

## Chromium, molybdenum and tungsten carbonyl derivatives of distibinomethane ligands †

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Substituted Group 6 carbonyl complexes of the distibinomethane ligands  $\text{Ph}_2\text{SbCH}_2\text{SbPh}_2$  (dpsm) and  $\text{Me}_2\text{SbCH}_2\text{SbMe}_2$  (dmsm) of types  $[\text{M}(\text{CO})_5(\eta^1\text{-dpsm})]$  ( $\text{M} = \text{Cr}, \text{Mo}$  or  $\text{W}$ ),  $[(\text{OC})_5\text{M}(\mu\text{-dpsm})\text{M}(\text{CO})_5]$  ( $\text{M} \neq \text{Mo}$ ),  $[(\text{OC})_5\text{M}(\mu\text{-dmsm})\text{M}(\text{CO})_5]$ ,  $[(\text{OC})_4\text{M}(\mu\text{-dpsm})_2\text{M}(\text{CO})_4]$ ,  $[(\text{OC})_4\text{M}(\mu\text{-dmsm})_2\text{M}(\text{CO})_4]$  and *fac*- $[\text{M}(\text{CO})_3(\eta^1\text{-dpsm})_3]$  have been isolated and characterised by chemical analysis, IR, NMR ( $^1\text{H}$ ,  $^{13}\text{C}\{-^1\text{H}\}$ ,  $^{95}\text{Mo}$ ) spectroscopy and FAB mass spectrometry. The crystal structures of  $[\text{W}(\text{CO})_5(\text{dpsm})]$ ,  $[\{\text{W}(\text{CO})_5\}_2(\text{dpsm})]$ ,  $[\{\text{W}(\text{CO})_4(\text{dpsm})\}_2]$  and  $[\{\text{W}(\text{CO})_4(\text{dmsm})\}_2]$  have been determined. Complexes of  $\eta^1\text{-dmsm}$  have been observed but are too unstable to isolate in a pure state. Both the ligands function as monodentate or bridging bidentates in the complexes characterised, but no examples with chelated distibinomethanes have been prepared. Comparisons are drawn with complexes of related diphosphine ligands.

In marked contrast to extensive work on the phosphorus and arsenic analogues, systematic studies of ligands containing two or more antimony donor atoms are rare.<sup>2</sup> In Part 1 we reported<sup>1</sup> complexes of the distibinomethane ligands bis(diphenylstibino)methane  $\text{Ph}_2\text{SbCH}_2\text{SbPh}_2$  (dpsm) and bis(dimethylstibino)methane  $\text{Me}_2\text{SbCH}_2\text{SbMe}_2$  (dmsm), with iron, cobalt, manganese and nickel carbonyls and carbonyl halides. The present manuscript describes detailed studies of complexes with Group 6 carbonyls. Some of these complexes have been reported previously<sup>3-6</sup> but with very limited spectroscopic (and no structural) characterisation and with relatively poor agreement in the data reported by different workers. As detailed below, this almost certainly results from the fact that many syntheses lead to mixtures of products unless carefully controlled, and the complexes once formed have limited stabilities and rearrange easily. Group 6 carbonyl complexes of  $\text{Ph}_2\text{SbESbPh}_2$  ( $\text{E} = \text{O}$  or  $\text{S}$ ) have been reported recently.<sup>7</sup> The much studied diphosphine analogues  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$  (dppm) and  $\text{Me}_2\text{PCH}_2\text{PMe}_2$  (dmpm) function as chelating, bridging bidentate or monodentate ligands.<sup>8,9</sup> The diarsine  $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2$  also exhibits all three coordination modes,<sup>10</sup> but for the distibinomethane ligands only monodentate ( $\eta^1$ ) or bridging bidentate (either across an M–M bond, or linking otherwise unconnected metal centres)<sup>1</sup> are definitely established. The claims<sup>3</sup> in the literature for chelation, *viz.*  $[\text{Mo}(\text{CO})_3(\text{dpsm})_2]$  and  $[\text{M}(\text{CO})_4(\text{dpsm})]$ , are based upon limited spectroscopic data, and are reinvestigated below.

### Results and Discussion

Substituted Group 6 carbonyl complexes have been extensively investigated and a variety of synthetic routes developed ranging from direct thermal or photochemical substitution of the hexacarbonyls through to displacement of the weakly bound ligands from complexes such as  $[\text{M}(\text{CO})_4(\text{diene})]$  or  $[\text{M}(\text{CO})_3(\eta^6\text{-arene})]$ .<sup>11</sup> Bis(diphenylstibino)methane is a weak donor<sup>1</sup> and reaction with  $[\text{M}(\text{CO})_6]$  in a variety of refluxing solvents including *n*-hexane, *n*-heptane, ethanol, toluene and diglyme (2,5,8-trioxanonane) gave poor yields (<10%) of  $[\text{M}(\text{CO})_5(\eta^1\text{-dpsm})]$  and traces (<2%) of higher substitution products, along with unchanged reagents. The reaction of  $[\text{M}(\text{CO})_6]$  with dpsm in ethanol using  $\text{NaBH}_4$  as a catalyst<sup>12</sup> increased the yields. For

$[\text{Cr}(\text{CO})_6]$  the products were a mixture of  $[\text{Cr}(\text{CO})_5(\eta^1\text{-dpsm})]$  and  $[\{\text{Cr}(\text{CO})_4(\text{dpsm})\}_2]$ , with  $[\text{W}(\text{CO})_6]$  mainly  $[\text{W}(\text{CO})_5(\eta^1\text{-dpsm})]$  with a little  $[\{\text{W}(\text{CO})_4(\text{dpsm})\}_2]$ , and unexpectedly for  $[\text{Mo}(\text{CO})_6]$  predominantly  $[\text{Mo}(\text{CO})_3(\eta^1\text{-dpsm})_3]$ . Substitution of other ligands also proved to be unpredictable and very dependent upon the conditions. For example,  $[\text{Mo}(\text{CO})_4(\text{pip})_2]$  (pip = piperidine) and dpsm in  $\text{CH}_2\text{Cl}_2$  gave  $[\text{Mo}(\text{CO})_3(\eta^1\text{-dpsm})_3]$  rather than the expected tetracarbonyl complex, whilst  $[\text{Mo}(\text{CO})_4(\text{cod})]$  (cod = cycloocta-1,5-diene) and dpsm in benzene gave a mixture including  $[\text{Mo}(\text{CO})_5(\eta^1\text{-dpsm})]$ ,  $[\{\text{Mo}(\text{CO})_4(\text{dpsm})\}_2]$  and  $[\text{Mo}(\text{CO})_6]$ . In addition to the weak nucleophilicity of dpsm, a second problem is the limited stability of the distibine complexes in solution and their tendency to rearrange or disproportionate into other complexes. The latter tendency was particularly noticeable during attempts to grow crystals for X-ray studies when a mixture of crystals of visually different habits was often obtained, some identified as free dpsm<sup>1</sup> or  $[\text{M}(\text{CO})_6]$ . The  $\text{Me}_2\text{SbCH}_2\text{SbMe}_2$  as expected was a better donor and its reactions are often cleaner, but the air sensitivity of the 'free'  $\text{SbMe}_2$  groups (the ligand is spontaneously inflammable in air) made it difficult to prepare complexes with  $\eta^1\text{-co-ordinated}$  dmsm. Despite these problems, syntheses for a range of complexes of both dpsm and dmsm in the pure state were developed and are now described. Small changes in the reaction conditions can lead to different or highly impure products.

### $[\text{M}(\text{CO})_5(\eta^1\text{-dpsm})]$ ( $\text{M} = \text{Cr}, \text{Mo}$ or $\text{W}$ )

Thermal substitution of dpsm into  $[\text{M}(\text{CO})_6]$  is an unsatisfactory route to these complexes; mixtures were always produced in poor overall yield which were not readily separated. This almost certainly accounts for the poor agreement in the spectroscopic data reported previously by different workers.<sup>3,4</sup> The complexes can be made by photolysis of  $[\text{M}(\text{CO})_6]$  in thf to yield  $[\text{M}(\text{CO})_5(\text{thf})]$  *in situ*, followed by addition of dpsm, whilst a clean chemical route is reaction of  $[\text{NET}_4][\text{M}(\text{CO})_5\text{Br}]$ <sup>13</sup> with dpsm in a 1 : 1 mol ratio in ethanol. The spectroscopic data (Experimental section), especially the three  $\nu(\text{CO})$  modes in the IR spectra (theory  $2A_1 + E$ ) and the two  $\delta(\text{CO})$  resonances (*ca.* 1 : 4 ratio) in the  $^{13}\text{C}\{-^1\text{H}\}$  NMR spectra, are consistent with the expected  $C_{4v}$  structure **I**, confirmed by the X-ray study of  $[\text{W}(\text{CO})_5(\text{dpsm})]$  (below). The FAB mass spectrum of  $[\text{Cr}(\text{CO})_5(\eta^1\text{-dpsm})]$  contains a parent ion with the correct

† Complexes of distibinomethane ligands. Part 2.<sup>1</sup>

**Table 1** Selected IR spectra (cm<sup>-1</sup>)

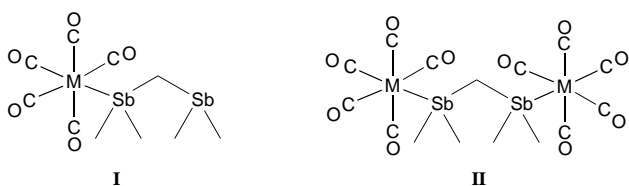
Complex	$\nu(\text{CO})$ , Nujol mull	$\nu(\text{CO})$ , CH <sub>2</sub> Cl <sub>2</sub> solution
[Cr(CO) <sub>5</sub> (dpsm)]	2056m, 1982m, 1922s	2060m, 1983w, 1941s
[Mo(CO) <sub>5</sub> (dpsm)]	2068m, 1991m, 1935s	2072m, 1993w, 1949s
[W(CO) <sub>5</sub> (dpsm)]	2066m, 1983m, 1918s	2070m, 1982w, 1943s
[Cr <sub>2</sub> (CO) <sub>10</sub> (dpsm)]	2058m, 1980w, 1962 (sh), 1915s	2060m, 1982 (sh), 1944s
[W <sub>2</sub> (CO) <sub>10</sub> (dpsm)]	2068m, 1958s, 1913s	2070m, 1985 (sh), 1946s
[Cr <sub>2</sub> (CO) <sub>10</sub> (dmsm)]	2058m, 1971w, 1939s, 1900 (sh)	2058m, 1967w, 1933s
[Mo <sub>2</sub> (CO) <sub>10</sub> (dmsm)]	2071m, 1988m, 1955s	2070m, 2023m, 1988 (sh), 1953s
[W <sub>2</sub> (CO) <sub>10</sub> (dmsm)]	2067m, 2014w, 1937s, 1908s	2068m, 2014w, 1980 (sh), 1939s
[Cr <sub>2</sub> (CO) <sub>8</sub> (dpsm) <sub>2</sub> ]	1999m, 1911s, 1900 (sh)	2013m, 1923s, 1910 (sh), 1897s
[Mo <sub>2</sub> (CO) <sub>8</sub> (dpsm) <sub>2</sub> ]	2016m, 1920 (sh), 1901s, 1880s	2021m, 1926s, 1915s, 1889 (sh)
[W <sub>2</sub> (CO) <sub>8</sub> (dpsm) <sub>2</sub> ]	2014m, 1913s, 1898s, 1862s	2020m, 1914s, 1903s, 1880 (sh)
[Cr <sub>2</sub> (CO) <sub>8</sub> (dmsm) <sub>2</sub> ]	1993s, 1920 (sh), 1890s (br)	2000s, 1908 (sh), 1894s, 1875 (sh)
[Mo <sub>2</sub> (CO) <sub>8</sub> (dmsm) <sub>2</sub> ]	2014s, 1920 (sh), 1880s (br)	2018m, 1919s, 1910 (sh), 1889m
[W <sub>2</sub> (CO) <sub>8</sub> (dmsm) <sub>2</sub> ]	2007s, 1905 (sh), 1880s (br)	2013s, 1902s (br), 1878 (sh)
[Cr(CO) <sub>3</sub> (dpsm) <sub>3</sub> ]	1910s, 1822s	1924s, 1836s
[Mo(CO) <sub>3</sub> (dpsm) <sub>3</sub> ]	1926s, 1835s	1944s, 1854s
[W(CO) <sub>3</sub> (dpsm) <sub>3</sub> ]	1924s, 1809s	1929s, 1834m (br)

Intensities: strong (s), medium (m), weak (w), shoulder (sh), broad (br).

**Table 2** Selected NMR spectroscopic data

Complex	<sup>1</sup> H NMR <sup>a</sup>			<sup>13</sup> C- <sup>1</sup> H NMR <sup>b</sup>				<sup>95</sup> Mo NMR <sup>c</sup>
	$\delta(\text{CH}_2)$	$\delta(\text{CH}_3)$	$\delta(\text{Ph})$	$\delta(\text{CH}_2)$	$\delta(\text{CH}_3)$	$\delta(\text{Ph})$	$\delta(\text{CO})$	
[Cr(CO) <sub>5</sub> (dpsm)]	2.35		7.2–7.5	4.6		128–136	217.6, 223.0	
[Mo(CO) <sub>5</sub> (dpsm)]	2.4		7.2–7.5	5.3		128–141	206.5, 210.5	–1856
[W(CO) <sub>5</sub> (dpsm)]	2.5		7.2–7.5	5.3		128–138	196.7 (126), 199.0 (162) <sup>d</sup>	<i>e</i>
[Cr <sub>2</sub> (CO) <sub>10</sub> (dpsm)]	2.65		7.1–7.4	2.2		129–135	217.2, 228.8	
[W <sub>2</sub> (CO) <sub>10</sub> (dpsm)]	2.8		7.2–7.5	3.0		128–136	196.5 (123), 198.2 (156) <sup>d</sup>	
[Cr <sub>2</sub> (CO) <sub>10</sub> (dmsm)]	2.05	1.5		0.8	1.6		218.5, 223.9	
[Mo <sub>2</sub> (CO) <sub>10</sub> (dmsm)]	1.8	1.3		0.9	1.3		206.2, 210.1	–1830
[W <sub>2</sub> (CO) <sub>10</sub> (dmsm)]	2.0	1.5		0.6	1.3		197.1 (127), 199.0 (164) <sup>d</sup>	
[Cr <sub>2</sub> (CO) <sub>8</sub> (dpsm) <sub>2</sub> ]	2.6		7.0–7.7	5.7		129–139	226.6, 228.4	
[Mo <sub>2</sub> (CO) <sub>8</sub> (dpsm) <sub>2</sub> ]	2.0		7.0–7.7	4.9		127–138	210.0, 214.6	–1760
[W <sub>2</sub> (CO) <sub>8</sub> (dpsm) <sub>2</sub> ]	2.6		7.0–7.7	4.6		129–140	200.7 (121), 203.5 (156) <sup>d</sup>	
[Cr <sub>2</sub> (CO) <sub>8</sub> (dmsm) <sub>2</sub> ]	1.45	1.3		2.5	2.1		222.8, 228.0	
[Mo <sub>2</sub> (CO) <sub>8</sub> (dmsm) <sub>2</sub> ]	1.6	1.3		2.4	1.9		210.6, 216.0	–1730
[W <sub>2</sub> (CO) <sub>8</sub> (dmsm) <sub>2</sub> ]	1.55	1.4		2.8	2.2		202.5 (130), 206.0 (158)	
[Cr(CO) <sub>3</sub> (dpsm) <sub>3</sub> ]	1.9		6.8–7.4	7.2		128–139	232.8	
[Mo(CO) <sub>3</sub> (dpsm) <sub>3</sub> ]	1.9		6.9–7.4	7.1		128–135	220.3	–1519
[W(CO) <sub>3</sub> (dpsm) <sub>3</sub> ]	2.0		7.0–7.4	6.5		127–140	210.8 (164) <sup>d</sup>	

<sup>a</sup> In CDCl<sub>3</sub>. <sup>b</sup> In 10% CDCl<sub>3</sub>–CH<sub>2</sub>Cl<sub>2</sub>. <sup>c</sup> Relative to aqueous Na<sub>2</sub>MoO<sub>4</sub>,  $\delta$  0; [Mo(CO)<sub>6</sub>] has  $\delta$  –1859. <sup>d</sup> <sup>1</sup>J(<sup>183</sup>W–<sup>13</sup>C)/Hz. <sup>e</sup> The low sensitivity and very long relaxation times of <sup>183</sup>W in carbonyl complexes, coupled with solution instability in some cases, prevented convincing <sup>183</sup>W resonances being observed.



isotope pattern, and ions resulting from CO loss down to [Cr(dpsm)]<sup>+</sup>; the molybdenum and tungsten complexes show [P – CO]<sup>+</sup> as the highest mass ions but similar fragments.

### [(OC)<sub>5</sub>M(μ-dpsm)M(CO)<sub>5</sub>] (M = Cr or W)

Thermal reactions of [M(CO)<sub>5</sub>(η<sup>1</sup>-dpsm)] with [M(CO)<sub>6</sub>] do not occur to a significant extent. The reaction of [M(CO)<sub>5</sub>Br]<sup>–</sup> with dpsm in a 2:1 mol ratio gave only [M(CO)<sub>5</sub>(η<sup>1</sup>-dpsm)] for M = Mo or W, and a mixture of [Cr(CO)<sub>5</sub>(η<sup>1</sup>-dpsm)] and [Cr(CO)<sub>5</sub>]<sub>2</sub>(dpsm) for chromium. This suggests that coordination of one stibine group reduces the reactivity of the second, but steric effects may also be important since [M(CO)<sub>5</sub>(η<sup>1</sup>-dpsm)] is a bulky ligand towards a second metal centre. The pure [M(CO)<sub>5</sub>]<sub>2</sub>(dpsm) (M = Cr or W) are best obtained from [M(CO)<sub>5</sub>(η<sup>1</sup>-dpsm)] and [M(CO)<sub>5</sub>(thf)]. Curiously, all attempts to prepare [Mo(CO)<sub>5</sub>]<sub>2</sub>(dpsm) resulted

only in recovery of [Mo(CO)<sub>5</sub>(η<sup>1</sup>-dpsm)]. The formulation of these complexes as [(OC)<sub>5</sub>M(μ-dpsm)M(CO)<sub>5</sub>] **II** follows from the very similar IR spectra (Table 1) to those of [M(CO)<sub>5</sub>(η<sup>1</sup>-dpsm)], and shows that the two M(CO)<sub>5</sub> groups are essentially isolated by the ligand bridge. Confirmation of the structure was obtained by the X-ray study of the tungsten complex (below). The chromium complex shows a parent ion [Cr<sub>2</sub>(CO)<sub>10</sub>(dpsm)]<sup>+</sup> in the FAB mass spectrum, but the highest significant feature for the tungsten complex is [P – 3(CO)]<sup>+</sup>, although both are good confirmation of the dimer formulation.

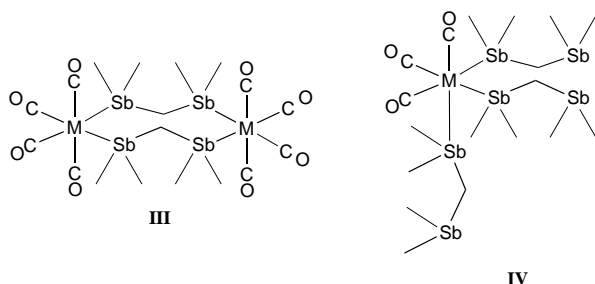
### [(OC)<sub>5</sub>M(μ-dmsm)M(CO)<sub>5</sub>] (M = Cr, Mo or W)

In marked contrast to the dpsm complexes, these dmsm compounds are readily made by reaction of [M(CO)<sub>6</sub>] with dmsm in a 2:1 mol ratio in a high-boiling solvent. The spectroscopic properties (Tables 1 and 2) are very similar to those of [(OC)<sub>5</sub>M(μ-dpsm)M(CO)<sub>5</sub>] and an analogous structure is proposed.

### cis-[[M(CO)<sub>4</sub>(L-L)]<sub>2</sub>] (M = Cr, Mo or W; L-L = dpsm or dmsm)

These complexes were prepared in relatively poor yields by displacement of the neutral ligands from [M(CO)<sub>4</sub>(nbd)] {M = Cr

or Mo; nbd = norbornadiene (bicyclo[2.2.1]hepta-2,5-diene) or  $[\text{W}(\text{CO})_4(\text{Me}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)]$ . Unless carefully controlled these reactions yield intractable mixtures of penta-, tetra- and tri-carbonyl complexes. The *cis* tetracarbonyl arrangement follows from the two  $^{13}\text{C}$  NMR carbonyl resonances (1 : 1 intensities) and the typical  $\nu(\text{CO})$  IR modes (theory  $2A_1 + B_1 + B_2$ ) (Tables 1 and 2). The formulation as dimers  $[(\text{OC})_4\text{M}(\mu\text{-L-L})_2\text{M}(\text{CO})_4]$  **III** rather than monomers  $[\text{M}(\text{CO})_4(\text{L-L})]$  is based upon the FAB mass spectra which show parent ions for the dmsm complexes (Experimental section), and dimetal fragments for the dpsm complexes of Mo and W, and was confirmed by single-crystal X-ray studies of  $[\{\text{W}(\text{CO})_4(\text{L-L})\}_2]$  (L-L = dpsm or dmsm) (below). Very small yields [5% (Mo), traces (Cr, W)] of monomer species  $[\text{M}(\text{CO})_4(\text{dpsm})]$  containing chelated dpsm reportedly<sup>3</sup> formed on prolonged photolysis (several days) of  $[\text{M}(\text{CO})_6]$  and ligand in hexane. We have been unable to confirm this. In our hands prolonged photolysis of  $[\text{Mo}(\text{CO})_6] + \text{dpsm}$  (1 : 1 mol ratio) in hexane gave  $[\text{Mo}(\text{CO})_3(\eta^1\text{-dpsm})]$ ,  $[\{\text{Mo}(\text{CO})_4(\text{dpsm})\}_2]$ , unchanged reagents and a large amount of grey insoluble carbonyl-free material. If complexes with a strained four-membered chelate ring were formed one would expect relatively large shifts in the  $\text{CH}_2$  resonances in the  $^1\text{H}$  or  $^{13}\text{C}\{-^1\text{H}\}$  NMR spectra,<sup>9,10</sup> but we have not observed examples of this. The pure  $[\{\text{M}(\text{CO})_4(\text{dmsm})\}_2]$  complexes appear air stable in the solid state, but in  $\text{CH}_2\text{Cl}_2$  solution they decompose quite rapidly.

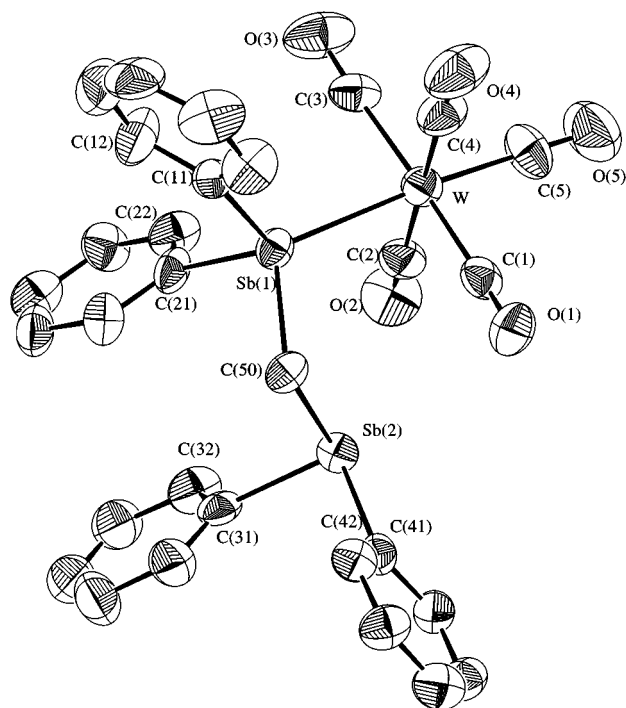


#### *fac*- $[\text{M}(\text{CO})_3(\eta^1\text{-dpsm})_3]$ (M = Cr, Mo or W)

The reaction of  $[\text{Mo}(\text{CO})_6]$  with dpsm in ethanol with  $\text{NaBH}_4$  as catalyst results in good yields of *fac*- $[\text{Mo}(\text{CO})_3(\eta^1\text{-dpsm})_3]$ , although the chromium and tungsten complexes do not form in this way. The *fac*- $[\text{Cr}(\text{CO})_3(\text{dpsm})_3]$  was made in low yield by heating  $[\text{Cr}(\text{CO})_4(\text{nbd})]$  with an excess of dpsm in ethanol or more slowly in methylcyclohexane, and *fac*- $[\text{W}(\text{CO})_3(\text{dpsm})_3]$  from  $[\text{W}(\text{CO})_3(\text{MeCN})_3]$  and dpsm. The single  $\delta(\text{CO})$  resonance in the  $^{13}\text{C}\{-^1\text{H}\}$  NMR spectrum of each complex and the two  $\nu(\text{CO})$  bands in the IR spectra are typical of *fac*- $\text{M}(\text{CO})_3\text{Sb}_3$  compounds **IV**, cf. *fac*- $[\text{Mo}(\text{CO})_3\{\text{MeC}(\text{CH}_2\text{-SbPh}_2)_3\}]$ .<sup>14</sup> The FAB mass spectra exhibit very weak parent ions with the correct isotope structure confirming the formulations. Unfortunately we have been unable to grow crystals of these complexes; the chromium and tungsten complexes decompose slowly in solution, and whilst the molybdenum complex is stable, repeated attempts to obtain crystals have produced only very thin needles which diffract too weakly. The complex formulated<sup>3</sup> as  $[\text{Mo}(\text{CO})_3(\text{dpsm})_2]$  and suggested to contain one chelated and one monodentate dpsm ligand, despite showing only a single  $\delta(\text{CH}_2)$  resonance in the  $^1\text{H}$  NMR spectrum, is one of the few claimed examples containing chelated dpsm. Comparison of the data reported for this complex with those obtained from  $[\text{Mo}(\text{CO})_3(\text{dpsm})_3]$  shows excellent agreement, and we conclude that the report of  $[\text{Mo}(\text{CO})_3(\text{dpsm})_2]$  is in error.

#### $\eta^1\text{-dmsm}$ Complexes

A number of attempts were made to isolate complexes of dmsm



**Fig. 1** The structure of  $[\text{W}(\text{CO})_5(\text{dpsm})]$  showing the atom labelling scheme. Ellipsoids are drawn at the 50% probability level

bonded only *via* one antimony. For example addition of dmsm to a solution of  $[\text{M}(\text{CO})_5(\text{thf})]$  (M = Mo or W) in thf (1 : 1 mol ratio), and removal of the solvent in vacuum, gave air-sensitive oils. The tungsten product had a  $^{13}\text{C}\{-^1\text{H}\}$  NMR spectrum showing  $\delta(\text{CO})$  200.1 and 197.5 in the expected ratio for a pentacarbonyl and weaker features at 199.0 and 197.0 assignable to  $[\text{W}_2(\text{CO})_{10}(\mu\text{-dmsm})]$ . The range  $\delta +5$  to  $-5$  showed seven main resonances attributable to the ditungsten complex, free dmsm<sup>1</sup> and  $[\text{W}(\text{CO})_5(\eta^1\text{-dmsm})]$ . Under an inert atmosphere the spectrum changed over a period of a few hours and on exposure to air a white solid deposited, no doubt due to oxidation at the free  $\text{Me}_2\text{Sb}$  groups.† Similar data were obtained from the molybdenum system and in addition the  $^{95}\text{Mo}$  NMR spectrum showed resonances at  $\delta -1859.0$   $\{[\text{Mo}(\text{CO})_6]\}$ ,  $-1856.0$   $\{[\text{Mo}_2(\text{CO})_{10}(\text{dmsm})]\}$  and  $-1856.5$   $\{[\text{Mo}(\text{CO})_5(\eta^1\text{-dmsm})]\}$ . The reaction of  $[\text{Mo}(\text{CO})_6]$  with an excess of dmsm in ethanol with added  $\text{NaBH}_4$  gave after work-up a grey powder, which was poorly soluble in chlorocarbons. It had major features in the  $^{13}\text{C}\{-^1\text{H}\}$  NMR spectrum at  $\delta$  227.0, 3.4, 2.2 and 0.7 and IR bands at 1933 and  $1840\text{ cm}^{-1}$  ( $\text{CH}_2\text{Cl}_2$ ) which are consistent with the presence of *fac*- $[\text{Mo}(\text{CO})_3(\eta^1\text{-dmsm})_3]$ . An analytically pure sample could not be obtained, and the  $\text{CH}_2\text{Cl}_2$  solution decomposed completely in a few hours. These results show that complexes of  $\eta^1\text{-co-ordinated}$  dmsm can be formed, but are unstable both to air oxidation and rearrangement into other complexes; the latter effectively prevents isolation of pure samples.

#### Crystal structures of $[\text{W}(\text{CO})_5(\text{dpsm})]$ , $[\{\text{W}(\text{CO})_5\}_2(\text{dpsm})]$ , $[\{\text{W}(\text{CO})_4(\text{dpsm})\}_2]$ and $[\{\text{W}(\text{CO})_4(\text{dmsm})\}_2]$

The molecules are shown in Figs. 1, 2, 3 and 4 respectively and selected bond lengths and angles presented in Table 3. The results confirm the structures and bonding modes of the distibines proposed above on the basis of spectroscopic data, and also reveal some unexpected trends in comparison to data on phosphine and arsine analogues. The first two examples can usefully be discussed together as they show co-ordination

† Unlike phosphines and arsines, stibines do not oxidise cleanly to the ligand oxide, but are converted into intractable polymeric materials.

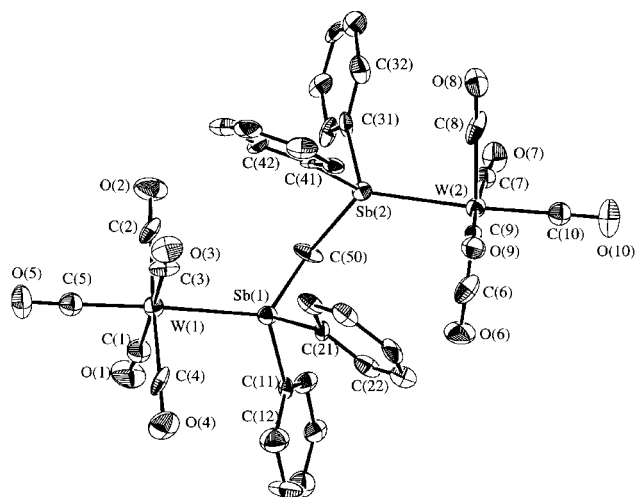


Fig. 2 The structure of  $[\{W(CO)_5\}_2(dpsm)]$ . Details as in Fig. 1

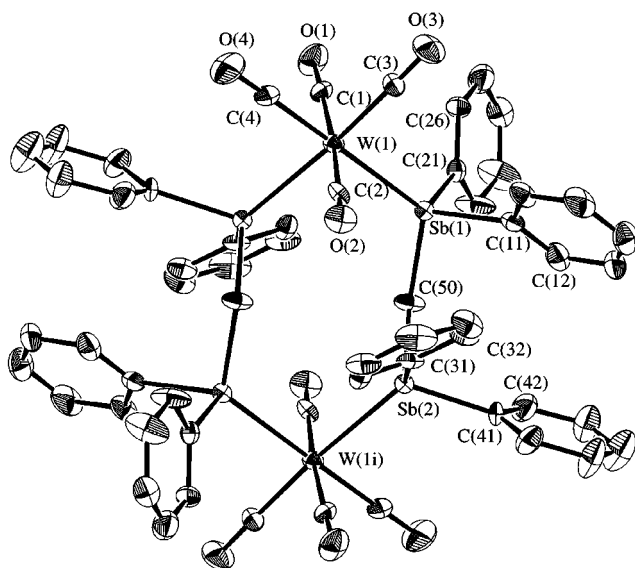


Fig. 3 The structure of  $[\{W(CO)_4(dpsm)\}_2]$ . Details as in Fig. 1

at one or two Sb atoms to unconnected square pyramidal  $W(CO)_5$  residues. The  $\eta^1$  derivative shows a smaller Sb–C–Sb angle [ $106.8(5)^\circ$ ] than free dpsm [ $117.3(2)^\circ$ ] and the C–Sb–C angles at the co-ordinated Sb are larger than the free C–Sb–C angles. Co-ordination to Sb(2) in the second compound results in an increase in the Sb–C–Sb angles by some  $15^\circ$  and the by now expected opening up of the C–Sb(2)–C angles. The complex  $[W(CO)_5(dpsm)]$  is isostructural with  $[Cr(CO)_5(Ph_2SbOSbPh_2)]$ ,<sup>7</sup> although in the latter the angle Sb–S–Sb is more acute ( $96.7^\circ$ ).

The two tetracarbonyl derivatives (Figs. 3 and 4) are centrosymmetric dimeric species with the Sb atoms bonded to different W atoms. The Sb–C–Sb angle [ $125.4(5)^\circ$ ] in  $[\{W(CO)_4(dpsm)\}_2]$  is a little larger ( $3^\circ$ ) than that in  $[\{W(CO)_5\}_2(dpsm)]$  and the C–Sb–C angles are as expected for a bonded Sb. A similar structure was found<sup>7</sup> for  $[\{Cr(CO)_4(Ph_2SbOSbPh_2)\}_2]$  with a wider Sb–O–Sb angle of  $136.9(1)^\circ$ .  $[\{W(CO)_4(dmsm)\}_2]$  is only the second structurally characterised example of a dmsm complex, the other being<sup>1</sup>  $[Co_2(CO)_4(\mu-CO)_2(\mu-dmsm)]$ . In both structures the C–Sb–C angles lie in the range *ca.*  $98$  to  $103^\circ$ , but the Sb–C–Sb angle is smaller in the cobalt complex [ $114.5(7)^\circ$ ] than in the present tungsten example [ $119.7(8)^\circ$ ].

Comparable structural data on the distibinomethane complexes and some phosphorus and arsenic analogues are collected in Table 4. Most notable are the effects of co-ordination upon the bond angles E–C–E and C–E–C (E = P, As or Sb). In

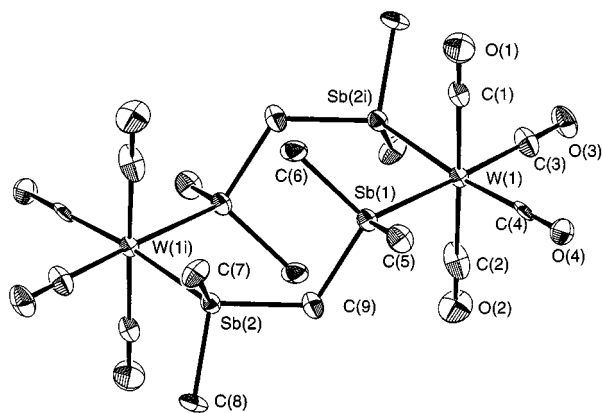


Fig. 4 The structure of  $[\{W(CO)_4(dmsm)\}_2]$ . Details as in Fig. 1

the case of dppm upon co-ordination to a metal there is no significant effect upon the C–P–C angles and although the data on complexes of  $Ph_2AsCH_2AsPh_2$  (dpam) are more restricted and of lower quality, the same seems to hold for the C–As–C angles. In marked contrast, in the stibines the C–Sb–C angles *increase* on co-ordination, most evident in comparing the angles at bound and free antimony centres in the  $\eta^1$ -dpsm complexes. A similar increase in the C–Bi–C angles was observed<sup>21,22</sup> on co-ordination of  $BiPh_3$  in  $[M(CO)_5(BiPh_3)]$ . On a simple hybridisation model these results suggest that on co-ordination more s character enters into the C–Sb bonds (conversely the donor ‘lone pair’ is now in an orbital with increased p character). A more detailed understanding of this effect must await high level MO calculations which are presently rare in organoantimony chemistry.<sup>23</sup>

The second effect, the changes in the E–CH<sub>2</sub>–E angles on co-ordination, also varies with the identity of E.  $\eta^1$  Co-ordination of dppm as in  $[Fe(CO)_4(dppm)]$  or  $[Cr(CO)_3(dppm)]$  (the latter contains one chelating and one monodentate dppm ligand) results in an *increase* in this angle, whereas in the  $\eta^1$ -dpsm complexes the angle *decreases*. The ‘free’  $SbPh_2$  group has no close contacts to other groups or to the metal and hence the decrease in the Sb–C–Sb angle does not result from any direct interaction. Co-ordination of a second metal centre to form a  $\mu$ -dpsm ligand results in Sb–C–Sb angles similar to or greater ( $\leq 10^\circ$ ) than that in free dpsm (Table 4). The case of the intermediate dpam is less clear due to limited data, but in the seven-co-ordinated carbonyl halides it appears that the As–C–As angle of  $\eta^1$ -dpam is not significantly different from that in free dpam.

### Some comparisons

Bis(diphenylphosphino)methane forms complexes with the Group 6 carbonyls of types  $[M(CO)_5(\eta^1-dppm)]$ ,  $[\{M(CO)_5\}_2(\mu-dppm)]$ , *mer*- and *fac*- $[M(CO)_3(dppm)_2]$ ,  $[M(CO)_4(dppm)]$  and  $[M(CO)_2(dppm)_2]$ ,<sup>8,18,24–26</sup> chelation being present in the last three types. The more nucleophilic dmpm appears more reluctant to form  $\eta^1$  complexes {although *fac*- $[M(CO)_3(dmpm)_3]$  are known}, but chelates readily as in  $[M(CO)_4(dmpm)]$ , and in *fac*- $[M_2(CO)_6(dmpm)_3]$  both bridging and chelating dmpm are present.<sup>9</sup> Bis(diphenylarsino)methane forms  $\eta^1$  complexes readily, *viz.*  $[M(CO)_5(dpam)]$ , *cis*- $[M(CO)_4(dpam)_2]$ , *fac*- $[M(CO)_3(dpam)_3]$ , but also chelates in  $[M(CO)_4(dpam)]$ ,<sup>10</sup> and both chelate and  $\eta^1$  forms are present in the carbonyl halides  $[Mo(CO)_2X_2(dpam)_2]$  (X = Cl or Br).<sup>27</sup> The crystal structures of the latter complexes reveal very strained non-planar four-membered rings formed by the chelated dpam.<sup>20</sup> The behaviour of the distibinomethanes described above extends these trends in that  $\eta^1$  and bridging behaviours are found, but we have no evidence for chelation, apparently the strain in a four-membered chelate ring containing two large antimony donors is too great.

**Table 3** Selected bond lengths (Å) and angles (°)

(a) [W(CO) <sub>5</sub> (dpsm)]			
Sb(1)–W	2.743(1)	Sb(1)⋯Sb(2)	3.497(1)
W–C	1.96(2)–2.05(2)	C–O	1.14(2)–1.17(2)
Sb(1)–C	2.10(1)–2.16(1)	Sb(2)–C	2.16(1)–2.19(1)
C–C	1.35(3)–1.44(2)		
W–Sb(1)–C	113.7(3)–118.4(4)	Sb(1)–C(50)–Sb(2)	106.8(5)
C–Sb(1)–C	99.4(5)–104.9(5)	C–Sb(2)–C	96.4(5)–97.4(5)
C–C–C	116(1)–123(1)	W–C–O	174(1)–179(2)
(b) [W(CO) <sub>5</sub> ] <sub>2</sub> (dpsm)]			
Sb(1)–W(1)	2.756(2)	Sb(2)–W(2)	2.753(2)
W–C	1.96(3)–2.12(3)	C–O	1.09(3)–1.18(3)
Sb(1)–C	2.11(3)–2.16(2)	Sb(2)–C	2.12(2)–2.17(2)
C–C	1.34(4)–1.46(4)	Sb(1)⋯Sb(2)	3.723(2)
W(1)–Sb(1)–C	111.5(5)–120.3(8)	W(2)–Sb(2)–C	111.3(6)–122.5(8)
C–Sb(1)–C	99.3(9)–104.5(9)	C–Sb(2)–C	98.1(9)–102.2(9)
C–C–C	116(3)–123(2)	Sb(1)–C(50)–Sb(2)	122(1)
W(1)–C–O	176(3)–179(2)	W(2)–C–O	172(2)–179(2)
(c) [W(CO) <sub>4</sub> (dpsm)] <sub>2</sub>			
Sb(1)–W(1)	2.7574(8)	Sb(2)–W(1i)	2.7420(8)
W(1)–C	1.96(1)–2.05(1)	C–O	1.12(1)–1.17(1)
Sb(1)–C	2.15(1)–2.18(1)	Sb(2)–C	2.12(1)–2.15(1)
C–C	1.35(2)–1.46(2)	Sb(1)⋯Sb(2)	3.847(1)
W(1)–Sb(1)–C	113.5(3)–122.8(3)	W(1i)–Sb(2)–C	111.2(3)–119.9(3)
C–Sb(1)–C	97.4(4)–100.1(4)	C–Sb(2)–C	97.4(5)–110.5(4)
C–C–C	117(1)–122(1)	Sb(1)–C(50)–Sb(2)	125.4(5)
W(1)–C–O	175(1)–179(1)		
(d) [W(CO) <sub>4</sub> (dmsm)] <sub>2</sub>			
Sb(1)–W(1)	2.754(1)	Sb(2)–W(1i)	2.752(1)
W(1)–C	1.96(2)–2.04(2)	C–O	1.13(2)–1.16(2)
Sb(1)–C	2.13(2)–2.17(2)	Sb(2)–C	2.14(2)–2.18(2)
Sb(1)⋯Sb(2)	3.710(2)		
W(1)–Sb(1)–C	114.6(4)–123.0(5)	W(1i)–Sb(2)–C	114.0(4)–125.3(5)
C–Sb(1)–C	98.5(7)–102.8(7)	C–Sb(2)–C	96.3(7)–102.8(6)
Sb(1)–C(9)–Sb(2)	119.7(8)	W(1)–C–O	178(1)–179(2)

Symmetry operation:  $i - x, -y, -z$ .**Table 4** Comparable structural data (E = P, As or Sb)

Compound	E–C–E/°	C–E–C/° (bonded)	C–E–C/° (free)	Sb⋯Sb/Å	Ref.
dpsm	117.3(2)		94.4(1)–98.7(1)	3.692(1)	1
[Fe(CO) <sub>4</sub> (η <sup>1</sup> -dpsm)]	107.9(3)	100.8(3)–106.8(3)	96.5(3)–97.7(3)	3.4806(9)	1
[W(CO) <sub>5</sub> (η <sup>1</sup> -dpsm)]	106.8(5)	99.4(5)–104.9(5)	96.4(5)–97.4(5)	3.497(1)	This work
[W(CO) <sub>5</sub> ] <sub>2</sub> (μ-dpsm)]	122(1)	98.1(9)–104.5(9)		3.723(2)	This work
[W(CO) <sub>4</sub> (μ-dpsm)] <sub>2</sub>	125.4(5)	97.4(4)–110.5(4)		3.847(1)	This work
[Pd(Ph)Cl(μ-dpsm)] <sub>2</sub>	115.0(2)	95.7(2)–103.8(2)			15
[Co <sub>2</sub> (CO) <sub>6</sub> (μ-dmsm)]	114.5(7)	99.0(7)–102.4(7)		3.572(2)	1
[W(CO) <sub>4</sub> (μ-dmsm)] <sub>2</sub>	119.7(8)	96.3(7)–102.8(6)		3.710(2)	This work
dppm	106.2(3)		99.9(2)–103.2(2)		16
[Fe(CO) <sub>4</sub> (η <sup>1</sup> -dppm)]	112.6(4)	102.4(4)–103.8(5)	101.7(4)–101.8(5)		17
[Cr(CO) <sub>3</sub> (dppm)] <sub>2</sub> *	115.3(6)	99.3(5)–104.1(5)	99.5(5)–102.5(6)		18
dpam	113(2)		96(2)–104(2)		19
[Mo(CO) <sub>2</sub> Br <sub>2</sub> (dpam)]*	113(2)	104(1)–105(1)	90(2)–103(2)		20
[Mo(CO) <sub>2</sub> Cl <sub>2</sub> (dpam)]*	113(2)	101(1)–106(1)	98(1)–101(1)		20

\* Data refer to the η<sup>1</sup>-co-ordinated ligand.

Evidence of the trends in electronic properties of the R<sub>2</sub>ECH<sub>2</sub>ER<sub>2</sub> ligands comes from the ν(CO) frequencies (in a common medium CH<sub>2</sub>Cl<sub>2</sub>) in these substituted carbonyl complexes. Examination of Table 1 shows that for analogous complexes the ν(CO) frequencies are lower in dmsm than in dpsm compounds, indicative of the expected greater σ-donor power of dmsm. If however one compares the ν(CO) frequencies of isostructural complexes of dppm, dpam<sup>20,24,25</sup> and dpsm, only small and erratic variations are observed. This probably reflects decreasing σ donation and π acceptance as Group 15 is des-

cended which overall leads to small electron-density changes at the metal centre.

A further probe for the ligand electronic effects is the magnitude of the <sup>1</sup>J(<sup>13</sup>C–<sup>183</sup>W) coupling constants observed on the CO<sub>trans-E</sub> as the donor is varied. Buchner and Schenk<sup>28</sup> have reported such coupling constants for a wide range of ligands in [W(CO)<sub>5</sub>L] complexes, and the values for the distibinmethanes (Table 2) ca. 163 Hz indicate that the ligands are relatively low in the *trans* influence series. The origin of this effect may lie in the weak σ donation from antimony.

## Experimental

Physical measurements were made as described elsewhere.<sup>1</sup> The <sup>95</sup>Mo NMR spectra were recorded from CH<sub>2</sub>Cl<sub>2</sub> solutions on a Bruker AM360 spectrometer at 23.5 MHz and referenced to external aqueous [MoO<sub>4</sub>]<sup>2-</sup>. The ligands were prepared as described.<sup>1</sup> All complex preparations were carried out in dry solvents under a dinitrogen atmosphere.

## Preparations

**[M(CO)<sub>5</sub>(dpsm)]** (M = Cr, Mo or W). A solution of [NEt<sub>4</sub>][M(CO)<sub>5</sub>Br]<sup>13</sup> (1.0 mmol) in ethanol (50 cm<sup>3</sup>) was added dropwise with stirring to a solution of dpsm (0.57 g, 1.0 mmol) in ethanol (50 cm<sup>3</sup>) and the mixture stirred at room temperature for 24 h. The pale coloured precipitate was filtered off, washed with water (3 × 5 cm<sup>3</sup>), dried, and then recrystallised from CH<sub>2</sub>Cl<sub>2</sub>-*n*-hexane. The resulting solid was dried *in vacuo*. Yield ca. 75%.

**[Cr(CO)<sub>5</sub>(dpsm)]** (Found: C, 48.0; H, 3.1. Calc. for C<sub>30</sub>H<sub>22</sub>CrO<sub>5</sub>Sb<sub>2</sub>: C, 47.5; H, 2.9%): FAB mass spectrum (3-nitrobenzyl alcohol) *m/z* 758, 730, 674 and 618; Calc. for [<sup>52</sup>Cr(CO)<sub>5</sub>(Ph<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbPh<sub>2</sub>)] 756, [<sup>52</sup>Cr(CO)<sub>4</sub>(Ph<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbPh<sub>2</sub>)] 728, [<sup>52</sup>Cr(CO)<sub>2</sub>(Ph<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbPh<sub>2</sub>)] 672 and [<sup>52</sup>Cr(Ph<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbPh<sub>2</sub>)] 616.

**[Mo(CO)<sub>5</sub>(dpsm)]** (Found: C, 44.4; H, 2.6. Calc. for C<sub>30</sub>H<sub>22</sub>MoO<sub>5</sub>Sb<sub>2</sub>: C, 44.8; H, 2.7%): FAB mass spectrum *m/z* 774, 718 and 662; Calc. for [<sup>92</sup>Mo(CO)<sub>4</sub>(Ph<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbPh<sub>2</sub>)] 768, [<sup>92</sup>Mo(CO)<sub>2</sub>(Ph<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbPh<sub>2</sub>)] 712 and [<sup>92</sup>Mo(Ph<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbPh<sub>2</sub>)] 656.

**[W(CO)<sub>5</sub>(dpsm)]** (Found: C, 40.1; H, 2.3. Calc. for C<sub>30</sub>H<sub>22</sub>O<sub>5</sub>Sb<sub>2</sub>W: C, 40.4; H, 2.5%): FAB mass spectrum *m/z* 862, 806 and 750; Calc. for [<sup>182</sup>W(CO)<sub>4</sub>(Ph<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbPh<sub>2</sub>)] 858, [<sup>182</sup>W(CO)<sub>2</sub>(Ph<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbPh<sub>2</sub>)] 802 and [<sup>182</sup>W(Ph<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbPh<sub>2</sub>)] 746.

**[M<sub>2</sub>(CO)<sub>10</sub>(dpsm)]** (M = Cr or W). A solution of [M(CO)<sub>5</sub>(thf)] (thf = tetrahydrofuran) in thf, made by photolysis of [M(CO)<sub>6</sub>] (0.25 mmol) in thf (20 cm<sup>3</sup>),<sup>29</sup> was added to a solution of [M(CO)<sub>5</sub>(dpsm)] (0.2 mmol) in thf (10 cm<sup>3</sup>), and the mixture stirred for 24 h. It was then evaporated to dryness, and the residue recrystallised from CH<sub>2</sub>Cl<sub>2</sub>-*n*-hexane. Yield ca. 40%.

**[W<sub>2</sub>(CO)<sub>10</sub>(dpsm)]** (Found: C, 34.3; H, 1.8. Calc. for C<sub>35</sub>H<sub>22</sub>O<sub>10</sub>Sb<sub>2</sub>W<sub>2</sub>: C, 34.6; H, 1.8%): FAB mass spectrum *m/z* 1130, 862 and 806; Calc. for [<sup>182</sup>W<sub>2</sub>(CO)<sub>7</sub>(Ph<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbPh<sub>2</sub>)] 1124, [<sup>182</sup>W(CO)<sub>4</sub>(Ph<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbPh<sub>2</sub>)] 858 and [<sup>182</sup>W(CO)<sub>2</sub>(Ph<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbPh<sub>2</sub>)] 802.

**[Cr<sub>2</sub>(CO)<sub>10</sub>(dpsm)]** (Found: C, 44.2; H, 2.3. Calc. for C<sub>35</sub>H<sub>22</sub>Cr<sub>2</sub>O<sub>10</sub>Sb<sub>2</sub>: C, 44.2; H, 2.3%): FAB mass spectrum *m/z* 950, 866, 810 and 758; Calc. for [<sup>52</sup>Cr<sub>2</sub>(CO)<sub>10</sub>(Ph<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbPh<sub>2</sub>)] 948, [<sup>52</sup>Cr<sub>2</sub>(CO)<sub>7</sub>(Ph<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbPh<sub>2</sub>)] 864, [<sup>52</sup>Cr<sub>2</sub>(CO)<sub>5</sub>(Ph<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbPh<sub>2</sub>)] 808 and [<sup>52</sup>Cr(CO)<sub>5</sub>(Ph<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbPh<sub>2</sub>)] 756.

**[W<sub>2</sub>(CO)<sub>10</sub>(dmsm)]**. The compound [W(CO)<sub>6</sub>] (1.6 g, 4.4 mmol) and dmsm (0.7 g, 2.2 mmol) were refluxed in diglyme (30 cm<sup>3</sup>) for 3 h, until evolution of CO had ceased. The solvent was removed by distillation under reduced pressure, and the residue recrystallised from CH<sub>2</sub>Cl<sub>2</sub>-*n*-hexane. Yield 0.68 g, 32% (Found: C, 18.5, H, 1.4. Calc. for C<sub>15</sub>H<sub>14</sub>O<sub>10</sub>Sb<sub>2</sub>W<sub>2</sub>: C, 18.7; H, 1.5%). FAB mass spectrum *m/z* 966, 938, 910, 854 and 614; Calc. for [<sup>182</sup>W<sub>2</sub>(CO)<sub>10</sub>(Me<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbMe<sub>2</sub>)] 960, [<sup>182</sup>W<sub>2</sub>(CO)<sub>9</sub>(Me<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbMe<sub>2</sub>)] 932, [<sup>182</sup>W<sub>2</sub>(CO)<sub>8</sub>(Me<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbMe<sub>2</sub>)] 904, [<sup>182</sup>W<sub>2</sub>(CO)<sub>6</sub>(Me<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbMe<sub>2</sub>)] 848 and [<sup>182</sup>W(CO)<sub>4</sub>(Me<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbMe<sub>2</sub>)] 610.

The complex [Mo<sub>2</sub>(CO)<sub>10</sub>(dmsm)] was made similarly to the tungsten complex using *n*-heptane as solvent. Yield 36% (Found: C, 22.7; H, 1.7. Calc. for C<sub>15</sub>H<sub>14</sub>Mo<sub>2</sub>O<sub>10</sub>Sb<sub>2</sub>: C, 22.8; H, 1.7%). The complex [Cr<sub>2</sub>(CO)<sub>10</sub>(dmsm)] was made similarly from [Cr(CO)<sub>6</sub>]. Yield 40% (Found: C, 25.9; H, 2.1. Calc. for C<sub>15</sub>H<sub>14</sub>Cr<sub>2</sub>O<sub>10</sub>Sb<sub>2</sub>: C, 25.7; H, 2.1%).

**[Cr<sub>2</sub>(CO)<sub>8</sub>(dpsm)]**. The complex [Cr(CO)<sub>4</sub>(nbd)]<sup>30</sup> (0.39 g, 1.5 mmol) and dpsm (0.86 g, 1.5 mmol) were stirred together in warm (38 °C) methylcyclohexane (100 cm<sup>3</sup>) for 8 d. The solvent was removed under reduced pressure, and the residue recrystallised from CHCl<sub>3</sub>-*n*-hexane to give a yellow powder (yield 0.28 g, 26%) (Found: C, 48.0; H, 3.2. Calc. for C<sub>29</sub>H<sub>22</sub>CrO<sub>4</sub>Sb<sub>2</sub>: C, 47.7; H, 3.0%). FAB mass spectrum *m/z* 1268, 1184 and 618; Calc. for [<sup>52</sup>Cr(CO)<sub>3</sub>(Ph<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbPh<sub>2</sub>)] 1264, [<sup>52</sup>Cr(Ph<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbPh<sub>2</sub>)] 1180 and [<sup>52</sup>Cr(Ph<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbPh<sub>2</sub>)] 616.

**[Mo<sub>2</sub>(CO)<sub>8</sub>(dpsm)]**. The complex [Mo(CO)<sub>4</sub>(nbd)]<sup>30</sup> (0.45 g, 1.5 mmol) and dpsm (0.84 g, 1.5 mmol) were stirred in methylcyclohexane (250 cm<sup>3</sup>) at room temperature for 24 h. The solution was concentrated to ca. 20 cm<sup>3</sup> under reduced pressure, and the resulting precipitate filtered off. The solid was recrystallised from CHCl<sub>3</sub>-*n*-hexane and dried *in vacuo*. Yield 0.33 g, 28% (Found: C, 44.7; H, 3.3. Calc. for C<sub>29</sub>H<sub>22</sub>MoO<sub>4</sub>Sb<sub>2</sub>: C, 45.0; H, 2.9%). FAB mass spectrum *m/z* 870, 774, 718 and 664; Calc. for [<sup>92</sup>Mo<sub>2</sub>(CO)<sub>4</sub>(Ph<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbPh<sub>2</sub>)] 860, [<sup>92</sup>Mo(CO)<sub>4</sub>(Ph<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbPh<sub>2</sub>)] 768, [<sup>92</sup>Mo(CO)<sub>2</sub>(Ph<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbPh<sub>2</sub>)] 712 and [<sup>92</sup>Mo(Ph<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbPh<sub>2</sub>)] 656.

**[W<sub>2</sub>(CO)<sub>8</sub>(dpsm)]**. The complex [W(CO)<sub>4</sub>(Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>-CH<sub>2</sub>NMe<sub>2</sub>)]<sup>31</sup> (0.21 g, 0.5 mmol) and dpsm (0.28 g, 0.5 mmol) were refluxed together in ethanol (30 cm<sup>3</sup>) for 25 min. A pale orange solid separated from the orange filtrate and was filtered off, washed with diethyl ether (2 × 10 cm<sup>3</sup>) and dried *in vacuo*. Yield 0.055 g, 13% (Found: C, 40.0; H, 2.5. Calc. for C<sub>29</sub>H<sub>22</sub>O<sub>4</sub>Sb<sub>2</sub>W: C, 40.4; H, 2.6%). FAB mass spectrum *m/z* 1130, 862, 806 and 750; Calc. for [<sup>182</sup>W<sub>2</sub>(CO)<sub>7</sub>(Ph<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbPh<sub>2</sub>)] 1124, [<sup>182</sup>W(CO)<sub>4</sub>(Ph<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbPh<sub>2</sub>)] 858, [<sup>182</sup>W(CO)<sub>2</sub>(Ph<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbPh<sub>2</sub>)] 802 and [<sup>182</sup>W(Ph<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbPh<sub>2</sub>)] 746.

**[Cr<sub>2</sub>(CO)<sub>8</sub>(dmsm)]**. The complex [Cr(CO)<sub>4</sub>(nbd)]<sup>30</sup> (0.19 g, 0.74 mmol) and dmsm (0.24 g, 0.75 mmol) were refluxed together in methylcyclohexane (25 cm<sup>3</sup>) for 1 min. The mixture was then immediately cooled to room temperature. The sticky yellow solid formed was separated by decanting the liquor off, dissolved in dichloromethane (20 cm<sup>3</sup>), filtered and the filtrate taken to dryness and triturated in *n*-pentane to give a yellow solid which was dried *in vacuo*. Yield 0.1 g, 28% (Found: C, 22.7; H, 3.1. Calc. for C<sub>9</sub>H<sub>14</sub>CrO<sub>4</sub>Sb<sub>2</sub>: C, 22.4; H, 2.9%). FAB mass spectrum *m/z* 963, 879, 851, 821 and 483; Calc. for [<sup>52</sup>Cr<sub>2</sub>(CO)<sub>8</sub>(Me<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbMe<sub>2</sub>)] 960, [<sup>52</sup>Cr<sub>2</sub>(CO)<sub>5</sub>(Me<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbMe<sub>2</sub>)] 876, [<sup>52</sup>Cr<sub>2</sub>(CO)<sub>4</sub>(Me<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbMe<sub>2</sub>)] 848, [<sup>52</sup>Cr<sub>2</sub>(CO)<sub>3</sub>(Me<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbMe<sub>2</sub>)] 820 and [<sup>52</sup>Cr(CO)<sub>4</sub>(Me<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbMe<sub>2</sub>)] 480.

The complex [Mo<sub>2</sub>(CO)<sub>8</sub>(dmsm)] was made similarly from [Mo(CO)<sub>4</sub>(nbd)]<sup>30</sup> (0.22 g, 0.73 mmol) and dmsm (0.24 g, 0.75 mmol). Yield 0.07 g, 18% (Found: C, 20.6; H, 2.8. Calc. for C<sub>9</sub>H<sub>14</sub>MoO<sub>4</sub>Sb<sub>2</sub>: C, 20.5; H, 2.7%). FAB mass spectrum *m/z* 993, 965, 911, 883, 855 and 527; Calc. for [<sup>92</sup>Mo<sub>2</sub>(CO)<sub>6</sub>(Me<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbMe<sub>2</sub>)] 984, [<sup>92</sup>Mo<sub>2</sub>(CO)<sub>5</sub>(Me<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbMe<sub>2</sub>)] 956, [<sup>92</sup>Mo<sub>2</sub>(CO)<sub>3</sub>(Me<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbMe<sub>2</sub>)] 900, [<sup>92</sup>Mo<sub>2</sub>(CO)<sub>2</sub>(Me<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbMe<sub>2</sub>)] 872, [<sup>92</sup>Mo<sub>2</sub>(CO)(Me<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbMe<sub>2</sub>)] 844 and [<sup>92</sup>Mo(CO)<sub>4</sub>(Me<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbMe<sub>2</sub>)] 520.

**[W<sub>2</sub>(CO)<sub>8</sub>(dmsm)]**. The complex [W(CO)<sub>4</sub>(Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>-CH<sub>2</sub>NMe<sub>2</sub>)]<sup>31</sup> (0.39 g, 0.93 mmol) and dmsm (0.30 g, 0.94 mmol) were refluxed together in ethanol (25 cm<sup>3</sup>) for 1 min. The mixture was then immediately cooled to room temperature and the pale yellow precipitate formed filtered off, washed with ethanol (2 × 10 cm<sup>3</sup>) and diethyl ether (2 × 10 cm<sup>3</sup>) and dried *in vacuo*. Yield 0.15 g, 26% (Found: C, 18.1; H, 2.4. Calc. for C<sub>9</sub>H<sub>14</sub>O<sub>4</sub>Sb<sub>2</sub>W: C, 17.6; H, 2.3%). FAB mass spectrum *m/z* 1227, 1170, 1117, 1090 and 614; Calc. for [<sup>182</sup>W<sub>2</sub>(CO)<sub>8</sub>(Me<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbMe<sub>2</sub>)] 1220, [<sup>182</sup>W<sub>2</sub>(CO)<sub>6</sub>(Me<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbMe<sub>2</sub>)]

**Table 5** Crystallographic details\*

	[W(CO) <sub>5</sub> (dpsm)]	[{W(CO) <sub>5</sub> } <sub>2</sub> (dpsm)]	[{W(CO) <sub>4</sub> (dpsm)} <sub>2</sub> ]	[{W(CO) <sub>4</sub> (dmsm)} <sub>2</sub> ]
Formula	C <sub>30</sub> H <sub>22</sub> O <sub>5</sub> Sb <sub>2</sub> W	C <sub>35</sub> H <sub>22</sub> O <sub>10</sub> Sb <sub>2</sub> W <sub>2</sub>	C <sub>58</sub> H <sub>44</sub> O <sub>8</sub> Sb <sub>4</sub> W <sub>2</sub>	C <sub>18</sub> H <sub>28</sub> O <sub>8</sub> Sb <sub>4</sub> W <sub>2</sub>
<i>M<sub>r</sub></i>	889.85	1213.75	1723.68	1227.11
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	<i>P2<sub>1</sub>/c</i> (no. 14)	<i>P</i> $\bar{1}$ (no. 2)	<i>P2<sub>1</sub>/n</i> (no. 14)	<i>P2<sub>1</sub>/n</i> (no. 14)
<i>a</i> /Å	9.160(5)	13.062(6)	12.657(1)	8.913(2)
<i>b</i> /Å	28.903(8)	14.665(10)	13.874(2)	16.163(2)
<i>c</i> /Å	11.394(7)	12.758(7)	16.544(1)	10.405(3)
<i>a</i> /°		115.36(5)		
<i>β</i> /°	98.21(5)	115.03(4)	101.934(8)	101.46(2)
<i>γ</i> /°		63.99(4)		
<i>U</i> /Å <sup>3</sup>	2985.5(2.6)	1899.6 (2.1)	2842.4(5)	1469.0(7)
2θ Range for cell/°	14.2–16.2	19.0–22.5	13.9–17.9	14.2–24.5
<i>T</i> /K	300	150	150	150
<i>D<sub>c</sub></i> /g cm <sup>-3</sup>	1.980	2.122	2.014	2.774
<i>Z</i>	4	2	2	2
<i>F</i> (000)	1672	1124	1616	1104
Crystal size/mm	0.50 × 0.27 × 0.10	0.50 × 0.10 × 0.05	0.30 × 0.10 × 0.10	0.30 × 0.10 × 0.10
Scan mode	ω	ω–2θ	ω–2θ	ω–2θ
Total no. observations	5727	7009	5494	2877
No. unique observations ( <i>R<sub>int</sub></i> )	5378 (0.067)	6690 (0.191)	5244 (0.048)	2699 (0.053)
<i>hkl</i> Ranges	0–10, 0–34, –13 to 13	0–15, –15 to 17, –15 to 13	0–15, 0–16, –19 to 19	0–10, 0–19, –12 to 12
Maximum, minimum transmission	1.000, 0.411	1.000, 0.342	1.000, 0.598	1.000, 0.696
No. data in refinement	3115 [ <i>I</i> > 3σ( <i>I</i> )]	4015 [ <i>I</i> > 3σ( <i>I</i> )]	3479 [ <i>I</i> > 2.5σ( <i>I</i> )]	1705 [ <i>I</i> > 2.5σ( <i>I</i> )]
No. parameters	343	412	325	145
μ/cm <sup>-1</sup>	57.70	74.99	60.54	116.6
<i>S</i>	1.76	2.49	1.31	1.23
Maximum shift/e.s.d.	0.02	0.05	0.001	0.00
Residual electron density/e Å <sup>-3</sup>	1.91 to –1.15	2.48 to –3.37	1.16 to –1.91	1.81 to –1.58
<i>R</i>	0.044	0.069	0.040	0.040
<i>R</i> '	0.047	0.079	0.046	0.047

\* In common:  $w^{-1} = \sigma^2(F_o)$ ;  $\psi$ -scan absorption correction; maximum 2θ = 50°;  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $R' = [\sum w(F_o - F_c)^2 / \sum w F_o^2]^{1/2}$ .

1164, [<sup>182</sup>W<sub>2</sub>(CO)<sub>4</sub>(Me<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbMe<sub>2</sub>)<sub>2</sub>] 1108, [<sup>182</sup>W<sub>2</sub>(CO)<sub>5</sub>(Me<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbMe<sub>2</sub>)<sub>2</sub>] 1080 and [<sup>182</sup>W(CO)<sub>4</sub>(Me<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbMe<sub>2</sub>)<sub>2</sub>] 610.

**[Cr(CO)<sub>3</sub>(dpsm)<sub>3</sub>].** The complex [Cr(CO)<sub>4</sub>(nbd)]<sup>30</sup> (0.19 g, 0.74 mmol) and dpsm (1.26 g, 2.23 mmol) were refluxed together in ethanol (50 cm<sup>3</sup>) for 30 min when a yellow solid precipitated. The mixture was cooled and stirred at room temperature for 30 min. The solid was filtered off, washed with diethyl ether (2 × 10 cm<sup>3</sup>) and dried *in vacuo*. Yield 0.03 g, 2%. The same reaction occurred over several days in warm (40 °C) methylcyclohexane solution (32%) (Found: C, 51.3; H, 3.7. Calc. for C<sub>78</sub>H<sub>66</sub>CrO<sub>3</sub>Sb<sub>6</sub>: C, 51.0; H, 3.6%). FAB mass spectrum *m/z* 1834, 1268, 1184 and 618; Calc. for [<sup>52</sup>Cr(CO)<sub>3</sub>(Ph<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbPh<sub>2</sub>)<sub>3</sub>] 1828, [<sup>52</sup>Cr(CO)<sub>3</sub>(Ph<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbPh<sub>2</sub>)<sub>2</sub>] 1264, [<sup>52</sup>Cr(Ph<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbPh<sub>2</sub>)<sub>2</sub>] 1180 and [<sup>52</sup>Cr(Ph<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbPh<sub>2</sub>)] 616.

**[Mo(CO)<sub>3</sub>(dpsm)<sub>3</sub>].** The compound [Mo(CO)<sub>6</sub>] (0.11 g, 0.4 mmol), dpsm (0.45 g, 0.8 mmol) and NaBH<sub>4</sub> (0.15 g, 4.0 mmol) were refluxed together in ethanol (30 cm<sup>3</sup>) for 6 h. The mixture was cooled, the solid which precipitated filtered off, washed with water (3 × 5 cm<sup>3</sup>), and dried *in vacuo*. Yield 0.18 g, 35% (Found: C, 50.0; H, 3.5. Calc. for C<sub>78</sub>H<sub>66</sub>MoO<sub>3</sub>Sb<sub>6</sub>: C, 50.0; H, 3.2%). FAB mass spectrum *m/z* 1876, 1312, 718 and 662; Calc. for [<sup>92</sup>Mo(CO)<sub>3</sub>(Ph<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbPh<sub>2</sub>)<sub>3</sub>] 1868, [<sup>92</sup>Mo(CO)<sub>3</sub>(Ph<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbPh<sub>2</sub>)<sub>2</sub>] 1304, [<sup>92</sup>Mo(CO)<sub>2</sub>(Ph<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbPh<sub>2</sub>)<sub>2</sub>] 712 and [<sup>92</sup>Mo(Ph<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbPh<sub>2</sub>)] 656.

**[W(CO)<sub>3</sub>(dpsm)<sub>3</sub>].** A mixture of [W(CO)<sub>6</sub>] (0.196 g, 0.55 mmol) and acetonitrile (50 cm<sup>3</sup>) were refluxed under argon for 4 d to generate *fac*-[W(CO)<sub>3</sub>(MeCN)<sub>3</sub>].<sup>32</sup> The solution was cooled and dpsm (1.0 g, 1.74 mmol) in dichloromethane (10 cm<sup>3</sup>) was added and the mixture stirred at room temperature for 3.5 d. The orange-brown solution was filtered and the filtrate reduced in volume to *ca.* 5 cm<sup>3</sup> and refiltered. The orange filtrate was

then taken to dryness, dissolved in dichloromethane (2 cm<sup>3</sup>) and added dropwise to a stirred solution of hexane (50 cm<sup>3</sup>) to give an orange-brown solid which was filtered off, washed with hexane (2 × 10 cm<sup>3</sup>) and dried *in vacuo*. Yield 0.19 g, 18% (Found: C, 47.4; H, 3.2. Calc. for C<sub>78</sub>H<sub>66</sub>O<sub>3</sub>Sb<sub>6</sub>W: C, 47.6; H, 2.6%). FAB mass spectrum *m/z* 1967, 806 and 750; Calc. for [<sup>182</sup>W(CO)<sub>3</sub>(Ph<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbPh<sub>2</sub>)<sub>3</sub>] 1958, [<sup>182</sup>W(CO)<sub>2</sub>(Ph<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbPh<sub>2</sub>)<sub>2</sub>] 802 and [<sup>182</sup>W(Ph<sub>2</sub><sup>121</sup>SbCH<sub>2</sub><sup>121</sup>SbPh<sub>2</sub>)] 746.

### Crystallography

Details of the crystallographic studies are presented in Table 5. Data were collected on a Rigaku AFC7S diffractometer equipped with Mo-Kα radiation (λ = 0.710 69 Å) and graphite monochromator. Selected crystals were mounted on glass fibres following oil immersion and held at 150 K using an Oxford Cryosystems low-temperature device or glued to a glass fibre for the room-temperature data (300 K). The Lorentz-polarisation corrections and any correction for the small amount of decay were applied during data reduction. Structure solution was by means of SHELXS 86<sup>33</sup> and full-matrix least-squares refinement on *F* was carried out to convergence with the TEXSAN package.<sup>34</sup> Hydrogen atoms were not included in the models and all atoms except as noted below were treated as anisotropic. Crystals were grown by the liquid-diffusion technique where ethanol was layered onto a CH<sub>2</sub>Cl<sub>2</sub> solution of the compound. Five C atoms of carbonyl groups mainly associated with W(2) in [{W(CO)<sub>5</sub>}<sub>2</sub>(dpsm)] gave rise to a non-positive definite condition and were treated as isotropic in the refinement.

CCDC reference number 186/848.

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