed in turn.

Pentacarbonyls

The pentacarbonyl-chromium and -tungsten complexes,‡ $[\{M(CO)_5\}_2\{O(CH_2CH_2BiPh_2)_2\}]$ (M = Cr or W), were readily prepared by photolysis of $M(CO)_6$ in thf to form $[M(CO)_5(thf)]$ *in situ*, followed by reaction with 0.5 mol. equivalents of $O(CH_2CH_2BiPh_2)_2$. The formulation as ligand bridged dimers with the bismuth donors bonded to C_{4v} pentacarbonyl metal units follows from the spectroscopic data which showed three carbonyl stretching modes in the IR spectra (theory 3; $2a_1$ + e), and two carbonyl resonances in the $^{13}C\{^1H\}$ NMR spectra at similar frequencies to those in $[M(CO)_5(BiPh_3)]$.[5] The complex $[\{Cr(CO)_5\}_2\{O(CH_2CH_2BiPh_2)_2\}]$ was the only one identified in the chromium system, but for tungsten, if less than a 2 : 1 mol. ratio of metal : ligand was used, varying amounts of a second complex were present. Although this was not isolated in a pure state, the ^1H and $^{13}C\{^1H\}$ NMR spectra showed it to be $[W(CO)_5\{\kappa^1\text{-}O(CH_2CH_2BiPh_2)_2\}]$; notably there was no evidence for a tetracarbonyl species as found in the antimony analogues (see below).

We also prepared $[M(CO)_5\{BiPh_2(o\text{-}C_6H_4OMe)\}]$ (M = Cr or W) by analogous routes, which have very similar spectroscopic properties, but are both rare examples of complexes of an unsymmetrical tertiary bismuthine (BiR_2R'),[1] and serve as comparators for the hybrid ligand complexes. The ligand $MeN(CH_2\text{-}2\text{-}C_6H_4BiPh_2)_2$ formed an orange-brown $[\{Cr(CO)_5\}_2\{MeN(CH_2\text{-}2\text{-}C_6H_4BiPh_2)_2\}]$; again the spectroscopic data (Experimental section) show pentacarbonylchromium units bridged by bismuth-coordinated ligand, and with the amine function uncoordinated. In contrast, repeated attempts to isolate a pure sample of $[\{W(CO)_5\}_2\{MeN(CH_2\text{-}2\text{-}C_6H_4BiPh_2)_2\}]$ failed. Although spectroscopic data showed the complex to be the major species initially formed from reaction of the ligand and two equivalents of $[W(CO)_5(thf)]$, the solutions darkened rapidly due to decomposition, including reformation of much $W(CO)_6$.

The reactions of $O(CH_2CH_2SbMe_2)_2$ with $[M(CO)_5(thf)]$ in a 1 : 2 mol. ratio unexpectedly produced mixtures of the $[\{M(CO)_5\}_2\{O(CH_2CH_2SbMe_2)_2\}]$ and tetracarbonyl complexes $[M(CO)_4\{O(CH_2CH_2SbMe_2)_2\}]$. The tetracarbonyls were obtained pure by a different route (below), but small amounts could also be separated from the mixtures by crystallisation at −18 °C. Using a higher M : L ratio, typically ~3 mol. equivalents of $[M(CO)_5(thf)]$ to 1 of $O(CH_2CH_2SbMe_2)_2$, gave $[\{M(CO)_5\}_2\{O(CH_2CH_2SbMe_2)_2\}]$ after work-up, essentially free of tetracarbonyl species, although some $M(CO)_6$ impurity (M = W $\upsilon(CO)$ = 1976 cm^{-1}, $\delta(^{13}C)$ = 192, M = Cr $\upsilon(CO)$ = 1980 cm^{-1}, $\delta(^{13}C)$ = 213) remained, hindering microanalysis (otherwise the complexes were spectroscopically pure). The ligand $O(CH_2CH_2SbPh_2)_2$ behaved similarly to the methyl analogue in producing mixtures of tetra- and penta-carbonyl species from stoichiometric quantities of reagents, but excess metal reagent led to $[\{W(CO)_5\}_2\{O(CH_2CH_2SbPh_2)_2\}]$, containing $W(CO)_6$ as the only significant impurity. The reactions of $MeN(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2$ with $[M(CO)_5(thf)]$ followed a similar course, but it was not possible to produce clean samples of the pentacarbonyls by using excess metal reagent. The pure tetracarbonyl complexes were made by a different route (below) and whilst the spectroscopic identification of the pentacarbonyls as $[\{M(CO)_5\}_2\{MeN(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2\}]$ is not in doubt, they are not described further.

Attempts to grow crystals of the pentacarbonyl complexes for X-ray study failed, due to slow decomposition of the complexes in solution.§ This leaves unanswered the question of hypervalent interactions in this series; in the $[\{(\eta^5\text{-}Cp)Fe(CO)_2\}_2(L)]^{2+}$ species hypervalent interaction between the heteroatom and *one* Sb centre in the solid state was established in several cases from the X-ray structures,[11] and was also evident from the presence of additional carbonyl stretching vibrations, reflecting the inequivalence of the iron centres. In solution the inequivalence was no longer observed, suggesting loss of any significant interaction. In the pentacarbonyl complexes, there was no evidence for inequivalence of the metal centres in the IR spectra obtained from Nujol mulls. Since symmetrical hypervalent interactions involving both metal centres are ruled out on steric grounds, we conclude that if any hypervalent interactions are present involving one Sb/Bi donor, they are insufficient to produce discernable splittings in the IR spectra.

Tetracarbonyls

The reaction of $[M(CO)_5(thf)]$ (M = Cr or W) with $O(CH_2CH_2SbMe_2)_2$ or $MeN(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2$ in a ≤1 : 1 mol. ratio gave mainly $[M(CO)_4(ligand)]$, with smaller amounts of pentacarbonyl complexes. Reaction of the ligands with $[Cr(CO)_4(nbd)]$ (nbd = norbornadiene) or $[W(CO)_4(pip)_2]$ (pip = piperidine) afforded the pure tetracarbonyl complexes directly. In contrast, as noted above, the hybrid bismuthine ligands did not produce any tetracarbonyl species on reaction with $[M(CO)_5(thf)]$, and they also failed to react with the tetracarbonyl precursors, probably due to the weak donor power of the bismuthine units. Only a few bismuthine complexes are known,[1] and all contain a single bismuthine donor on the metal centre. The ready formation of $[M(CO)_4$(hybrid distibine)$]$ complexes was unexpected since the chelate rings formed are large, 10-membered for $MeN(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2$ and 8-membered for $O(CH_2CH_2SbMe_2)_2$, and therefore no strong chelate effect is expected. It is possible that hypervalent interactions may promote some pre-organisation of the ligands towards chelation. Group 6 tetracarbonyl complexes are known with distibines giving rise to 5- ($o\text{-}C_6H_4(SbMe_2)_2$),[13] 6- ($R_2Sb(CH_2)_3SbR_2$),[14] and 7-membered ($o\text{-}C_6H_4(CH_2SbMe_2)_2$)[15] rings. Distibinomethane ligands ($R_2SbCH_2SbR_2$) form dinuclear complexes $[\{M(CO)_4\}_2(R_2SbCH_2SbR_2)_2]$ with distibine bridges in 8-membered rings.[16]

Crystal structures of four examples with the hybrid ligands were determined: $[M(CO)_4\{O(CH_2CH_2SbMe_2)_2\}]$ (M = Cr

---

‡ Molybdenum carbonyl complexes with bismuthine ligands are often much less stable than chromium or tungsten analogues[4–6] and were not generally included in the present study.

§ In some cases crystals of the corresponding tetracarbonyl complex or $M(CO)_6$ resulted.

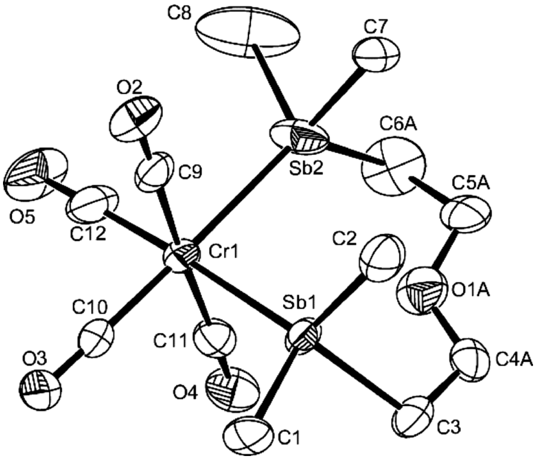

Fig. 1 Structure of [Cr(CO)$_4${O(CH$_2$CH$_2$SbMe$_2$)$_2$}] showing the atom labelling scheme. There is disorder in the Sb ligand backbone which was modelled as two conformations (A/B) with A being shown. Ellipsoids are drawn at the 40% probability level and H atoms are omitted for clarity.

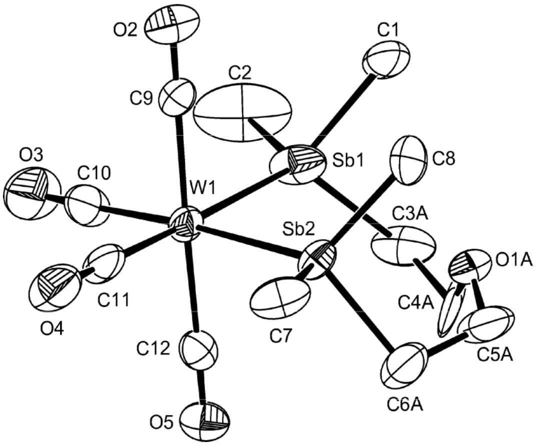

Fig. 2 Structure of [W(CO)$_4${O(CH$_2$CH$_2$SbMe$_2$)$_2$}] showing the atom labelling scheme. There is disorder in the Sb ligand backbone which was modelled as two conformations (A/B) with A being shown. Ellipsoids are drawn at the 40% probability level and H atoms are omitted for clarity.

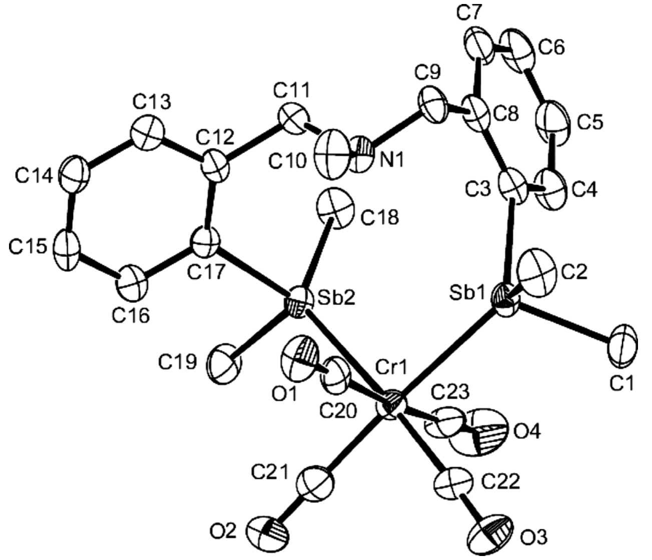

Fig. 3 Structure of [Cr(CO)$_4${MeN(CH$_2$-2-C$_6$H$_4$SbMe$_2$)$_2$}] showing the atom labelling scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

Table 1 Selected bond lengths (Å) and angles (°) for [Cr(CO)$_4$-{O(CH$_2$CH$_2$SbMe$_2$)$_2$}]

Cr1–C9	1.895(11)	Cr1–C10	1.833(11)
Cr1–C11	1.890(11)	Cr1–C12	1.842(12)
Cr1–Sb1	2.601(2)	Cr1–Sb2	2.588(2)
Sb1 · · · O1A	3.06(2)	Sb2 · · · O1A	2.86(2)
C10–Cr1–C12	88.9(6)	C10–Cr1–C11	90.3(5)
C12–Cr1–C11	90.7(5)	C10–Cr1–C9	91.8(5)
C12–Cr1–C9	91.0(5)	C12–Cr1–Sb2	89.9(5)
C11–Cr1–Sb2	90.5(3)	C9–Cr1–Sb2	87.4(3)
C10–Cr1–Sb1	88.5(4)	C11–Cr1–Sb1	88.3(3)
C9–Cr1–Sb1	90.2(3)	Sb2–Cr1–Sb1	92.69(5)

Table 2 Selected bond lengths (Å) and angles (°) for [W(CO)$_4$-{O(CH$_2$CH$_2$SbMe$_2$)$_2$}]

W1–C9	2.026(14)	W1–C10	2.00(2)
W1–C11	1.94(2)	W1–C12	2.04(2)
W1–Sb1	2.7250(14)	W1–Sb2	2.7378(13)
Sb1 · · · O1A	3.44(2)	SB2 · · · O1A	3.16(2)
C11–W1–C10	88.6(8)	C11–W1–C9	91.2(6)
C10–W1–C9	91.5(6)	C11–W1–C12	90.7(6)
C10–W1–C12	89.3(6)	C10–W1–Sb1	90.5(5)
C9–W1–Sb1	87.8(4)	C12–W1–Sb1	90.3(4)
C11–W1–Sb2	88.9(5)	C9–W1–Sb2	91.3(4)
C12–W1–Sb2	88.1(4)	Sb1–W1–Sb2	92.03(4)

or W) which are isomorphous, and [M(CO)$_4${MeN(CH$_2$-2-C$_6$H$_4$SbMe$_2$)$_2$}] (Fig. 1 to 4, Tables 1 to 4). The coordination environments in [M(CO)$_4${MeN(CH$_2$-2-C$_6$H$_4$SbMe$_2$)$_2$}], are similar to that in the molybdenum analogue reported earlier,[9] showing a near to octahedral geometry and M–C$_{\text{transSb}}$ shorter than M–C$_{\text{transCO}}$. Notably, the tungsten complex shows one hypervalent N · · · Sb interaction to antimony (Sb2 · · · N = 2.997(3) Å). This correlates with a slightly longer W–Sb bond (2.7745(4) Å) compared to W–Sb1 (2.7402(4) Å) which lacks any hypervalent interaction (Sb1 · · · N = 4.055(2) Å). This behaviour is similar to that observed for the molybdenum complex (Mo–Sb1 = 2.7792(5), Mo–Sb2 = 2.7509(6), N · · · Sb1 = 3.05 Å).[9] However, in the chromium complex (Table 3), the Cr–Sb bonds do not differ significantly (2.5914(12), 2.5934(12) Å). The Sb · · · N distances are also quite similar (3.467(6), 3.645(6) Å) and close to the sum of the Van der Waals radii (3.55 Å),[17] which suggests no hypervalent interaction is present in the chromium system. The availability of structural data on the three Group 6 carbonyl complexes illustrates the subtleties surrounding the hypervalent interactions. Fig. 5 shows the conformations of the tungsten and chromium complexes (the molybdenum analogue[9] is essentially superimposable on the tungsten), which reveal that the formation of the hypervalent interaction in the tungsten complex requires significant changes in the conformation of the ligand backbone to orientate the lone pair on the nitrogen appropriately, bringing it closer to one Sb. In the chromium complex the ligand has a more "folded" conformation with the lone pair pointing away from the antimony atoms. In order for the hypervalent interaction to occur, the energy gain from the N · · · Sb bond must be greater than the energy needed to reorientate the ligand conformation, and this subtle balance qualitatively rationalises the occurrence or absence of hypervalency in these systems. The ^{1}H and ^{13}C{^{1}H} NMR

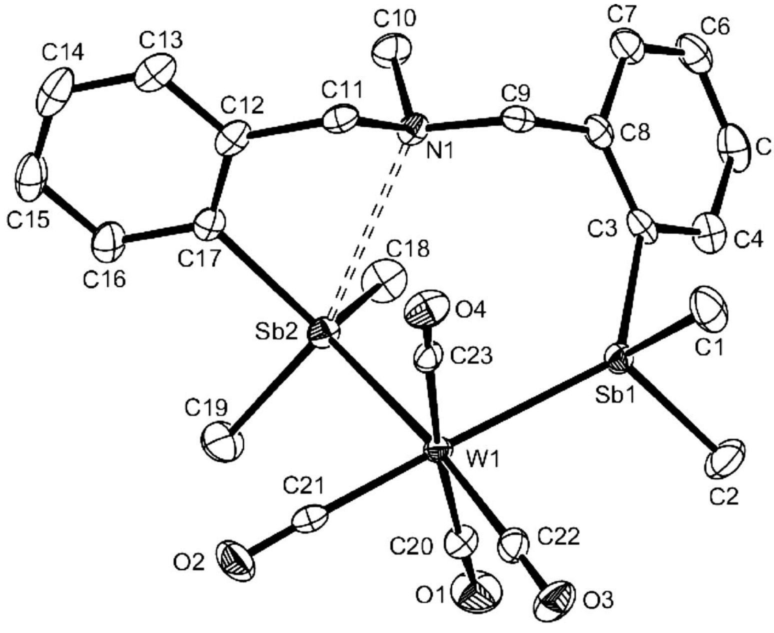

Fig. 4 Structure of [W(CO)$_4${MeN(CH$_2$-2-C$_6$H$_4$SbMe$_2$)$_2$}] showing the atom labelling scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

Table 3 Selected bond lengths (Å) and angles (°) for [Cr(CO)$_4$-{MeN(CH$_2$-2-C$_6$H$_4$SbMe$_2$)$_2$}]

Cr1–C20	1.902(8)	Cr1–C21	1.835(8)
Cr1–C22	1.859(8)	Cr1–C23	1.862(8)
Cr1–Sb1	2.5934(12)	Cr1–Sb2	2.5914(12)
Sb1 · · · N1	3.467(6)	Sb2 · · · N1	3.643(6)
C21–Cr1–C22	88.7(3)	C21–Cr1–C23	92.1(3)
C22–Cr1–C23	92.4(3)	C21–Cr1–C20	91.1(3)
C22–Cr1–C20	92.5(3)	C21–Cr1–Sb2	87.9(2)
C23–Cr1–Sb2	87.5(2)	C20–Cr1–Sb2	87.8(2)
C22–Cr1–Sb1	88.5(2)	C23–Cr1–Sb1	86.2(3)
C20–Cr1–Sb1	90.8(2)	Sb2–Cr1–Sb1	94.84(4)

Table 4 Selected bond lengths (Å) and angles (°) for [W(CO)$_4$-{MeN(CH$_2$-2-C$_6$H$_4$SbMe$_2$)$_2$}]

W1–C20	2.035(3)	W1–C21	1.978(3)
W1–C22	1.976(3)	W1–C23	2.032(3)
W1–Sb1	2.7402(4)	W1–Sb2	2.7745(4)
Sb1 · · · N1	4.055(2)	Sb2 · · · N1	2.997(3)
C22–W1–C21	89.15(13)	C22–W1–C23	86.68(12)
C21–W1–C23	90.95(12)	C22–W1–C20	90.88(12)
C21–W1–C20	93.09(12)	C22–W1–Sb1	89.30(9)
C23–W1–Sb1	89.30(9)	C20–W1–Sb1	86.59(9)
C21–W1–Sb2	87.20(9)	C23–W1–Sb2	98.03(8)
C20–W1–Sb2	84.67(9)	Sb1–W1–Sb2	94.325(14)

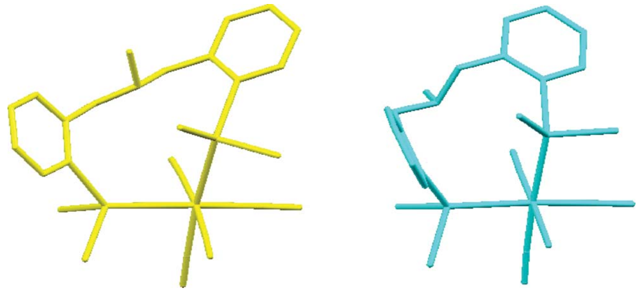

Fig. 5 The conformations present in [W(CO)$_4${MeN(CH$_2$-2-C$_6$H$_4$SbMe$_2$)$_2$}] (left) and [Cr(CO)$_4${MeN(CH$_2$-2-C$_6$H$_4$SbMe$_2$)$_2$}] (right) as a consequence of the presence and absence of hypervalent interactions.

spectra do not show any inequivalence of the antimony groups for either complex in solution; either the hypervalency in the tungsten complex is lost in solution (as in most of the complexes with [CpFe(CO)$_2$]$^+$)[11] or the effects are too small to resolve. For a *cis* tetracarbonyl, four IR active carbonyl vibrations are expected irrespective of any hypervalent contact, so IR spectroscopy does not help in this case.

The structures of the two [M(CO)$_4${O(CH$_2$CH$_2$SbMe$_2$)$_2$}] (M = Cr or W) show similar trends in the M–C distances. Unfortunately, both show disorder in the -CH$_2$CH$_2$OCH$_2$CH$_2$- unit, and although this was relatively successfully modeled over two sites, the Sb · · · O distances are unreliable. Tetracarbonyl complexes with S(CH$_2$-2-C$_6$H$_4$SbMe$_2$)$_2$ were not isolated.

Tricarbonyls

The chemistry of these hybrid ligands described thus far,[9–11] and above, showed a preference for coordination only *via* the antimony or bismuth donor atoms. We were interested to explore whether it would be possible to coordinate the lighter heteroatoms (O, N or S) in tandem, hence leading to tridentate coordination and disparate donor properties. To this end, S(CH$_2$-2-C$_6$H$_4$SbMe$_2$)$_2$ was reacted with [M(CO)$_3$(MeCN)$_3$][18] (M = Cr or Mo), the nitrile being substituted cleanly at room temperature in MeCN solution. However, no reaction occurred with S(CH$_2$-2-C$_6$H$_4$BiR$_2$)$_2$ under similar conditions, and under reflux the hybrid bismuthine ligands fragmented. The structure of [Cr(CO)$_3${S(CH$_2$-2-C$_6$H$_4$SbMe$_2$)$_2$}] (Fig. 6, Table 5) shows the expected *fac*-octahedral geometry which maximises the Cr–CO bonding; notably the Cr–C and Cr–Sb distances differ little from those in [Cr(CO)$_4${O(CH$_2$CH$_2$SbMe$_2$)$_2$}].

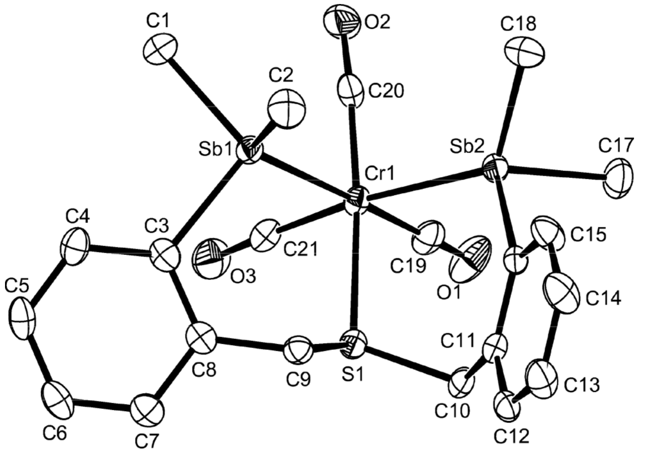

Fig. 6 Structure of [$\mathrm{Cr(CO)_3\{S(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2\}}$] showing the atom labelling scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

Table 5 Selected bond lengths (Å) and angles (°) for [$\mathrm{Cr(CO)_3\{S(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2\}}$]

Cr1–C19	1.842(4)	Cr1–C20	1.838(4)
Cr1–C21	1.835(4)	Cr1–S1	2.4114(11)
Cr1–Sb1	2.5982(6)	Cr1–Sb2	2.5985(6)
C21–Cr1–C20	90.5(2)	C21–Cr1–C19	87.0(2)
C20–Cr1–C19	91.9(2)	C21–Cr1–S1	86.77(12)
C19–Cr1–S1	91.69(12)	C21–Cr1–Sb1	90.16(12)
C20–Cr1–Sb1	87.58(12)	S1–Cr1–Sb1	88.73(3)
C20–Cr1–Sb2	94.01(11)	C19–Cr1–Sb2	88.20(12)
S1–Cr1–Sb2	88.99(3)	Sb1–Cr1–Sb2	94.72(2)

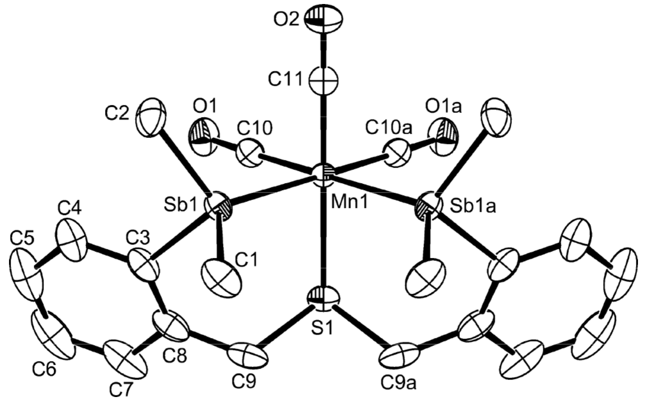

Fig. 7 Structure of [$\mathrm{Mn(CO)_3\{S(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2\}}$]$^+$ showing the atom labelling scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operation: a = x, $\frac{1}{2}$ − y, z.

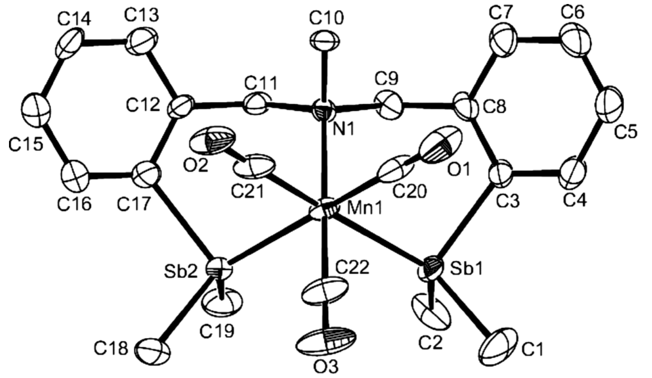

Fig. 8 Structure of [$\mathrm{Mn(CO)_3\{MeN(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2\}}$]$^+$ showing the atom labelling scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

Table 6 Selected bond lengths (Å) and angles (°) for [$\mathrm{Mn(CO)_3\{S(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2\}}$][$\mathrm{CF_3SO_3}$]. Symmetry operation: a = x, $\frac{1}{2}$ − y, z

Mn1–C10	1.822(3)	Mn1–C11	1.788(4)
Mn1–Sb1	2.5716(4)	Mn1–S1	2.3649(11)
C11–Mn1–C10	90.32(11)	C10–Mn1–C10a	92.5(2)
C10–Mn1–S1	88.54(8)	C11–Mn1–Sb1	89.88(8)
C10–Mn1–Sb1	86.52(8)	S1–Mn1–Sb1	91.23(2)
Sb1–Mn1–Sb1a	94.45(2)		

Table 7 Selected bond lengths (Å) and angles (°) for [$\mathrm{Mn(CO)_3\text{-}\{MeN(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2\}}$][$\mathrm{CF_3SO_3}$]

Mn1–C20	1.797(9)	Mn1–C21	1.817(9)
Mn1–C22	1.806(9)	Mn1–N1	2.236(6)
Mn1–Sb1	2.5656(13)	Mn1–Sb2	2.5628(14)
C20–Mn1–C22	89.5(4)	C20–Mn1–C21	89.3(4)
C22–Mn1–C21	90.5(4)	C20–Mn1–N1	91.9(3)
C21–Mn1–N1	91.1(3)	C22–Mn1–Sb2	88.2(3)
C21–Mn1–Sb2	88.6(3)	N1–Mn1–Sb2	90.5(2)
C20–Mn1–Sb1	86.3(3)	C22–Mn1–Sb1	87.4(3)
N1–Mn1–Sb1	91.1(2)	Sb2–Mn1–Sb1	95.64(4)

The ^{1}H and ^{13}C{^{1}H} NMR spectra show the [$\mathrm{M(CO)_3\{S(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2\}}$] (M = Cr or Mo) are stable in solution in $\mathrm{CH_2Cl_2}$, and both show two δ(Me) resonances of equal intensity, reflecting the MeSb- groups *syn* to CO and *syn* to S respectively. The solution IR spectra in $\mathrm{CH_2Cl_2}$ show one sharp and one very broad stretch, which correspond to the a_1 + e modes of the *fac*-tricarbonyl unit, the broadening of the e mode reflecting the lower actual symmetry (C_s), although splitting (into a′ + a″) was not clearly resolved. Curiously, both complexes show *four* carbonyl stretches in the Nujol mull IR spectra, which is attributed to a solid state effect, since the spectra are unchanged after recrystallisation of the complexes and the effect is not present in solution.

In order to probe the potential for these hybrid ligands towards tridentate coordination more broadly, we have also investigated their chemistry with the *fac*-[$\mathrm{Mn(CO)_3}$]$^+$ fragment. The reactions of $\mathrm{S(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2}$ or $\mathrm{MeN(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2}$ with [$\mathrm{Mn(CO)_3(Me_2CO)_3}$][$\mathrm{CF_3SO_3}$] [19] in acetone solution, followed by recrystallisation from $\mathrm{CH_2Cl_2}$, gave yellow [$\mathrm{Mn(CO)_3\{S(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2\}}$][$\mathrm{CF_3SO_3}$] and [$\mathrm{Mn(CO)_3\{MeN(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2\}}$][$\mathrm{CF_3SO_3}$] (the latter was briefly mentioned in our earlier study[9]), but attempts to obtain a similar complex with $\mathrm{O(CH_2CH_2SbMe_2)_2}$ failed, presumably due to the weak affinity of the ether oxygen donor for the soft manganese centre. Crystal structures of the two complexes were determined (Fig. 7 and 8, Tables 6 and 7) and show the expected *facial* isomers. The geometries are close to octahedral and the Mn–Sb and Mn–$\mathrm{C_{transSb}}$ distances differ little between the two species, (*fac*-[$\mathrm{Mn(CO)_3\{S(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2\}}$][$\mathrm{CF_3SO_3}$] adopts crystallographic *m* symmetry with the Mn, S and one CO ligand occupying the mirror plane).

For *fac*-[$\mathrm{Mn(CO)_3\{S(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2\}}$][$\mathrm{CF_3SO_3}$] the solution IR, ^{1}H and ^{13}C{^{1}H} NMR spectra are consistent with the solid state structure, confirming its retention in solution. However, careful examination of the ^{1}H and ^{13}C{^{1}H} NMR spectra of *fac*-[Mn(CO)$_3${MeN(CH$_2$-2-C$_6$H$_4$SbMe$_2$)$_2$}]CF$_3$SO$_3$ reveal that a second (similar) species is present even in non-coordinating solvents like CH$_2$Cl$_2$ and CHCl$_3$. This results in two distinct sets of resonances. There are also two closely spaced ^{19}F NMR resonances due to coordinated and ionic triflate. The major species is clearly the cation found in the crystal structure and the second complex is assigned as [Mn(CO)$_3${κ^2-MeN(CH$_2$-2-C$_6$H$_4$SbMe$_2$)$_2$}(κ^1-CF$_3$SO$_3$)] where the relatively weakly bound tertiary amine has been replaced by a κ^1-coordinated triflate.

Conclusions

The metal pentacarbonyl dibismuthines reported here confirm that metal complexes with different substituents at the bismuth centre may be formed (as do the analogues with BiPh$_2$(*o*-C$_6$H$_4$OMe)), whereas almost all other well characterised examples contained symmetrically substituted bismuthines (BiR$_3$).[1] However, the weak binding power of bismuth prevents coordination *via* more than one bismuth atom per metal centre. A possible approach to overcome this would be to use dibismuthines with rigid linkers, pre-organised for chelation–such compounds are not known at present.

The hybrid tridentates containing antimony provide rare examples of polydentate stibine complexes, and also establish a wider range of coordination modes including bridging bidentate, chelating bidentate (both Sb$_2$-coordinated) and chelating tridentate (Sb$_2$S- or Sb$_2$N-coordinated). The failure to obtain tridentate coordination from ligands with an ether oxygen in the backbone reflects the very poor affinity of this group for low valent metal centres. Particularly notable are the complexes exhibiting hypervalency. In the three Group 6 complexes [M(CO)$_4${κ^2-MeN(CH$_2$-2-C$_6$H$_4$SbMe$_2$)$_2$}], hypervalent interactions between N and one Sb are clearly present in the Mo[9] and W species, but absent from the Cr complex. This can be rationalised as a trade-off between the small energy gain from the extra N···Sb bonding interaction and the energy needed to achieve the ligand conformation necessary to bring the N and Sb into the correct orientation. These complexes, together with the Fe species described in our earlier paper,[11] provide rare examples in which a single Sb (or Bi) atom behaves as a donor to a transition metal atom and an acceptor to a lighter heteroatom simultaneously.

Experimental

Infrared spectra were recorded as Nujol mulls between NaCl plates using a Perkin Elmer Spectrum 100 spectrometer over the range 4000–600 cm^{-1} and solution spectra used NaCl solution cells over the range 2200–1800 cm^{-1}. ^{1}H NMR spectra were recorded from CD$_2$Cl$_2$ or CDCl$_3$ solutions using a Bruker AV300 spectrometer and low temperature ^{1}H and ^{13}C{^{1}H} NMR spectra of the complexes were recorded from CDCl$_3$ or CD$_2$Cl$_2$ solutions using a Bruker DPX400 spectrometer and are referenced to the protio-solvent signal. ^{55}Mn NMR spectra were obtained on the Bruker DPX400 spectrometer and are referenced to aqueous KMnO$_4$. Microanalyses on new complexes were undertaken by Medac Ltd. FAB mass spectra were obtained using 3-NOBA as matrix from Medac Ltd and electrospray (ES$^+$) mass spectra were obtained using a VG Biotech platform. Preparations were undertaken using standard Schlenk and glove box techniques under a dry N$_2$ atmosphere. Solvents were dried by distillation from CaH$_2$ (CH$_2$Cl$_2$) or Na/benzophenone ketyl (thf, hexane and diethyl ether). Photochemical syntheses were carried out using a 125 W medium pressure mercury lamp (Photochemical Reactors Ltd.) emitting at 365 nm.

The O(CH$_2$CH$_2$SbR$_2$)$_2$ (R = Me or Ph),[10] O(CH$_2$CH$_2$BiPh$_2$)$_2$,[11] BiPh$_2$(o-C$_6$H$_4$OMe),[7] MeN(CH$_2$-2-C$_6$H$_4$SbMe$_2$)$_2$,[9] MeN(CH$_2$-2-C$_6$H$_4$BiR$_2$)$_2$,[11] S(CH$_2$-2-C$_6$H$_4$SbMe$_2$)$_2$, S(CH$_2$-2-C$_6$H$_4$BiR$_2$)$_2$,[11] [M(CO)$_5$(thf)] (M = Cr, W),[20] [Cr(CO)$_4$(nbd)],[21] [W(CO)$_4$-(pip)$_2$],[22] [M(CO)$_3$(MeCN)$_3$][18] (M = Cr, Mo) and [Mn(CO)$_3$-(acetone)$_3$][CF$_3$SO$_3$][19] were made as described.

[Cr(CO)$_5${Ph$_2$Bi(*o*-C$_6$H$_4$OMe)}]

Cr(CO)$_6$ (0.3 g, 1.36 mmol) was dissolved in thf (40 mL) and the solution photolysed for 1 h, producing a bright orange solution. Ph$_2$Bi(*o*-C$_6$H$_4$OMe) (0.64 g, 1.36 mmol), dissolved in thf (10 mL) was added and the mixture stirred for 45 min. The solvent was removed *in vacuo*, leaving a yellow/brown residue. The addition of hexane (20 mL) gave a yellow solution and some darker solids, which were removed by filtration. The solvent was again removed *in vacuo*, yielding a bright yellow solid (0.26 g, 29%). Required for C$_{24}$H$_{17}$BiCrO$_6$: C, 43.5; H, 2.6. Found: C, 44.0; H, 2.5%. IR (CH$_2$Cl$_2$/cm^{-1}): 2064w, 1980 m, 1945s; (Nujol/cm^{-1}): 2062w, 1985w, 1947s. ^{1}H NMR (CD$_2$Cl$_2$): δ 3.79 ([3H], s, OMe), 6.82–7.65 ([14H], m, aromatic). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 253 K): δ 55.3 (OMe), 110.1, 123.1, 129.1, 130.0, 130.3, 135.8, 136.0, 140.1, 161.0 (C$_{\text{aromatic}}$), 217.0 (4CO), 222.7 (CO). MS (FAB): m/z = 662 [M]$^+$, 606 [M – 2CO]$^+$, 550 [M – 4CO]$^+$, 522 [M – 5CO]$^+$.

[W(CO)$_5${Ph$_2$Bi(*o*-C$_6$H$_4$OMe)}]

W(CO)$_6$ (0.41 g, 1.17 mmol) was dissolved in thf (40 mL) and the solution photolysed for 1 h, producing a dark yellow solution. Ph$_2$Bi(*o*-C$_6$H$_4$OMe) (0.44 g, 0.93 mmol, dissolved in thf (10 mL) was added and the mixture stirred for 1 h. The solvent was removed *in vacuo*, leaving a dark brown residue. Extraction with hexane (20 mL) and removal of all solvents gave a yellow/brown solid. A second extraction with hexane (20 mL), followed by removal of the solvent, precipitated a pale yellow solid (0.12 g, 16%). Required for C$_{24}$H$_{17}$BiO$_6$W: C, 36.3; H, 2.2. Found: C, 36.0; H, 2.0%. IR (CH$_2$Cl$_2$/cm^{-1}): 2074s, 1976s, 1944s; (Nujol/cm^{-1}): 2070s, 1981s, 1945s. ^{1}H NMR (CD$_2$Cl$_2$): δ 3.78 ([3H], s, OMe), 6.90–7.53 ([14H], m, PhBi). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 253 K): δ 56.0 (OMe), 110.9, 123.6, 129.8, 130.1, 130.8, 136.3, 136.6, 139.3, 161.7 (C$_{\text{aromatic}}$), 198.1 ($^{1}J_{\text{WC}}$ = 126 Hz, 4CO), 199.2 ($^{1}J_{\text{WC}}$ = 181 Hz, CO). MS (FAB): m/z = 794 [M]$^+$, 738 [M – 2CO]$^+$.

[{Cr(CO)$_5$}$_2${O(CH$_2$CH$_2$BiPh$_2$)$_2$}]

Cr(CO)$_6$ (0.20 g, 0.91 mmol) was dissolved in thf (40 mL) and the solution irradiated for 1 h, producing an orange solution. O(CH$_2$CH$_2$BiPh$_2$)$_2$ (0.29 g, 0.36 mmol) dissolved in thf (10 mL) was added and the mixture stirred for 45 min. The solvent was removed *in vacuo*, leaving an orange/brown solid which was redissolved in hexane (20 mL) and filtered to remove insoluble dark impurities. The solvent was removed from the filtrate, yielding the complex as viscous yellow/orange oil (0.14 g, 33%). Required for $C_{38}H_{28}Bi_2Cr_2O_{11}$: C, 38.6; H, 2.4. Found: C, 39.5; H, 2.5%. IR (CH_2Cl_2/cm^{-1}): 2063s, 1980s, 1942s; (Nujol/cm^{-1}): 2063m, 1985w, 1946s. ^{1}H NMR (CD_2Cl_2): δ 2.87 ([4H], t, $^3J_{HH}$ = 7 Hz, CH_2Bi), 4.00 ([4H], t, $^3J_{HH}$ = 7 Hz, CH_2O), 7.30–7.71 ([20H], m, PhBi). ^{13}C{^{1}H} NMR (CD_2Cl_2, 253 K): δ 27.8 (CH_2Bi), 68.2 (CH_2O), 129.2, 130.1, 135.7 (C$_{aromatic}$), 217.2 (4CO), 222.4 (CO). MS (FAB): *m*/*z* = 1051 [M + Na − 2Ph]$^+$.

[{W(CO)$_5$}$_2${O(CH$_2$CH$_2$BiPh$_2$)$_2$}]

W(CO)$_6$ (0.18 g, 0.51 mmol) was dissolved in thf (40 mL) and the solution photolysed for 1 h, producing a dark yellow solution. O($CH_2CH_2BiPh_2$)$_2$ (0.16 g, 0.20 mmol) dissolved in thf (10 mL) was added and the mixture stirred at room temperature for 45 min. The solvent was removed *in vacuo*, leaving a dark brown residue. Extraction with hexane (20 mL) and removal of all volatiles gave a yellow/brown solid (0.05 g, 22%). Required for $C_{38}H_{28}Bi_2O_{11}W_2\cdot C_6H_{14}$: C, 34.9; H, 2.8. Found: C, 34.7; H, 2.9%. IR (CH_2Cl_2/cm^{-1}): 2073s, 1976s, 1943s; (Nujol/cm^{-1}): 2074m, 1982s, 1948s. ^{1}H NMR (CD_2Cl_2, 253 K): δ 2.94 ([4H], t, $^3J_{HH}$ = 7 Hz, CH_2Bi), 4.00 ([4H], t, $^3J_{HH}$ = 7 Hz, CH_2O), 7.24–7.86 ([20H], m, Ph), (0.88, 1.27, C_6H_{14}). ^{13}C{^{1}H} NMR (CD_2Cl_2, 253 K): δ 27.2 (CH_2Bi), 68.4 (CH_2O), 129.2, 130.8, 135.5 (C$_{aromatic}$), 197.3 ($^1J_{WC}$ = 128 Hz, 4CO), 198.0 ($^1J_{WC}$ = 180 Hz, CO), (14.4, 23.2, 32.2, ^{n}C$_6$H$_{14}$).

[{W(CO)$_5$}$_2${O(CH$_2$CH$_2$SbMe$_2$)$_2$}]

W(CO)$_6$ (0.32 g, 0.91 mmol) was dissolved in thf (40 mL), and photolysed for 1 h, producing a dark yellow solution. A solution of O($CH_2CH_2SbMe_2$)$_2$ (0.137 g, 0.36 mmol) in thf (10 mL) was added and the mixture stirred for 1.5 h at room temperature. All volatiles were removed *in vacuo* leaving a yellow-brown residue. Hexane (20 mL) was added and the mixture was stirred for 10 min. The solution was filtered and the filtrate reduced *in vacuo* to *ca.* 10 mL, then stored in a freezer (−18 °C, 16 h). The off-white solid deposited was separated by filtration at 0 °C and dried *in vacuo* (0.11 g, 30%). Required for $C_{18}H_{20}O_{11}Sb_2W_2$: C, 21.1; H, 2.0. Found: C, 21.2; H, 2.0%. IR (CH_2Cl_2/cm^{-1}): 2068s, 1971(sh), 1936s; (Nujol/cm^{-1}): 2066m, 1975s, 1936s. ^{1}H NMR ($CDCl_3$): δ 1.30 ([12H], s, MeSb), 2.12 ([4H], t, CH_2Sb), 3.77 ([4H], t, CH_2O). ^{13}C{^{1}H} NMR ($CDCl_3$): δ −1.5 (MeSb), 17.6 (CH_2Sb), 67.4 (CH_2O), 197.4 ($^1J_{WC}$ = 124 Hz, 4CO), 200.0 ($^1J_{WC}$ = 162 Hz, CO). MS (FAB): *m*/*z* = 1047 [M + Na]$^+$, 1025 [M]$^+$.

[{Cr(CO)$_5$}$_2${O(CH$_2$CH$_2$SbMe$_2$)$_2$}]

Cr(CO)$_6$ (0.20 g, 0.91 mmol) was dissolved in thf (40 mL) and the solution photolysed for 1 h, producing an orange solution. O($CH_2CH_2SbMe_2$)$_2$ (0.137 g, 0.36 mmol) in thf (10 mL) was added and the mixture stirred for 1.5 h at room temperature. The solvent was removed *in vacuo* to leave a yellow/brown residue. Hexane (20 mL) was added and the mixture stirred for 10 min at room temperature. The solution was filtered and the solvent removed *in vacuo* yielding a bright yellow viscous oil (0.06 g, 22%). IR (CH_2Cl_2/cm^{-1}): 2057s, 1979w, 1935s; (Nujol/cm^{-1}): 2057(s), 1985m, 1938s. ^{1}H NMR ($CDCl_3$) δ 1.21 ([12H], s, MeSb), 2.12 ([4H], t, CH_2Sb), 3.8 ([4H], t, CH_2O). ^{13}C{^{1}H} NMR ($CDCl_3$): δ −2.0 (MeSb), 18.2 (CH_2Sb), 66.8 (CH_2O), 218.5 (4CO), 223.9 (CO).

[{W(CO)$_5$}$_2${O(CH$_2$CH$_2$SbPh$_2$)$_2$}]

W(CO)$_6$ (0.35 g, 1.00 mmol) was dissolved in thf (40 mL) and photolysed for 1 h, producing a dark yellow solution. A solution of O($CH_2CH_2SbPh_2$)$_2$ (0.25 g, 0.40 mmol) in thf (10 mL) was added and the mixture stirred for 2.5 h at room temperature. All volatiles were removed *in vacuo* leaving a yellow/brown residue. Hexane (20 mL) was added and the mixture stirred for 10 min at which point most of the solids dissolved. The yellow solution was then filtered and the solvent removed *in vacuo* to yield a brown solid (0.13 g, 27%). IR (CH_2Cl_2/cm^{-1}): 2071m, 1976, 1941s; (Nujol/cm^{-1}): 2071w, 1981w, 1944s. ^{1}H NMR ($CDCl_3$): δ 2.39 (4H, t, CH_2Sb), 3.65 (4H, t, CH_2O), 7.4–7.5 (m, PhSb). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 21.4 (CH_2Sb), 68.0 (CH_2O), 130.0, 130.2, 130.9, 135.3 (C$_{aromatic}$), 197.0 ($^1J_{WC}$ = 124 Hz, 4CO), 199.1 ($^1J_{WC}$ = 166 Hz, CO).

[{Cr(CO)$_5$}$_2${MeN(CH$_2$-2-C$_6$H$_4$BiPh$_2$)$_2$}]

Cr(CO)$_6$ (0.13 g, 0.59 mmol) was dissolved in thf (40 mL) and the solution photolysed for 1 h, producing a dark orange solution. MeN(CH_2-2-$C_6H_4BiPh_2$)$_2$ (0.25 g, 0.27 mmol) dissolved in thf (10 mL) was added and the mixture stirred for 1 h. The solvent was removed *in vacuo*, leaving an orange/brown solid. The addition of hexane (20 mL) gave an orange solution and some darker solids, which were removed by filtration. Removal of the solvent from the filtrate gave an orange/brown solid (0.17 g, 48%). IR (CH_2Cl_2/cm^{-1}): 2063s, 1980s, 1944s; (Nujol/cm^{-1}): 2063m, 1985s, 1946s. ^{1}H NMR (CD_2Cl_2, 253 K): δ 1.71 ([3H], s, MeN), 3.49 ([4H], s, CH_2N), 7.0–7.7 ([28H], m, aromatic CH). ^{13}C{^{1}H} NMR (CD_2Cl_2, 253 K): δ 41.2 (MeN), 64.7 (CH_2N), 127.8, 130.4, 130.7, 131.1, 136.6, 138.0, 140.3, 144.6 (C$_{aromatic}$), 157.7 and 159.2 (BiC$_{ipso}$), 217.6 (4CO), 222.8 (CO).

[W(CO)$_4${O(CH$_2$CH$_2$SbMe$_2$)$_2$}]

[W(CO)$_4$(pip)$_2$] (0.12 g, 0.27 mmol) was suspended in toluene (50 mL) and O($CH_2CH_2SbMe_2$)$_2$ (0.10 g, 0.27 mmol) was added. The mixture was refluxed for 18 h, resulting in a cloudy orange solution. The volatiles were removed *in vacuo* and dichloromethane (20 mL) added, resulting in a pale yellow solution and some orange solid. The solution was isolated by filtration, the volume of the filtrate reduced *in vacuo* to *ca.* 5 mL. Hexane (5 mL) was added and the solution stored in a freezer (−18 °C,16 h), yielding a pale orange precipitate (0.06 g, 22%). Required for $C_{12}H_{20}O_5Sb_2W$: C, 21.5; H, 3.0. Found: C, 21.8; H, 3.1%. IR (CH_2Cl_2/cm^{-1}): 2009, 1905sh, 1893s, 1871sh; (Nujol/cm^{-1}): 2012s, 1916s, 1896s, 1864sh. ^{1}H NMR ($CDCl_3$): δ 1.88 ([6H], s, MeSb), 2.04 ([2H], br t, SbCH_2), 3.76 ([2H], br t, CH_2O). ^{13}C{^{1}H} NMR ($CDCl_3$): δ −0.1 (MeSb), 18.5 (CH_2Sb), 68.4 (CH_2O), 204.0 ($^1J_{WC}$ = 130 Hz, CO), 207.7 ($^1J_{WC}$ = 148 Hz, CO). MS (FAB): *m*/*z* = 672 [M]$^+$, 588 [M − 3CO]$^+$.

The route using a 1 : 1 ratio of [W(CO)$_5$(thf)] : L yields a mixture of penta- and tetra-carbonyl complexes. Crystals of the tetracarbonyl complex were isolated from this mixture.

[Cr(CO)$_4${O(CH$_2$CH$_2$SbMe$_2$)$_2$}]

[Cr(CO)$_4$(nbd)] (0.10 g, 0.40 mmol) and Me$_2$Sb(CH_2)$_2$-O(CH_2)$_2$SbMe$_2$ (0.15 g, 0.40 mmol) were refluxed overnight in hexane (50 mL). The volatiles were removed *in vacuo* and the resultant yellow residue dissolved in CH_2Cl_2 (20 mL). The solution was concentrated *in vacuo* to *ca.* 5 mL causing precipitation of a yellow solid (0.04 g, 19%). Required for $C_{12}H_{20}CrO_5Sb_2$: C, 26.7; H, 3.7. Found: C, 26.8; H, 3.8%. IR (CH_2Cl_2/cm^{-1}): 1996s, 1904sh, 1888s, 1869sh; (Nujol/cm^{-1}): 2000m, 1912m, 1891sh. ^{1}H NMR ($CDCl_3$): δ 1.12 (12H, s, MeSb), 2.05 (4H, t, CH_2Sb), 3.80 (4H, t, CH_2O). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ −1.5 (MeSb), 18.4 (CH_2Sb), 67.3 (CH_2O), 223.8 (CO), 229.6 (CO). MS (CI): $m/z = 540$ [M]$^+$.

A mixture of tetra- and penta-carbonyl complexes forms from the photolysis route using a 1 : 1 ratio of reactants. Crystals of the tetracarbonyl were grown from a sample made by this route.

[W(CO)$_4$\{MeN(CH$_2$-2-C$_6$H$_4$SbMe$_2$)$_2$\}]

$W(CO)_6$ (0.12 g, 0.35 mmol) was dissolved in thf (40 mL) and the solution photolysed for 1 h, giving a dark yellow solution. $MeN(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2$ (0.15 g, 0.29 mmol) dissolved in CH_2Cl_2 (10 mL) was added and the reaction mixture stirred for 2 h. The solvent was removed *in vacuo* leaving a dark brown residue. Extraction with hexane (20 mL) produced a yellow solution and residual brown solid, which was removed by filtration. Storage of the hexane solution (4 °C, 16 h) gave the complex as yellow crystalline blocks (0.15 g, 63%). Required for $C_{23}H_{27}NO_4Sb_2W$: C, 34.2; H, 3.4; N, 1.7. Found: C, 34.4; H, 3.3; N, 1.7%. IR (CH_2Cl_2/cm^{-1}): 2011s, 1907sh, 1893s, 1872s; (Nujol/cm^{-1}): 2011s, 1916sh, 1897s, 1858s. ^{1}H NMR ($CDCl_3$): δ 1.25 ([12H], s, MeSb), 1.87 ([3H], s, MeN), 3.61 ([4H], s, CH_2N), 7.23–7.49 ([8H], m, aromatic CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 2.9 (MeSb), 42.3 (MeN), 65.2 (CH_2), 128.9, 130.0, 132.4, 134.5, 134.6 ($C_{aromatic}$), 143.4 (C_{ipso}), 203.3 ($^1J_{WC} = 124$ Hz, CO), 206.5 ($^1J_{WC} = 161$ Hz, CO). MS (FAB): $m/z = 808$ [M]$^+$, 793 [M − Me]$^+$.

[Cr(CO)$_4$\{MeN(CH$_2$-2-C$_6$H$_4$SbMe$_2$)$_2$\}]

[$Cr(CO)_4$(nbd)] (0.10 g, 0.39 mmol) and $MeN(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2$ (0.20 g, 0.39 mmol) were dissolved in hexane (40 mL) and refluxed for 7 h, then stirred overnight. The solution was filtered and the filtrate reduced *in vacuo* to *ca.* 7 mL, causing precipitation of a yellow solid, which was isolated by filtration (0.05 g, 19%). Yellow crystals were grown from the filtrate (4 °C). Required for $C_{23}H_{27}CrNO_4Sb_2$: C, 40.8; H, 4.0; N, 2.1. Found: C, 41.8; H, 4.2; N, 2.0%. IR (CH_2Cl_2/cm^{-1}): 1999s, 1906s, 1890s, 1870sh; (Nujol/cm^{-1}): 1999m, 1915m, 1893s, 1859m. ^{1}H NMR ($CDCl_3$): δ 1.09 (12H, s, MeSb), 1.95 (3H, s, MeN), 3.53 (4H, s, CH_2N), 7.14–7.62 (8H, m, aromatic CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 1.49 (MeSb), 43.1 (MeN), 65.2 (CH_2N), 128.7, 129.6, 132.1, 134.6, 136.6 ($C_{aromatic}$), 143.3 (C_{ipso}), 223.0 (CO), 229.3 (CO). MS (FAB): $m/z = 676$ [M]$^+$, 564 [M − 4CO]$^+$.

This compounds was also identified as a major product from the reaction of [$Cr(CO)_5$(thf)] with the ligand, but could not readily be separated from the pentacarbonyl [\{$Cr(CO)_5$\}$_2$\{$MeN(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2$\}] also produced.

fac-[Cr(CO)$_3$\{S(CH$_2$-2-C$_6$H$_4$SbMe$_2$)$_2$\}]

$Cr(CO)_6$ (0.13 g, 0.58 mmol) was dissolved in acetonitrile (50 mL) and refluxed for 20 h, resulting in a bright yellow solution and some green solid. A solution of $S(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2$ (0.29 g, 0.58 mmol) in acetonitrile (40 mL) and dichloromethane (5 mL) was added, and the resulting mixture stirred for 1 h at room temperature. The volatiles were removed *in vacuo* and the resulting solids redissolved in dichloromethane (20 mL). The solution was filtered and the volume reduced *in vacuo* to *ca.* 5 mL. Diethyl ether (5 mL) was added and the solution was then concentrated further until it reached clouding point. The Schlenk was then stored in a freezer (−18 °C, 16 h), yielding bright yellow rhombic crystals (0.04 g, 13%). Required for $C_{21}H_{24}CrO_3SSb_2$: C, 38.7; H, 3.7. Found: C, 39.6; H, 3.3%. IR (CH_2Cl_2/cm^{-1}): 1927s, 1829vbr; (Nujol/cm^{-1}): 1922s, 1916s, 1827s, 1815s. ^{1}H NMR ($CDCl_3$): δ 1.13 ([6H], s, MeSb) and 1.36 ([6H s, MeSb), 3.41 ([4H], br m, CH_2S), 7.0–7.6 ([8H], m, aromatic CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 0.9 and 1.7 (MeSb), 45.9 (CH_2S), 129.7, 130.2, 130.5, 131.5, 132.3, 140.5 ($C_{aromatic}$), 230.8 (CO), 233.3 (CO). MS (FAB): $m/z = 652$ [M]$^+$, 568 [M − 3CO]$^+$.

fac-[Mo(CO)$_3$\{S(CH$_2$-2-C$_6$H$_4$SbMe$_2$)$_2$\}]

$Mo(CO)_6$ (0.13 g, 0.48 mmol) was dissolved in acetonitrile (50 mL) and the solution refluxed for 16 h under a flow of argon, resulting in a pale yellow solution. A solution of $S(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2$ (0.25 g, 0.48 mmol) in acetonitrile (40 mL) was added and the mixture allowed to stir for 5 h at room temperature. The solvent was removed *in vacuo*, yielding a brown residue which was dissolved in dichloromethane (20 mL), filtered and the filtrate concentrated *in vacuo* to *ca.* 5 mL. The addition of hexane (5 mL) precipitated a beige powder (0.15 g, 46%), which was collected by filtration. Required for $C_{21}H_{24}MoO_3SSb_2\cdot\frac{1}{2}CH_2Cl_2$: C, 34.4; H, 3.4. Found: C, 35.0; H, 3.1%. IR (CH_2Cl_2/cm^{-1}): 1939s, 1841s,br; (Nujol/cm^{-1}): 1933s, 1928sh, 1839s, 1825s. ^{1}H NMR ($CDCl_3$): δ 1.09 ([6H], s, MeSb) and 1.37 ([6H], s, MeSb), 3.58 ([2H], s, CH_2S), 3.61 ([2H], s CH_2S), 7.1–7.6 ([8H] aromatic CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ −0.3 and 0.7 (MeSb), 46.2 (CH_2S), 130.3, 130.4, 131.9, 132.4, 140.2, 148.0 ($C_{aromatic}$), 218.7 (CO), 223.3 (CO). MS (CI): $m/z = 696$ [M]$^+$.

[Mn(CO)$_3$\{S(CH$_2$-2-C$_6$H$_4$SbMe$_2$)$_2$\}][CF$_3$SO$_3$]

$Mn(CO)_5Br$ (0.08 g, 0.29 mmol) and Ag[CF_3SO_3] (0.075 g, 0.29 mmol) were dissolved in acetone (40 mL) and refluxed in the dark for 1 h. The resulting yellow solution was allowed to cool to room temperature, and filtered to remove the AgBr precipitate. $S(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2$ (0.15 g, 0.29 mmol) was added and the mixture refluxed for 20 min, then stirred at room temperature for 18 h. The volatiles were removed *in vacuo*, resulting in yellow/brown oil, which was dissolved in dichloromethane (10 mL), filtered to give a bright yellow solution, and then concentrated to *ca.* 5 mL. The addition of diethyl ether (5 mL) afforded a yellow precipitate (0.05 g, 21%), which was isolated by filtration. The filtrate was stored at 4 °C (16 h), yielding yellow block shaped crystals. Required for $C_{22}H_{24}F_3MnO_6S_2Sb_2$: C, 32.9, 3.0. Found: C, 32.3; H, 3.1%. IR (CH_2Cl_2/cm^{-1}): 2031s, 1963m, 1953m; (Nujol/cm^{-1}): 2020s, 1943s, 1927s. ^{1}H NMR ($CDCl_3$): δ 1.51 ([6H], s, MeSb) and 1.67 ([6H], s, MeSb), 3.72 ([4H], br m, CH_2S), 7.3–7.6 ([8H], m, $CH_{aromatic}$). ^{13}C NMR ($CDCl_3$): δ −1.94, −1.38 (MeSb), 42.8 (CH_2S), 125.9, 130.8, 132.2, 132.4, 132.7 and 138.5 ($C_{aromatic}$), 217 vbr (CO). ^{55}Mn NMR ($CDCl_3$): δ −1418 ($W_{\frac{1}{2}} = 3000$ Hz). MS (ESI$^+$): $m/z = 655$ [$Mn(CO)_3\{S(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2\}$]$^+$, 571 [$Mn\{S(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2\}$]$^+$.

Table 8 Crystal data and structure refinement details[a]

Compound	$[Cr(CO)_4\{O(CH_2CH_2SbMe_2)_2\}]$	$[W(CO)_4\{O(CH_2CH_2SbMe_2)_2\}]$	$[W(CO)_4\{MeN(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2\}]$	$[Cr(CO)_4\{MeN(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2\}]$	$[Cr(CO)_3\{S(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2\}]$	$[Mn(CO)_3\{S(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2\}][CF_3SO_3]$	$[Mn(CO)_3\{MeN(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2\}][CF_3SO_3]$
Formula	$C_{12}H_{20}CrO_5Sb_2$	$C_{12}H_{20}O_5Sb_2W$	$C_{23}H_{27}NO_4Sb_2W$	$C_{23}H_{27}CrNO_4Sb_2$	$C_{21}H_{24}CrO_3SSb_2$	$C_{22}H_{24}F_3MnO_6S_2Sb_2$	$C_{23}H_{27}F_3MnNO_6SSb_2$
M	539.78	671.63	808.81	676.96	651.96	803.97	800.96
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/m$ (no. 11)	$P2_1/n$ (no. 14)
a/Å	7.2837(5)	7.229(2)	8.9364(15)	9.6141(15)	12.6781(10)	8.7926(10)	11.2440(15)
b/Å	13.933(2)	14.047(5)	18.427(3)	26.060(4)	11.2606(10)	14.589(2)	14.737(2)
c/Å	17.804(3)	18.191(6)	16.230(3)	10.2948(15)	16.5520(15)	11.1433(10)	17.721(3)
α/°	90	90	90	90	90	90	90
β/°	94.690(10)	95.26(2)	100.494(7)	97.699(10)	90.357(5)	106.534(8)	107.168(10)
γ/°	90	90	90	90	90	90	90
U/Å^3	1800.8(4)	1839.4(10)	2627.9(7)	2556.0(7)	2363.0(4)	1370.3(3)	2805.7(7)
Z	4	4	4	4	4	2	4
μ(Mo-Kα)/mm^{-1}	3.583	9.167	6.434	2.543	2.828	2.619	2.487
F(000)	1032	1232	1520	1320	1264	780	1560
Total no. reflections	18994	13234	17567	20852	29464	14910	27167
Unique reflections	3512	3519	5975	5710	5402	3233	5493
R_{int}	0.031	0.044	0.028	0.049	0.041	0.030	0.065
Min., max. Transmission	0.804, 1.000	0.530, 1.000	0.779, 1.000	0.780, 1.000	0.8574, 1.000	0.7585, 1.000	0.8942 to 1.000
No. of parameters, restraints	218, 86	218, 47	285, 0	280, 0	253, 0	175, 0	334, 0
$R_1{}^b$ $[I_o > 2\sigma(I_o)]$	0.064	0.057	0.023	0.059	0.033	0.025	0.062
R_1 (all data)	0.074	0.069	0.025	0.077	0.041	0.027	0.089
w$R_2{}^b$ $[I_o > 2\sigma(I_o)]$	0.161	0.132	0.049	0.109	0.061	0.057	0.112
wR_2 (all data)	0.172	0.143	0.050	0.118	0.064	0.059	0.126

[a] Common items: $T = 120$ K; λ(Mo-Kα) = 0.71073 Å; θ(max) = 27.5°. [b] $R_1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$. $wR_2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2 / \Sigma w F_o{}^4]^{1/2}$.

$[Mn(CO)_3\{MeN(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2\}][CF_3SO_3]$

$Mn(CO)_5Br$ (0.08 g, 0.29 mmol) and $Ag[CF_3SO_3]$ (0.075 g, 0.29 mmol) were dissolved in acetone (40 mL) and refluxed in the dark for 1 h. The resulting yellow solution was allowed to cool to room temperature, and filtered to remove the AgBr precipitate. $MeN(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2$ (0.15 g, 0.29 mmol) was added and the mixture refluxed for 20 min, then stirred for 18 h. The volatiles were removed *in vacuo*, leaving a yellow/green oil, which was redissolved in dichloromethane (10 mL), filtered to give a bright yellow solution, and concentrated to *ca.* 5 mL. The addition of hexane (10 mL) afforded a yellow precipitate (0.18 g, 77%), which was isolated by filtration. The filtrate was stored at 4 °C (16 h), yielding yellow crystals. IR (CH_2Cl_2/cm^{-1}): 2023s, 1950s, 1935s; (Nujol/cm^{-1}): 2014s, 1935sh, 1929s. ^1H NMR ($CDCl_3$): δ 1.15*, 1.52 (br, s, MeSb), 2.01*, 2.83 (s, MeN), 3.48*, 4.01–4.12 (br m, CH_2N), 7.3–7.8 (m, $CH_{aromatic}$) (* minor species). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ −5.4, −3.0*, −1.7*, −1.0 (MeSb), 59.0 (MeN)†, 74.9*, 76.7 (CH_2), 125.8 129.9, 130.4, 130.6, 131.6, 132.5, 133.1, 134.0, 134.8, 139.9, 140.4 ($C_{aromatic}$), 215.1, 216.2*, 218.0*, 219.6 (CO). ^{19}F NMR ($CDCl_3$) δ −77.0 (s), −77.8 (vbr). ^{55}Mn NMR (CH_2Cl_2) δ −1745 ($W_{\frac{1}{2}}$ = 4500 Hz). MS (ESI$^+$): m/z = 652 $[Mn(CO)_3\{MeN(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2\}]^+$, 568 $[Mn\{MeN(CH_2\text{-}2\text{-}C_6H_4SbMe_2)_2\}]^+$. († the second MeN- resonance is obscured by solvent).

X-Ray crystallography

Details of the crystallographic data collection and refinement parameters are given in Table 8. Crystals were obtained as described above. Data collection used a Nonius Kappa CCD diffractometer fitted with monochromated (confocal mirrors) Mo-Kα X-radiation (λ = 0.71073 Å). Crystals were held at 120 K in a nitrogen gas stream. Structure solution and refinement were routine except as described below,[23–25] with hydrogen atoms on C added to the model in calculated positions. Both $[M(CO)_4\{O(CH_2CH_2SbMe_2)_2\}]$ (M = Cr or W) showed some disorder in the $CH_2CH_2OCH_2CH_2$ unit. This was modelled satisfactorily using partial atom occupancies, giving two different conformations in approximately 50 : 50 ratio. However, the disorder precludes detailed analysis of bond distances in this region.

CCDC 817769–817775 contain the supplementary crystallographic data for this paper.†

Acknowledgements

We thank EPSRC for support (EP/F038763), for a studentship (S.L.B) and Dr M. Webster for assistance with the X-ray crystallographic analyses.

References

1 N. R. Champness and W. Levason, *Coord. Chem. Rev.*, 1994, **133**, 115; W. Levason and G. Reid, *Coord. Chem. Rev.*, 2006, **250**, 2565; W. Levason and G. Reid, in *Comprehensive Coordination Chemistry II*, J. A. McCleverty and T. J. Meyer, (Eds), Elsevier Oxford, 2003, vol. 1, 391.

2 H. Werner, *Angew. Chem., Int. Ed.*, 2004, **43**, 938.

3 *Gmelin Handbuch der Anorganische Chemie*, 8th ed. *Bismuth-organic Compounds*, Springer Verlag, NY, 1978; K. Y. Akiba and Y. Yamamoto, *Chem. Org. Arsenic Antimony Bismuth Compounds*, S. Patai, (Ed), Wiley NY, 1994, 761H. Suzuki and Y. Matano, in *The Chemistry of Arsenic*

Antimony and Bismuth, N. C. Norman, (Ed), Blackie, London 1998, 207.

4 H. Schumann and L. Eguren, *J. Organomet. Chem.*, 1991, **403**, 183; H. J. Breunig, E. Lork, C. I. Rat and R. P. Wagner, *J. Organomet. Chem.*, 2007, **692**, 3430; H. J. Breunig, T. Borrmann, E. Lork, O. Moldovan, C. I. Rat and R. P. Wagner, *J. Organomet. Chem.*, 2009, **694**, 427.

5 N. J. Holmes, W. Levason and M. Webster, *J. Organomet. Chem.*, 1997, **545–546**, 111.

6 N. J. Holmes, W. Levason and M. Webster, *J. Organomet. Chem.*, 1999, **584**, 179.

7 W. Levason, C. A. McAuliffe and R. D. Sedgwick, *J. Organomet. Chem.*, 1976, **122**, 531; W. Levason, B. Sheihk and F. P. McCullough, *J. Coord. Chem.*, 1982, **12**, 53; W. Levason, C. A. McAuliffe and S. G. Murray, *J. Chem. Soc., Dalton Trans.*, 1977, 711.

8 A. F. Chiffey, J. Evans, W. Levason and M. Webster, *Organometallics*, 1996, **15**, 1280.

9 M. Jura, W. Levason, G. Reid and M. Webster, *Dalton Trans.*, 2009, 7811.

10 M. F. Davis, M. Jura, W. Levason, G. Reid and M. M. Webster, *J. Organomet. Chem.*, 2007, **692**, 5589.

11 S. L. Benjamin, W. Levason, G. Reid and M. C. Rogers, *Organometallics*, 2011, **30**, 895.

12 See for example: A. Soran, H. J. Breunig, V. Lippolis, M. Arca and C. Silvestru, *Dalton Trans.*, 2009, 77; H. J. Breunig, L. Koenigsmann, E. Lork, N. Philipp, M. Nema, C. Silvestru, A. Soran, R. A. Varga and R. R Wagner, *Dalton Trans.*, 2008, 1831; L. Balazs, H. J. Breunig, E. Lork, A. Soran and C. Silvestru, *Inorg. Chem.*, 2006, **45**, 2341; S. Yasuike, Y. Kishi, S. Kawara, K. Yamaguchi and J. Kurita, *J. Organomet. Chem.*, 2006, **691**, 2213; L. M. Opris, A. M. Preda, R. A. Varga, H. J. Breunig and C. Silvestru, *Eur. J. Inorg. Chem.*, 2009, 1187; X.-W. Zhang, J. Xia, H.-W. Yan, S.-L. Li, S.-F. Yin, C.-T. Au and W.-Y. Wong, *J. Organomet. Chem.*, 2009, **694**, 3019.

13 E. Schewchuk and S. B. Wild, *J. Organomet. Chem.*, 1977, **128**, 115.

14 M. D. Brown, W. Levason, J. M. Manning and G. Reid, *J. Organomet. Chem.*, 2005, **690**, 1540.

15 W. Levason, M. L. Matthews, G. Reid and M. Webster, *Dalton Trans.*, 2004, 51.

16 A. M. Hill, N. J. Holmes, A. R. J. Genge, W. Levason, M. Webster and S. Rutschow, *J. Chem. Soc., Dalton Trans.*, 1998, 825.

17 See web-site: www.ccdc.cam.ac.uk/products/csd/radii for values used; literature reference is: B. Cordero, V. Gomez, A. E. Platero-Prats, M. Reves, J. Echeverria, E. Cremades, F. Barragan and S. Alvarez, *Dalton Trans.*, 2008, 2832.

18 D. P. Tate, W. R. Knipple and J. M. Augl, *Inorg. Chem.*, 1962, **1**, 433.

19 R. Uson, V. Riera, J. Gimeno, M. Laguna and M. P. Gamasa, *J. Chem. Soc., Dalton Trans.*, 1979, 996.

20 W. Strohmeier, *Angew. Chem.*, 1964, **76**, 873.

21 E. Subasi, S. Karahan and A. Ercag, *Russ. J. Coord. Chem.*, 2007, **33**, 886.

22 G. R. Dobson and G. C. Faber, *Inorg. Chim. Acta*, 1970, **4**, 87.

23 G. M. Sheldrick, *SHELXS-97 Program for crystal structure solution*, University of Göttingen, Germany, 1997.

24 G. M. Sheldrick, *SHELXL-97 Program for crystal structure refinement*, University of Göttingen, Germany, 1997.

25 H. D. Flack, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1983, **39**, 876.