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Chelation of Group 6 metal tetracarbonyl fragments by dicobalt thioalkyne complexes

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Abstract

Reactions of [$Co_2(\mu$-$RSCH_2C{\equiv}CCH_2SR)(\mu$-dppm$)(CO)_4$] (dppm = bis(diphenylphosphino)methane) with [$M(CO)_4$nbd] (nbd = norbornadiene) afford [$Co_2\{\mu$-$C_2(CH_2SR)_2M(CO)_4\}(\mu$-dppm$)(CO)_4$] (M = Mo, W; R = Me, Et, ^{n}Bu, ^{t}Bu, Bz and M = Cr; R = Me, Et). The molecular structure of [$Co_2\{\mu$-$C_2(CH_2SMe)_2Mo(CO)_4\}(\mu$-dppm$)(CO)_4$] has been established by X-ray diffraction, and comprises a $Co_2(\mu$-dppm$)(CO)_4$ unit transversely bridged by 2,7-dithio-4-octyne co-ordinated through the thioether sulphur atoms to a molybdenum tetracarbonyl moiety. The chelation of [$Co_2(\mu$-$MeSCH_2C{\equiv}CCH_2SMe)(\mu$-dppm$)(CO)_4$] to the molybdenum centre produces a seven-membered ring which adopts a chair conformation, and the thiomethyl groups adopt a *cis* configuration with respect to the plane defined by the molybdenum and the two sulphur atoms. The mass spectra and NMR spectra of the new compounds are reported. The compounds display dynamic NMR behaviour which can be interpreted in terms of alkyne rocking and sulphur inversion.

1. Introduction

In previous studies, we showed that co-ordination of the acetylenic bond of bis(diphenylphosphino)acetylene (dppa) to a mononuclear tungsten centre produces sufficient distortion of the dppa skeleton to allow the two phosphorus centres to chelate a $M(CO)_4$ (M = Cr, Mo, W) fragment [1]. We describe below the chelation of Group 6 tetracarbonyl moieties by a recently prepared range of dicobalt alkyne complexes, [$Co_2(\mu$-$RSCH_2C{\equiv}CCH_2SR)(\mu$-dppm$)(CO)_4$] (R = Me, Et, ^{n}Bu, ^{t}Bu and Bz) [2,3].

The chelation of Group 6 tetracarbonyl fragments by dithioethers has been studied in some detail. An extensive series of dithioethane complexes is known, [$M(CO)_4(RSCH_2CH_2SR)$] (R = Me, Et, ^{i}Pr, ^{t}Bu [4], Ph [5], Bz [6], C_6H_4X (X = H, Me, Cl, NO_2) [7]), and the complexes [$W(CO)_4\{^tBuS(CH_2)_nS^tBu\}$] ($n = 1$–$5$) [8] have been studied in order to assess the effect of backbone length on the rate of substitution of the dithioether. In general, the ease of displacement increases with chain length. Cyclic systems such as 2,5,8,11-tetrathia[12](2,5)thiophenophane [9] and 2,6,15,19-tetrathia[7,7]paracyclophane (TTPH) [10] have been found to co-ordinate to Group 6 tetracarbonyl fragments, as has *cis*-1,4-cyclohexadienebisepisulphide [11]. Studies have been made of complexes with dithioether systems containing unsaturated backbones, for example, [$M(CO)_4$(*cis*-RSCH=CHSR)] (M = Cr, Mo, W; R = Me, ^{t}Bu) [4,12]. Similar complexes can also be prepared from tetrakis(thioalkyl)ethenes in which one pair of *cis* sulphur centres co-ordinates to the transition metal [13]. The unsaturated backbone can also incorporate an aromatic system such as benzene, as in [$M(CO)_4\{C_6(SMe)_6\}$] [14,15] or [$W(CO)_4\{o$-$(MeS)_2C_6H_4\}$] [16], or a cyclopentadienyl ring as in [$Mn(CO)_3\{C_5(SMe)_5\}Mo(CO)_4$] [17].

The low activation energy for sulphur inversion in co-ordinated thioethers results in observation of interconversion of invertomers on the NMR timescale [18,19]. The solid state structures of several derivatives

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have been determined by X-ray crystallography and normally represent the dominant invertomer observed in solution [4]. Structural data for the chelate systems containing a CH_2CH_2 linkage show a preference for the thioether substituents to adopt a *trans* geometry with respect to the plane defined by the two sulphur atoms and the metal [20–22], while the structure of $[W(CO)_4\{{}^tBuS(CH_2)_3S{}^tBu\}]$ has a *cis* conformation [22]. It has been suggested for the ethylene systems that the geometry is controlled by non-bonded interactions between the alkyl groups on the sulphur atoms [4]. This contrasts with the structures of the compounds containing unsaturated backbones, in which the *cis* invertomers predominate [15–17,23], and it has been suggested in the case of $[Mo(CO)_4(cis\text{-}{}^tBuSCH{=}CHS{}^tBu)]$ that this is due to alkyl-group carbonyl-group interactions [27].

2. Results and discussion

Reactions of $[Co_2(\mu\text{-}RSCH_2C{\equiv}CCH_2SR)(\mu\text{-}dppm)(CO)_4]$ (R = Me, Et) with $[M(CO)_4nbd]$ (M = Cr, Mo, W) in refluxing CH_2Cl_2 afford compounds **1** and **2**, and analogous reactions of $[Co_2(\mu\text{-}RSCH_2C{\equiv}CCH_2SR)(\mu\text{-}dppm)(CO)_4]$ (R = ^{n}Bu, ^{t}Bu, Bz) with $[M(CO)_4nbd]$ (M = Mo, W) afford compounds **3–5**. The bridging dppm is crucial to the success of the reactions as it suppresses the Pauson–Khand reaction between the norbornadiene and the dicobalt alkyne complexes [24]. All the compounds except for **2c** gave satisfactory analytical data (see Table 1), and it was observed that the chromium derivatives were appreciably less stable than the molybdenum and tungsten derivatives. Fast atom bombardment (FAB) mass spectra were recorded for selected compounds (see Table 2), and all show isotope envelopes assigned to the respective molecular ions, $[M^+]$, or $[M+H]^+$ and a series of carbonyl-loss peaks down to $[M-8CO]^+$. In addition, the spectra of **1a**, **1c** and **5a** show isotope envelopes assigned to $[M-M(CO)_4]^+$. The IR and NMR spectra of **1–5** (see Tables 1 and 3) will be discussed after the crystal structure of **1a**.

Suitable crystals of **1a** were obtained by slow crystallization from CH_2Cl_2/light petroleum. Selected structural parameters are listed in Table 4 and the molecular structure is shown in Fig. 1. The molecular structure consists of a $Co_2(\mu\text{-}dppm)(CO)_4$ unit transversely bridged by 2,7-dithio-4-octyne co-ordinated *via* the thioether sulphur atoms to a molybdenum tetracarbonyl moiety. The dppm occupies two equatorial sites as has been observed previously in $[Co_2(\mu\text{-}alkyne)(\mu\text{-}dppm)(CO)_4]$ complexes [25]. The chelation of $[Co_2(\mu\text{-}MeSCH_2C{\equiv}CCH_2SMe)(\mu\text{-}dppm)(CO)_4]$ to the molybdenum centre results in the formation of a seven-membered ring, which adopts a chair conformation in order to minimize steric interactions between the axial molybdenum and axial cobalt carbonyl ligands. The thiomethyl groups adopt a *cis* conformation with re-

TABLE 1. Analytical [a] and physical data

Compound	Appearance	Yield (%)	$\nu_{max}(CO)$ (cm^{-1})	Analysis (%)	
				C	H
1a	Pink solid	48	2032m, 2023m, 2003s, 1979m, 1913s, 1866m [b]	47.8 (48.4)	3.2 (3.3)
1b	Pink solid	47	2028m, 2017s, 1998vs, 1965s, 1876s, 1847w [b]	43.6 (44.4)	3.5 (3.1)
1c	Pink/orange solid	43	2022m, 2019s, 1995vs, 1966s, 1895m, 1850w [b]	51.1 (50.7)	4.0 (3.5)
2a	Red solid	64	2029m, 2021m, 1999vs, 1955w, 1973m, 1908s, 1850m [c]	48.7 (49.4)	3.5 (3.6)
2b	Orange solid	54	2025s, 2015(sh), 1999s, 1973m, 1885s, 1843m [c]	44.9 (45.4)	3.3 (3.4)
2c	Red solid	49	2027m, 2012m, 1998s, 1973m, 1899s, 1847m [c]	–	–
3a	Red/orange solid	84	2029m, 2020m, 1999vs, 1973m, 1954w, 1897s, 1893s, 1850m [c]	50.8 (51.3)	4.0 (4.2)
3b	Red/orange solid	68	2029m, 2014m, 1999s, 1973m, 1956w, 1893s, 1843m [c]	47.4 (47.4)	3.8 (3.4)
4a	Red solid	72	2027m, 2020m, 1998vs, 1972m, 1955(sh), 1908s, 1890s, 1844m [c]	51.5 (52.4)	4.2 (4.1)
4b	Red/purple solid	64	2027m, 2015m, 1998s, 1972m, 1956(sh), 1897s, 1885m, 1839m [c]	47.7 (47.4)	3.8 (3.4)
5a	Orange solid	78	2029m, 2022m, 2000vs, 1974m, 1957w, 1913s, 1893m, 1852m [c]	54.6 (54.6)	4.0 (3.6)
5b	Purple solid	79	2029m, 2017m, 1999vs, 1975m, 1901s, 1889s, 1845m [c]	51.4 (50.7)	3.5 (3.3)

[a] Calculated values are given in parentheses. [b] In light petroleum. [c] In dichloromethane.

TABLE 2. Fast atom bombardment (FAB) data

Compound	$[M+H]^+$ (m/z)	$[M]^+$ (m/z)	$[M-n\mathrm{CO}]^+$ (m/z)								$[M-M(CO)_4]^+$ (m/z)
			1	2	3	4	5	6	7	8	
1a	969	–	–	914	886	857	828	800	772	744	760
1c	924	–	895	868	841	812	784	756	–	701	760
2a	–	997	–	–	913	885	857	829	801	773	–
2c	–	1085	–	1029	1001	974	945	916	888	861	–
4a	–	1025	–	–	969	–	913	885	857	829	–
5a	–	1122	–	–	1038	1009	982	954	926	897	914

spect to the plane defined by the molybdenum and the two sulphur atoms, and inspection of models of **1a** suggests that a *trans* configuration would result in significant steric interactions between one of the methyl groups and an axial cobalt carbonyl ligand.

The molybdenum–sulphur bond lengths (2.547(1) and 2.588(1) Å) can be compared with those found in $[Mn(CO)_3\{C_5(SMe)_5\}Mo(CO)_4]$ (2.564(1) and 2.547(1) Å) [17] and $[(TTPH)\{Mo(CO)_4\}_2]$ (2.569(3) and 2.570(3) Å) [10]. The longest bond is to S(2), which is on the same side of the molecule as the dppm. The angle S(1)–Mo–S(2) (87.3(1)°) is only slightly smaller than that expected for octahedral co-ordination at the molybdenum centre. A *trans* effect shortening of Mo–C(2) and Mo–C(3) (1.956(7) and 1.968(6) Å) compared to Mo–C(1) and Mo–C(4) (2.032(7) and 2.030(6) Å) is observed. All the bond lengths and angles about the pseudo-tetrahedral Co_2C_2 core are within the ranges normally expected for this type of structure [26]. The alkyne bend-back angles (140.4(4) and 143.8(4)°) are somewhat disparate, and can be compared with the analogous angles in $[Co_2(\mu\text{-}PhC{\equiv}CPh)(\mu\text{-dppm})(CO)_4]$ (137.7(9) and 143.2(9)°) in which the asymmetry can again be ascribed to the dppm ligand [25]. The remaining angles in the seven-membered ring (C(15)–C(14)–S(1) 112.2(3), C(10)–C(11)–S(2) 110.7(3), C(14)–S(1)–Mo 111.1(2) and C(11)–S(2)–Mo 111.4(1)°) are as expected, and there is no evidence for any significant ring strain, in contrast to the situation for the complexes $[W\{(Ph_2PC{\equiv}CPPh_2)M(CO)_4\}(CO)(S_2CNEt_2)_2]$ (M = Cr, Mo, W), which contain five-membered rings [1].

It is possible to interpret the solution IR spectra of **1**–**5** (see Table 1) in terms of the presence of $M(CO)_4$ and $Co_2(\mu\text{-dppm})(CO)_4$ groups. The precursors, $[Co_2(\mu\text{-}RSCH_2C{\equiv}CCH_2SR)(\mu\text{-dppm})(CO)_4]$, have an IR spectrum in CH_2Cl_2 of 2021m, 1991s, 1964m and 1945(sh). So, for example, the absorptions in the spectrum of **4a** at 2020m, 1998vs, 1972m and 1955(sh) can be assigned to the $Co_2(\mu\text{-dppm})(CO)_4$ fragment. The shift of frequencies to higher wavenumber can be ascribed to the lowering of electron density following the co-ordination of the $Mo(CO)_4$ fragment. The remaining four absorptions at 2027m, 1908s, 1890m and 1844m can be assigned to the $Mo(CO)_4$ fragment, and can be compared with those found in, for example, $[Mo(^tBuSCH{=}CHS^tBu)(CO)_4]$ at 2030m, 1915vs, 1899vs and 1865m [27].

The ^1H NMR spectra of the new complexes (see Table 3) can be readily interpreted by comparison with those of the precursors $[Co_2(\mu\text{-}RSCH_2C{\equiv}CCH_2SR)(\mu\text{-dppm})(CO)_4]$. For example, **1a** has resonances due to the phenyl groups at δ 7.5–7.2, the methylene protons at δ 4.2, the dppm methylene at δ 3.5 and the methyl groups at δ 2.5. In the spectrum of $[Co_2(\mu\text{-}MeSCH_2C{\equiv}CCH_2SMe)(\mu\text{-dppm})(CO)_4]$ the corresponding resonances occur at δ 7.6–7.1, 4.0, 3.5 and 2.2. The observation of only one set of methylene and methyl resonances indicates that alkyne rocking produces a mirror plane on the NMR timescale through the cobalt and phosphorus centres. This is also apparent in the room temperature $^{13}C\text{-}\{^1H\}$ NMR spectra of **1**–**5**. All the spectra show only one resonance for the acetylenic carbons, shifted to high field by 5–7 ppm compared with the values for the precursors, and one resonance for the methylene groups, shifted to high field by 8–11 ppm. Also only one set of resonances is observed for the thioether substituents and the equatorial molybdenum carbonyl ligands. The axial molybdenum carbonyls are also equivalent, as are the cobalt carbonyls, indicating that inversion at the sulphur centres creates a mirror plane bisecting the cobalt–cobalt bond on the NMR timescale.

In order to investigate these fluxional processes in more detail, low temperature NMR spectra of **1a** and **1c** were recorded. Similar results were obtained from both samples and will be discussed in detail for **1a**. The ^1H NMR of these cobalt-containing compounds consistently lost resolution at low temperature, and the ^{13}C spectra were found to be more informative. At 183 K, the lowest temperature at which spectra were recorded, there is clear evidence that both of the fluxional processes are becoming slow on the NMR timescale. Only

TABLE 3. Hydrogen-1 and carbon-13 NMR data [a]

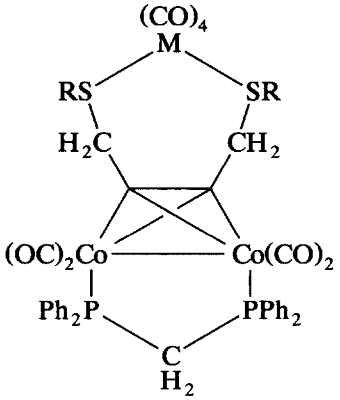
Compound	$^1H(\delta)$	$^{13}C(\delta)$ [b]
1a	7.5–7.2 (m, 20H, Ph); 4.2 (t, 4H, CCH_2, *J*(PH)3); 3.5 (t, 2H, PCH_2, *J*(PH)11); 2.5 (s, 6H, CH_3)	217.1 (*eq*-Mo(CO)$_2$); 206.6 (*ax*-Mo(CO)$_2$); 204.0 (Co(CO)); 137–128 (Ph); 89.1 (C_2); 50.2 (CCH_2); 43.4 (t, PCH_2, *J*(PC)19); 27.6 (CH_3)
1b	7.6–7.2 (m, 20H, Ph); 4.4 (br s, 4H, CCH_2); 3.4 (t, 2H, PCH_2, *J*(PH)10); 2.6 (s, 6H, CH_3)	208.0 (*eq*-W(CO)$_2$, *J*(WC)168); 203.8 (Co(CO)); 202.6 (*ax*-W(CO)$_2$); 137–128 (Ph), 88.6 (C_2); 51.7 (CCH_2); 43.5 (t, PCH_2, *J*(PC)19); 29.4 (CH_3)
1c	7.3–7.2 (m, 20H, Ph); 4.1 (t, 4H, CCH_2, *J*(PH)3), 3.4 (t, 2H, PCH_2, *J*(PH)10); 2.4 (s, 6H, CH_3)	226.2 (*eq*-Cr(CO)$_2$); 216.4 (*ax*-Cr(CO)$_2$); 204.2 (Co(CO)); 137–128 (Ph); 89.2 (C_2); 49.2 (CCH_2); 43.2 (t, PCH_2, *J*(PC)19); 26.5 (CH_3)
2a	7.4–7.2 (m, 20H, Ph); 4.2 (t, 4H, CCH_2, *J*(PH)3); 3.5 (t, 2H, PCH_2, *J*(PH)10); 2.9 (q, 4H, CH_2Me, *J*(HH)7); 1.4 (t, 6H, CH_3, *J*(HH)7)	217.3 (*eq*-Mo(CO)$_2$); 206.7 (*ax*-Mo(CO)$_2$); 204.1 (Co(CO)); 137–128 (Ph); 89.3 (C_2); 47.0 (CCH_2); 43.5 (t, PCH_2, *J*(PC)19); 37.1 (CH_2Me); 13.4 (CH_3)
2b	7.4–7.2 (m, 20H, Ph); 4.4 (br s, 4H, CCH_2); 3.5 (t, 2H, PCH_2, *J*(PH)11); 2.9 (q, 4H, CH_2Me, *J*(HH)7); 1.4 (t, 6H, CH_3, *J*(HH)7)	208.1 (*eq*-W(CO)$_2$, *J*(WC)166); 203.9 (Co(CO)); 202.7 (*ax*-W(CO)$_2$, *J*(WC)136); 137–129 (Ph); 88.8 (C_2); 48.6 (CCH_2); 43.5 (t, PCH_2, *J*(PC)20); 38.9 (CH_2Me); 13.6 (CH_3)
2c	7.4–7.2 (m, 20H, Ph); 4.1 (br s, 4H, CCH_2); 3.5 (t, 2H, PCH_2, *J*(PH)11); 2.8 (q, 4H, CH_2Me, *J*(HH)7); 1.4 (t, 6H, CH_3, *J*(HH)7)	226.3 (*eq*-Cr(CO)$_2$); 216.5 (*ax*-Cr(CO)$_2$); 203.9 (Co(CO)); 137–126 (Ph); 89.2 (C_2); 46.1 (CCH_2); 43.2 (t, PCH_2, *J*(PC)18); 36.2 (CH_2Me); 13.2 (CH_3)
3a	7.4–7.3 (m, 20H, Ph); 4.2 (s, 4H, CCH_2); 3.5 (t, 2H, PCH_2, *J*(PH)10), 2.8 (t, 4H, CH_2Pr, *J*(HH)7); 1.7–1.4 (m, 8H, CH_2CH_2); 1.0 (t, 6H, CH_3, *J*(HH)7)	217.4 (*eq*-Mo(CO)$_2$); 206.8 (*ax*-Mo(CO)$_2$); 204.1 (Co(CO)); 137–128 (Ph); 89.4 (C_2); 47.5 (CCH_2); 43.5 (t, PCH_2, *J*(PC)20); 42.7, 30.3, 21.9 (CH_2); 13.7 (CH_3)
3b	7.4–7.2 (m, 20H, Ph); 4.5 (t, 4H, CCH_2, *J*(PH)3); 3.5 (t, 2H, PCH_2, *J*(PH)10); 3.0 (m, 4H, CH_2Pr); 1.9–1.0 (m, 8H, CH_2CH_2); 0.9 (t, 6H, CH_3, *J*(HH)7)	208.3 (*eq*-W(CO)$_2$); 203.9 (Co(CO)); 202.8 (*ax*-W(CO)$_2$); 137–128 (Ph); 88.9 (C_2); 49.2 (CCH_2); 44.4 (SCH_2); 43.7 (t, PCH_2, *J*(PC)20); 30.4, 21.8 (CH_2CH_2); 13.7 (CH_3)
4a	7.4–7.2 (m, 20H, Ph); 4.2 (s, 4H, CCH_2); 3.5 (t, 2H, PCH_2, *J*(PH)10); 1.4 (s, 18H, CH_3)	218.7 (*eq*-Mo(CO)$_2$); 207.1 (*ax*-Mo(CO)$_2$); 204.1 (Co(CO)); 137–128 (Ph); 90.3 (C_2), 49.2 (C^tBu); 43.6 (CCH_2); 42.9 (t, PCH_2, *J*(PC)20), 29.5 (CH_3)
4b	7.5–7.2 (m, 20H, Ph); 4.4 (t, 4H, CCH_2, *J*(PH)3); 3.5 (t, 2H, PCH_2, *J*(PH)9); 1.4 (s, 18H, CH_3)	209.1 (*eq*-W(CO)$_2$, *J*(WC) 167), 204.1 (Co(CO)); 203.3 (*ax*-W(CO)$_2$, *J*(WC)132); 137–128 (Ph); 89.9 (C_2); 50.9 (C^tBu); 45.2 (CCH_2); 43.0 (t, PCH_2, *J*(PC)20); 29.4 (CH_3)
5a	7.4–7.2 (m, 30H, Ph); 4.2 (s, 4H, CH_2); 4.1 (s, 4H, CH_2); 3.2 (t, 2H, PCH_2, *J*(PH)10)	217.3 (*eq*-Mo(CO)$_2$); 206.3 (*ax*-Mo(CO)$_2$); 203.8 (Co(CO)); 137–128 (Ph); 88.5 (C_2); 47.9, 46.5 (CH_2); 40.4 (t, PCH_2, *J*(PC)20)
5b	7.6–7.2 (m, 30H, Ph); 4.4 (t, 4H, CCH_2, *J*(PH)3); 4.2 (s, 4H, SCH_2), 3.4 (t, 2H, PCH_2, *J*(PH)9)	208.2 (*eq*-W(CO)$_2$); 203.7 (Co(CO)); 202.2 (*ax*-W(CO)$_2$); 137–128 (Ph); 88.1 (C_2); 49.7, 48.1 (CH_2); 40.5 (t, PCH_2, *J*(PC)20)

[a] Chemical shifts (δ) in ppm, coupling constants in Hz. Measured in $CDCl_3$ unless otherwise stated. [b] Hydrogen-1 decoupled.

one invertomer is detected at low temperature, and this is presumeably the *cis* invertomer, in accord with the solid-state structure. The slowing of alkyne rocking results in two acetylenic carbon resonances at 93.6 and 81.9 ppm, and two methylene resonances at 51.0 and 47.6 ppm. From determination of the coalescence temperatures, 223 ± 5 and 213 ± 5 K, the activation energy for this process can be estimated as *ca.* 40 kJ mol^{-1}. This can be compared with that determined for $[Co_2(\mu\text{-PhC}{\equiv}\text{CPh})(\mu\text{-dppm})(CO)_4]$ of *ca.* 48 kJ mol^{-1} [28]. The equatorial molybdenum carbonyls give rise to only one resonance even at 183 K, while the axial carbonyls appear as a pair of peaks at 206.7 and 206.3 ppm possibly reflecting a greater asymmetry in their environments in the static structure. The cobalt carbonyls produce three resonances, at 205.4, 203.6 and 201.5 ppm, the first peak having double intensity. In the $^{13}C\text{-}\{^1H\}$ NMR spectrum of **1c** at 183 K four distinct resonances are observed for the cobalt carbonyls, while as for **1a**, the equatorial chromium carbonyls give rise to a single resonance and the axial carbonyls produce a pair of peaks. The $^{31}P\text{-}\{^1H\}$ NMR spectra of **2a–c** were found to contain single resonances, which were broadened by quadrapolar interac-

TABLE 4. Selected internuclear distances (Å) and angles (°) for complex **1a**

Co(1)–Co(2)	2.473(1)	C(4)–O(4)	1.142(6)	S(2)–C(11)	1.833(4)
Mo–S(1)	2.547(1)	Co(1)–C(5)	1.779(5)	C(10)–C(11)	1.480(6)
Mo–S(2)	2.588(1)	C(5)–O(5)	1.141(5)	S(2)–C(12)	1.790(5)
Co(1)–P(1)	2.227(1)	Co(1)–C(6)	1.782(6)	S(1)–C(13)	1.819(5)
Co(2)–P(2)	2.231(1)	C(6)–O(6)	1.122(6)	S(1)–C(14)	1.827(4)
Mo–C(1)	2.032(7)	Co(2)–C(7)	1.769(6)	Co(1)–C(15)	1.949(4)
C(1)–O(1)	1.126(7)	C(7)–O(7)	1.136(6)	Co(2)–C(15)	1.942(4)
Mo–C(2)	1.956(7)	Co(2)–C(8)	1.790(6)	C(10)–C(15)	1.346(6)
C(2)–O(2)	1.141(7)	C(8)–O(8)	1.134(6)	C(14)–C(15)	1.483(6)
Mo–C(3)	1.968(6)	Co(1)–C(10)	1.945(4)	P(1)–C(9)	1.847(4)
C(3)–O(3)	1.151(6)	Co(2)–C(10)	1.974(4)	P(2)–C(9)	1.832(4)
Mo–C(4)	2.030(6)	C(11)–C(10)	1.480(6)		
P(2)–Co(2)–Co(1)	98.4(1)	S(2)–Mo–S(1)	87.3(1)	C(56)–P(2)–C(9)	102.7(2)
C(7)–Co(2)–Co(1)	149.9(2)	C(1)–Mo–S(1)	88.9(2)	C(56)–P(2)–C(46)	100.6(2)
C(7)–Co(2)–P(2)	103.2(2)	C(1)–Mo–S(2)	89.7(2)	O(1)–C(1)–Mo	177.0(6)
C(8)–Co(2)–Co(1)	97.7(2)	C(2)–Mo–S(1)	176.5(2)	O(2)–C(2)–Mo	178.4(6)
C(8)–Co(2)–P(2)	100.1(2)	C(2)–Mo–S(2)	93.7(2)	O(3)–C(3)–Mo	178.4(6)
C(8)–Co(2)–C(7)	98.8(2)	C(2)–Mo–C(1)	87.8(3)	O(4)–C(4)–Mo	175.3(5)
C(10)–Co(2)–Co(1)	50.3(1)	C(3)–Mo–S(1)	93.9(2)	O(5)–C(5)–Co(1)	177.9(4)
C(10)–Co(2)–P(2)	104.9(1)	C(3)–Mo–S(2)	178.8(2)	O(6)–C(6)–Co(1)	177.5(5)
C(10)–Co(2)–C(7)	103.2(2)	C(3)–Mo–C(1)	89.9(2)	O(7)–C(7)–Co(2)	177.4(5)
C(10)–Co(2)–C(8)	141.5(2)	C(3)–Mo–C(2)	85.1(2)	O(8)–C(8)–Co(2)	177.7(5)
C(15)–Co(2)–Co(1)	50.6(1)	C(4)–Mo–S(1)	90.8(1)	P(2)–C(9)–P(1)	111.6(2)
C(15)–Co(2)–P(2)	142.0(1)	C(4)–Mo–S(2)	87.7(1)	Co(2)–C(10)–Co(1)	78.3(2)
C(15)–Co(2)–C(7)	100.6(2)	C(4)–Mo–C(1)	177.4(2)	C(11)–C(10)–Co(1)	134.7(3)
C(15)–Co(2)–C(8)	105.0(2)	C(4)–Mo–C(2)	92.6(2)	C(11)–C(10)–Co(2)	136.6(3)
C(15)–Co(2)–C(10)	40.2(2)	C(4)–Mo–C(3)	92.7(2)	C(15)–C(10)–Co(1)	69.9(3)
C(13)–S(1)–Mo	108.2(2)	P(1)–Co(1)–Co(2)	96.2(1)	C(15)–C(10)–Co(2)	68.6(3)
C(14)–S(1)–Mo	111.1(2)	C(5)–Co(1)–Co(2)	151.7(2)	C(15)–C(10)–C(11)	140.0(4)
C(14)–S(1)–C(13)	97.5(2)	C(5)–Co(1)–P(1)	102.5(2)	C(10)–C(11)–S(2)	110.7(3)
C(11)–S(2)–Mo	111.4(1)	C(6)–Co(1)–Co(2)	98.2(2)	C(15)–C(14)–S(1)	112.2(3)
C(12)–S(2)–Mo	107.4(2)	C(6)–Co(1)–P(1)	102.6(2)	Co(2)–C(15)–Co(1)	79.0(2)
C(12)–S(2)–C(11)	98.3(3)	C(6)–Co(1)–C(5)	98.2(2)	C(10)–C(15)–Co(1)	69.6(3)
C(9)–P(1)–Co(1)	110.7(1)	C(10)–Co(1)–Co(2)	51.4(1)	C(10)–C(15)–Co(2)	71.2(3)
C(26)–P(1)–Co(1)	117.7(1)	C(10)–Co(1)–P(1)	100.0(1)	C(14)–C(15)–Co(1)	135.4(3)
C(26)–P(1)–C(9)	106.4(2)	C(10)–Co(1)–C(5)	103.9(2)	C(14)–C(15)–Co(2)	130.4(3)
C(36)–P(1)–Co(1)	118.3(2)	C(10)–Co(1)–C(6)	143.9(2)	C(14)–C(15)–C(10)	143.8(4)
C(36)–P(1)–C(9)	101.4(2)	C(15)–Co(1)–Co(2)	50.4(1)		
C(36)–P(1)–C(26)	100.8(2)	C(15)–Co(1)–P(1)	137.5(1)		
C(9)–P(2)–Co(2)	110.4(1)	C(15)–Co(1)–C(5)	102.5(2)		
C(46)–P(2)–Co(2)	119.0(2)	C(15)–Co(1)–C(6)	107.1(2)		
C(46)–P(2)–C(9)	103.9(2)	C(15)–Co(1)–C(10)	40.5(2)		
C(56)–P(2)–Co(2)	118.2(2)				



	M	R
1a	Mo	Me
1b	W	Me
1c	Cr	Me
2a	Mo	Et
2b	W	Et
2c	Cr	Et
3a	Mo	^{n}Bu
3b	W	^{n}Bu
4a	Mo	^{t}Bu
4b	W	^{t}Bu
5a	Mo	Bz
5b	W	Bz

tion with the ^{59}Co nuclei, at 33.7, 42.3 and 35.9 ppm, respectively. The spectrum of **2a** remains unchanged at 223 K. In contrast, the spectra of **1a–c** at room temperature all contain two broad resonances (**1a** 32.8, 30.8; **1b** 33.8, 32.3; **1c** 34.1, 32.2 ppm), indicating that sulphur inversion is slow on the NMR timescale. This is in accord with the presence of less bulky methyl substituents which raises the barrier to inversion [4].

3. Experimental details

The general experimental procedures have been described previously [3]. ^{1}H NMR spectra were recorded with a JEOL PMX 60 instrument, which was found to give better resolution for the cobalt containing compounds than a JEOL GX 270 instrument used to record the ^{13}C-{^{1}H} NMR spectra. The FAB mass spectra were obtained by the SERC mass spectrometry service with a VG ZAB-E instrument. The compounds [$Co_2(\mu$-$RSCH_2C{\equiv}CCH_2SR)(\mu$-dppm$)(CO)_4$] [3] and [$Mo(CO)_4$(nbd)] [29] were prepared by published methods. Analytical and other data for the new compounds are given in Tables 1 and 2.

3.1. Preparation of [$Co_2\{\mu$-$C_2(CH_2SR)_2M(CO)_4\}(\mu$-dppm$)(CO)_4$]

Compounds **1–5** were prepared by the same general procedure, which will be described in detail only for **1a**. To [$Co_2(\mu$-$MeSCH_2C{\equiv}CCH_2SMe)(\mu$-dppm$)(CO)_4$] (0.20 g, 0.26 mmol) and [$Mo(CO)_4$(nbd)] (0.08 g, 0.27 mmol) was added CH_2Cl_2 (50 cm^{3}). The resulting solution was heated to reflux for 3.5 h, and the solvent was then removed *in vacuo*. The residue was chromatographed on a Florisil column (10 × 1.5 cm^{2}), with light petroleum/CH_2Cl_2 (1 : 1) as eluent, to give a red band. Crystallization (CH_2Cl_2/light petroleum) afforded [$Co_2\{\mu$-$C_2(CH_2SMe)_2Mo(CO)_4\}(\mu$-dppm$)(CO)_4$] (0.122 g, 0.12 mmol).

3.2. Crystal structure determination

Crystals of **1a** were obtained by solvent diffusion from CH_2Cl_2/light petroleum as red prisms with crystal dimensions *ca.* 0.33 × 0.25 × 0.05 mm. Data were collected using a Enraf-Nonius CAD4 diffractometer (293 K, Mo Kα X-radiation, graphite monochromator, = 0.710 69 Å). Of the 7137 data collected ($\omega/2\theta$ scan

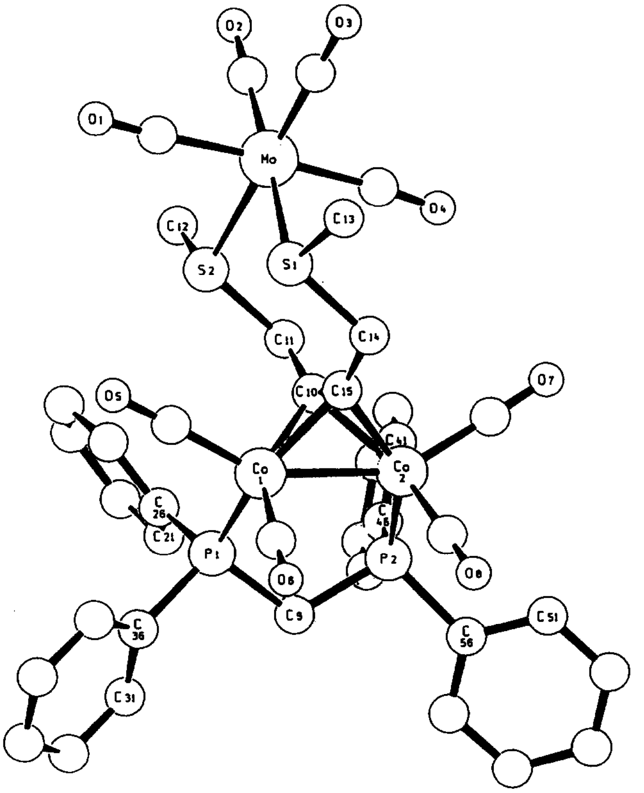


Fig. 1. The molecular structure of **1a** showing the atom labelling system.

TABLE 5. Atomic positional (fractional coordinates) parameters ($\times 10^4$) with estimated standard deviations in parentheses, for compound **1a**

Atom	x	y	z
Mo	0.21737(4)	0.15872(3)	0.04549(2)
Co(1)	0.20615(5)	0.15118(4)	0.28933(3)
Co(2)	0.07556(5)	0.03286(4)	0.27173(3)
S(1)	0.3438(1)	0.0975(1)	0.1361(1)
S(2)	0.1213(1)	0.2436(1)	0.1269(1)
P(1)	0.0959(1)	0.2262(1)	0.3448(1)
P(2)	−0.0575(1)	0.0758(1)	0.3298(1)
C(1)	0.3317(6)	0.2508(4)	0.0402(3)
O(1)	0.3952(5)	0.3011(3)	0.0346(3)
C(2)	0.1281(6)	0.2096(4)	−0.0254(3)
O(2)	0.0783(5)	0.2393(4)	−0.0675(2)
C(3)	0.2891(5)	0.0959(4)	−0.0178(3)
O(3)	0.3287(5)	0.0587(3)	−0.0555(2)
C(4)	0.1002(5)	0.0696(4)	0.0540(2)
O(4)	0.0336(4)	0.0215(3)	0.0628(2)
C(5)	0.2976(4)	0.2269(3)	0.2622(2)
O(5)	0.3587(3)	0.2747(2)	0.2462(2)
C(6)	0.3028(5)	0.1057(3)	0.3479(3)
O(6)	0.3663(4)	0.0766(3)	0.3832(2)
C(7)	0.0035(5)	−0.0392(3)	0.2206(3)
O(7)	−0.0396(4)	−0.0853(3)	0.1863(2)
C(8)	0.1499(5)	−0.0381(3)	0.3246(3)
O(8)	0.2002(4)	−0.0815(3)	0.3580(2)
C(9)	−0.0036(4)	0.1593(3)	0.3819(2)
C(10)	0.1009(4)	0.1272(3)	0.2168(2)
C(11)	0.0316(4)	0.1781(3)	0.1706(2)
C(12)	0.0130(5)	0.3043(4)	0.0855(3)
C(13)	0.4334(5)	0.0199(4)	0.1053(3)
C(14)	0.2647(4)	0.0281(3)	0.1823(2)
C(15)	0.1876(4)	0.0736(3)	0.2200(2)
C(21)	−0.0980(4)	0.3279(3)	0.3178(3)
C(22)	−0.1553(5)	0.3910(4)	0.2867(3)
C(23)	−0.1061(6)	0.4352(4)	0.2415(3)
C(24)	0.0010(5)	0.4168(3)	0.2283(2)
C(25)	0.0588(4)	0.3532(3)	0.2597(2)
C(26)	0.0105(4)	0.3074(3)	0.3043(2)
C(31)	0.1000(5)	0.3087(3)	0.4599(2)
C(32)	0.1520(5)	0.3513(4)	0.5103(3)
C(33)	0.2640(6)	0.3707(4)	0.5120(3)
C(34)	0.3252(5)	0.3454(4)	0.4653(3)
C(35)	0.2747(4)	0.3017(3)	0.4149(2)
C(36)	0.1613(4)	0.2834(3)	0.4116(2)
C(41)	−0.2074(4)	0.1121(3)	0.2276(2)
C(42)	−0.3055(5)	0.1430(4)	0.1968(3)
C(43)	−0.3856(5)	0.1792(4)	0.2302(3)
C(44)	−0.3674(5)	0.1842(4)	0.2938(3)
C(45)	−0.2703(4)	0.1525(4)	0.3241(3)
C(46)	−0.1885(4)	0.1173(3)	0.2912(2)
C(51)	−0.1329(5)	−0.0779(3)	0.3630(3)
C(52)	−0.1800(6)	−0.1353(4)	0.4007(3)
C(53)	−0.2072(5)	−0.1141(4)	0.4580(3)
C(54)	−0.1843(6)	−0.0370(5)	0.4797(3)
C(55)	−0.1363(6)	0.0212(4)	0.4425(3)
C(56)	−0.1127(4)	0.0016(3)	0.3835(2)

mode, $2\theta \leq 50°$, scan width from $0.75 + 0.35 \tan \theta$), 4506 unique data had $F \geq 5\sigma(F)$, and only these were used for the structure refinement. The data were corrected for Lorentz, polarization and X-ray absorption effects, the latter by a method based upon azimuthal ψ-scans.

3.2.1. *Crystal data for 1a*

$C_{39}H_{32}Co_2MoO_8P_2S_2$, $M = 968.6$, monoclinic, space group $P2_1/n$, $a = 11.930(3)$, $b = 16.181(4)$, $c = 21.595(4)$ Å, $\beta = 95.08(2)°$, $U = 4152.2$ Å^3, $Z = 4$, $D_c = 1.55$ g cm^{-3}, $F(000) = 1952$, $\mu = $ (Mo Kα) $= 12.3$ cm^{-1}.

The structure was solved by conventional heavy atom methods and successive difference Fourier syntheses were used to locate all non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were included in calculated positions (C–H = 0.96 Å) with fixed isotropic thermal parameters ($U = 0.08$ Å^2). A weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.0005 |F|^2]$ gave a satisfactory analysis of variance. Refinement by full matrix least squares using a Digital Vax 8800 computer with the SHELX system of programs led to $R = 0.034$ ($R_w = 0.037$) [30]. Scattering factors with corrections for anomalous dispersion were taken from [31]. Atomic co-ordinates are listed in Table 5.

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