Synthesis, Reactivity and Crystal Structures of Cobalt Complexes $[Co_2(CO)_2(\mu\text{-}X)(\mu\text{-}Y)(dppm)_2]$ (X = CO, S or SO_2; Y = CO or SO_2; dppm = $Ph_2PCH_2PPh_2$)[‡]

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The reaction of SO_2 with the M–M bond of the cobalt(0) complex $[Co_2(CO)_2(\mu\text{-}CO)(dppm)_2]$ **1** [dppm = bis(diphenylphosphino)methane] results in the substitution of the bridging CO group by SO_2 and the addition of a second SO_2 group to give $[Co_2(CO)_2(\mu\text{-}SO_2)_2(dppm)_2]$ **2**. The reaction of **1** with thiirane, C_2H_4S, or CO gives the insertion products $[Co_2(CO)_2(\mu\text{-}CO)(\mu\text{-}X)(dppm)_2]$ (X = CO **3**, or S **4**). The X-ray molecular structure analysis of the sulfur-bridged dimer **4** shows the presence of a distorted A-frame skeleton. These crystals contain 1.5 molecules of acetone per asymmetric unit and are monoclinic, space group $P2_1/n$, a = 14.950(5), b = 25.480(5), c = 15.682(2) Å, β = 98.18(2)°, T = 200 K and Z = 2; final R = 0.074. The complexes **3** and **4** react with SO_2 by substitution to give the SO_2-bridged complexes $[Co_2(CO)_2(\mu\text{-}X)(\mu\text{-}SO_2)(dppm)_2]$ (X = CO **5**, or S **6**). The X-ray molecular structure analysis of $[Co_2(CO)_2(\mu\text{-}S)(\mu\text{-}SO_2)(dppm)_2]$ **6** shows the sulfur and sulfur dioxide ligands in symmetrically bridging position between both cobalt centres. The crystals are monoclinic, space group $P2_1/n$, a = 12.850(5), b = 27.660(4), c = 16.056(5) Å, β = 93.85(3)°, T = 205 K and Z = 4; final R = 0.063.

Transition-metal dimers linked by two bridging diphosphine ligands represent a large and important class of molecules. They often possess A-frame structures and reactive metal–metal bonds which enable the insertion of small molecules.[1,2] The synthesis of several homo- and hetero-bimetallic A-frame species with bridging μ-SO_n ligands (n = 0–2) of various metals by different methods has been reported,[3–9] including direct formation *via* oxidative addition of $SOCl_2$ to a nickel(0) complex.[10] The stepwise conversion of μ-S, μ-SO and μ-SO_2 ligands by redox reactions,[11,12] which are sometimes reversible, has also been studied. This is of interest in bioinorganic chemistry where model systems of redox enzymes are investigated, *e.g.* sulfite reductase, which contains a sirohaem complex of iron which enables the reduction of sulfite to sulfide. Another such enzyme is sulfite oxidase, which contains a thiolato complex of molybdenum(VI) and oxidizes sulfite to sulfate. In this context, it was recently shown by McAuliffe and co-workers[13] and by us,[14] that SO_2 can be oxidized by special metal- and ligand-induced reactions to yield discrete sulfuric acid or its ligand adducts. Because of the important role of sulfur in such enzymes, we are interested in complexes which have one or more sulfur ligands displaying different oxidation states of sulfur. Recently we have reported A-frame complexes of rhodium and iridium with bridging sulfur, sulfur monoxide or sulfur dioxide ligands.[4,12,15] Now, we report the insertion reactions of carbon monoxide, sulfur and sulfur dioxide into the Co–Co bond of $[Co_2(CO)_2(\mu\text{-}CO)(dppm)_2]$ **1** [dppm = bis(diphenylphosphino)methane], the reactions of the resultant new complexes of cobalt[16–19] with SO_2 and their structures, and the X-ray molecular structure of $[Co_2(CO)_2(\mu\text{-}CO)(\mu\text{-}S)(dppm)_2]$ and $[Co_2(CO)_2(\mu\text{-}S)(\mu\text{-}SO_2)(dppm)_2]$.

Results and Discussion

Synthesis and Solution Studies.—Reduction of the dimeric salt $[Co_2(CO)_2(\mu\text{-}CO)(\mu\text{-}I)(dppm)_2]I$ with zinc[16] in acetonitrile gives the neutral green complex $[Co_2(CO)_2(\mu\text{-}CO)(dppm)_2]$ **1** within one or two days; treatment of **1** with $NaBH_4$ to effect reduction was unsuccessful. Complex **1** is reported to possess formally a Co–Co double bond[16] and should easily react with electrophiles. Thus, **1** reacts with SO_2 in toluene at −30 °C to give red-brown $[Co_2(CO)_2(\mu\text{-}SO_2)_2(dppm)_2]$ **2** [Scheme 1(*iii*)] whilst at higher reaction temperatures decomposition is observed. At 0 °C in acetone, however, **1** reacts with CO to form $[Co_2(CO)_2(\mu\text{-}CO)_2(dppm)_2]$ **3** [Scheme 1(*i*)] which has been prepared previously[20] by a different procedure. This unusual CO-rich complex shows two terminal and two bridging CO ligands and can be used as a starting material for further syntheses. Thus sulfur generated from thiirane (C_2H_4S) in acetone substitutes one bridging CO ligand in **3** to give $[Co_2(CO)_2(\mu\text{-}CO)(\mu\text{-}S)(dppm)_2]$ **4**. Although complex **4** was prepared previously by Lisic and Hanson[16] by treating $[Co_2(CO)_6(dppm)]$ in boiling tetrahydrofuran with dppm and sulfur, we obtained **4** almost quantitatively by treating **1** with thiirane in toluene [Scheme 1(*iv*)]. Both complexes **3** and **4** react readily with SO_2: **3** reacts at −30 °C to give the corresponding SO_2 complex $[Co_2(CO)_2(\mu\text{-}CO)(\mu\text{-}SO_2)(dppm)_2]$ **5** [Scheme 1(*ii*)] by substitution of one bridging CO ligand. At higher temperature some decomposition is observed, but also along with the formation of **2**. Complex **4** reacts at room temperature to give the stable violet sulfur dioxide complex $[Co_2(CO)_2(\mu\text{-}S)(\mu\text{-}SO_2)(dppm)_2]$ **6** (Scheme 1(*v*)]. While complexes **2**, **3** and **5** are not very stable in solution, **4** and **6** are stable even in halogenated hydrocarbon solvents. Although the μ-SO_2 complexes **2**, **5** and **6** have been synthesised, none of the starting complexes **1**, **3** or **4** react with thiirane *S*-oxide to give the corresponding μ-SO complexes. On the other hand, there are many examples[4,5,11] for the stepwise oxidation of sulfur bridges by H_2O_2 or *m*-chloroperbenzoic acid to the corresponding SO or SO_2 bridged complexes. In the present systems, however, there is no reaction between **4** or **6** and 2 equivalents of *m*-chloroperbenzoic acid at room temperature. The crystal structures of **4** and **6** show a possible explanation for this behaviour. Because of the small P–Co–P angles (145°), the

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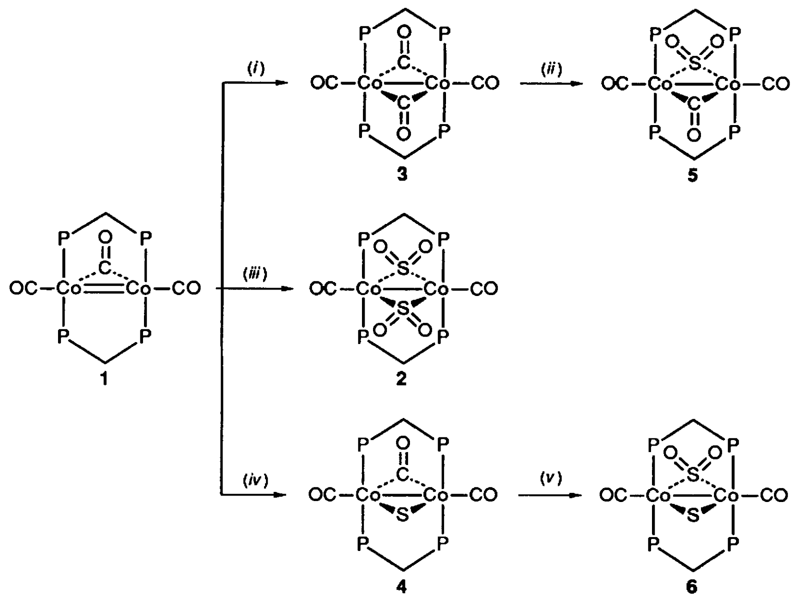
[‡] *Supplementary data available:* Additional material for the X-ray structure analyses may be obtained from Fachinformationszentrum Karslruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, Germany, by quoting the depository number CSD 55819, the names of the authors and the journal citation.



Scheme 1 (*i*) $+\mathrm{CO}$; (*ii*) $+\mathrm{SO_2}, -\mathrm{CO}$; (*iii*) $+2\mathrm{SO_2}, -\mathrm{CO}$; (*iv*) $+\mathrm{C_2H_4S}, -\mathrm{C_2H_4}$; (*v*) $+\mathrm{SO_2}, -\mathrm{CO}$

Table 1 IR, ^{31}P-{^{1}H}, ^{1}H NMR and FAB mass spectral data for the complexes **2**–**6**

	IR[a]/cm^{-1}		NMR		
Complex	ν(CO)	ν(SO)	δ(P)[b]	δ(H)[c]	*m*/*z*
2	2060s	1207m	53.3 (s)	2.8 (m)	1070 [*M*]$^+$
	2030s	1040s			941 [*M* − 2SO$_2$]$^+$
3	1940s		41.4 (s)	3.6 (m)	970 [*M* − CO]$^+$
	1913s				942 [*M* − 2CO]$^+$
	1755m				
	1706m				
4	1959s		47.8 (s)	4.1 (m)[d]	1002 [*M*]$^+$
	1910s			2.4 (m)	918 [*M* − CO]$^+$
	1754s				
5	2032s	1189m	59.2 (m)[e]	3.5 (m)	950 [*M* − 3CO]$^+$
	1995s	1042s	48.7 (m)		
	1782m				
6[f]	1956s, br	1177m	32.9 (s)	3.7 (m)	1038 [*M*]$^+$
		1036s		2.9 (m)	1013 [*M* − CO]$^+$

[a] KBr: s = strong, m = medium. [b] In CDCl$_3$ or (CD$_3$)$_2$CO at 25 °C: m = multiplet, s = broad singlet. [c] In CH$_2$Cl$_2$ at −30 °C: m = multiplet. [d] *J*(HH′) = 14.8, *J*(HP) = 5.0 Hz, *J*(H′P) = 2.4 Hz. [e] *J*(AA′) = *J*(BB′) = 10, *J*(AB) = *J*(A′B′) = 153, *J*(AB′) = *J*(A′B) = −3 Hz. [f] ^{13}C-{^{1}H} NMR data in CDCl$_3$ at 25 °C: δ(CH$_2$) 32.9 (br s), δ(*ipso*) 139.2 (br s), δ(*ortho*) 129.7 (br s)/129.1 (br s), δ(*meta*) 128.1 (br s)/127.6 (br s), δ(*para*) 132.8 (br s).

phosphorus ligands are bent towards the sulfur atom which is therefore sterically hindered to oxidation by *m*-chloroperbenzoic acid. At higher temperatures and higher molarities of the oxidizing agent decomposition of the starting materials **4** and **6** is observed.

All the complexes **2**–**6** have been spectroscopically characterized by IR, ^{31}P-{^{1}H}, ^{1}H, ^{13}C-{^{1}H} NMR and mass spectra (Table 1), and complexes **4** and **6** additionally by X-ray structure analyses.

Complexes **3**–**5** show three carbonyl absorptions; two terminal ν(CO) between 2032 and 1910 cm^{-1} and one or two bridging ν(CO) between 1782 and 1706 cm^{-1} while complexes **2** and **6** show only one or two terminal bands. The ν(CO) modes of the complexes **2**, **5** and **6** lie at higher wavenumbers than those of the corresponding starting materials **1**, **3** and **4**. The ν(SO$_2$) vibrations for complexes **2**, **5** and **6** occur at 1207–1177 and *ca.* 1040 cm^{-1} as expected for μ-SO$_2$ ligands.[21]

The ^{31}P-{^{1}H} NMR spectra of complexes **2**–**4** and **6** show only one singlet between δ 33 and 60, while **5** shows an AA′BB′ system at δ 59.2 and 48.7 with $J_{\mathrm{AA'}} = J_{\mathrm{BB'}} = 10$, $J_{\mathrm{AB}(trans)} = J_{\mathrm{A'B'}(trans)} = 153$ and $J_{\mathrm{AB'}} = J_{\mathrm{A'B}} = -3$ Hz. The origin of this AA′BB′ system is not clear, although it is likely that one of the dppm ligands in **5** is *trans* and the other is *cis*.[22–24] Most of the analogous A-frame complexes of iridium also show singlets,[25] while the corresponding rhodium complexes behave as AA′A″A‴XX′ systems.[4]

In the ^{1}H NMR spectra of complexes **4** and **6** the two methylene protons of each dppm ligand are inequivalent because of the A-frame structure so that they appear as a basic AB quartet. Each line of this quartet should be further split into a 1:4:6:4:1 quintet due to the coupling with the phosphorus atoms. Indeed complex **4** shows this splitting, while **6** shows unresolved multiplets. The symmetrically-bridged complexes **2** and **3** and the presumably *cis*–*trans* co-ordinated[22,24] complex **5** only shows one broad unresolved multiplet. The signals of the methylene protons are observed in the range δ 2.4 to 4.3 whereas those of the phenyl protons lie at δ 7–8.

The ^{13}C-{^{1}H} NMR spectrum can only be measured for complex **6**, since the other complexes decompose rapidly in halogenated solvents and are barely soluble in most other solvents. The methylene bridge appears as an unresolved multiplet at δ 32.9. The different phenyl carbon atoms are

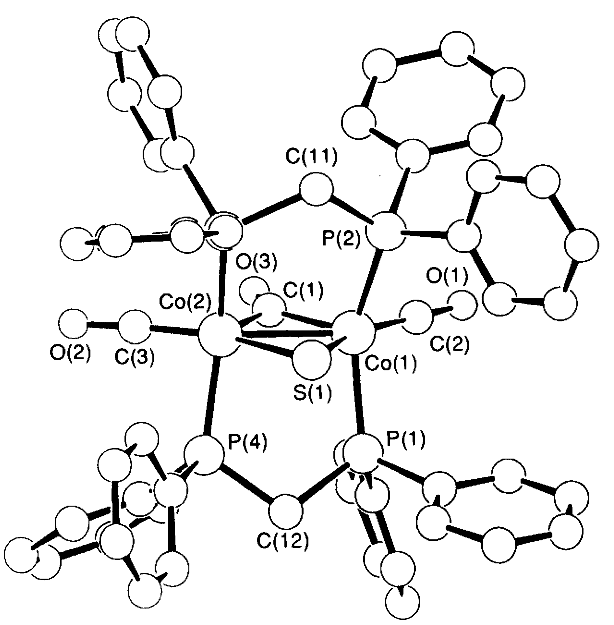


Fig. 1 Perspective view of $[Co_2(CO)_2(\mu\text{-}CO)(\mu\text{-}S)(dppm)_2]$ **4**

Table 2 Interatomic distances (Å) and angles (°) in $[Co_2(CO)_2(\mu\text{-}CO)(\mu\text{-}S)(dppm)_2]$ **4** with estimated standard deviations (e.s.d.s) in parentheses

Co(1)–Co(2)	2.559(3)	P(1)–C(121)	1.81(1)
Co(1)–S(1)	2.262(6)	P(2)–C(11)	1.88(2)
Co(1)–P(1)	2.193(4)	P(2)–C(211)	1.84(1)
Co(1)–P(2)	2.179(4)	P(2)–C(221)	1.82(1)
Co(1)–C(1)	1.94(1)	P(3)–C(11)	1.86(2)
Co(1)–C(2)	1.74(1)	P(3)–C(311)	1.84(2)
Co(2)–S(1)	2.275(5)	P(3)–C(321)	1.84(2)
Co(2)–P(3)	2.200(4)	P(4)–C(12)	1.88(2)
Co(2)–P(4)	2.186(4)	P(4)–C(411)	1.82(2)
Co(2)–C(1)	1.95(1)	P(4)–C(421)	1.86(1)
Co(2)–C(3)	1.72(2)	O(2)–C(2)	1.14(2)
P(1)–C(12)	1.86(2)	O(3)–C(3)	1.17(3)
P(1)–C(111)	1.83(1)	O(1)–C(1)	1.14(2)
S(1)–Co(1)–P(1)	83.0(2)	S(1)–Co(2)–C(3)	158.5(5)
S(1)–Co(1)–P(2)	80.7(2)	P(3)–Co(2)–P(4)	144.7(2)
S(1)–Co(1)–C(1)	104.8(5)	P(3)–Co(2)–C(1)	103.9(4)
S(1)–Co(1)–C(2)	156.9(5)	P(3)–Co(2)–C(3)	94.7(5)
P(1)–Co(1)–P(2)	147.2(2)	P(4)–Co(2)–C(1)	109.8(4)
P(1)–Co(1)–C(1)	106.8(4)	P(4)–Co(2)–C(3)	91.3(5)
P(1)–Co(1)–C(2)	92.6(5)	C(1)–Co(2)–C(3)	97.4(7)
P(2)–Co(1)–C(1)	104.8(4)	Co(1)–S(1)–Co(2)	68.7(1)
P(2)–Co(1)–C(2)	91.3(5)	Co(2)–C(1)–O(1)	140(1)
C(1)–Co(1)–C(2)	98.3(6)	Co(1)–C(2)–O(2)	176(1)
S(1)–Co(2)–P(3)	82.3(2)	Co(2)–C(3)–O(3)	177(1)
S(1)–Co(2)–P(4)	79.7(2)	Co(1)–C(1)–Co(2)	82.5(5)
S(1)–Co(2)–C(1)	104.1(5)	Co(1)–C(1)–O(1)	139(1)

resolved, so that two different *ipso*, *o*- and *m*-resonances and one *p*-resonance can be observed between δ 127.6 and 139.2. The *ipso*, *o*- and *m*-C-atoms appear as broad unresolved multiplets because of coupling to the phosphorus atoms (unresolved AXX′ systems).

The fast atom bombardment (FAB) mass spectra show signals for $[M]^+$ and fragments $[M - nX]^+$ (n = 1–3, X = CO; n = 1 or 2, X = CO or SO_2) for complexes **2**, **4** and **6**, while complexes **3** and **5** only show fragment peaks.

Crystal Structures of $[Co_2(CO)_2(\mu\text{-}CO)(\mu\text{-}S)(dppm)_2]\cdot 1.5Me_2CO$ *and* $[Co_2(CO)_2(\mu\text{-}S)(\mu\text{-}SO_2)(dppm)_2]\cdot CH_2Cl_2$.—The crystal of **4** was found to be a Me_2CO solvate with the formulation $[Co_2(CO)_2(\mu\text{-}CO)(\mu\text{-}S)(dppm)_2]\cdot 1.5Me_2CO$. The structure consists of discrete complexes and non-co-ordinating Me_2CO solvate molecules. Fig. 1 shows a perspective view of the molecule including atom labels. Selected distances and angles are presented in Table 2.

The two Co atoms in **4** are bridged by two bis(diphenylphosphino)methane ligands in a distorted *trans* arrangement, one sulfur atom and one CO ligand. An interesting feature of the structure are the angles between the Co and P atoms, which deviate by more than 30° from a linear arrangement. The P–M–P angles of *trans*-co-ordinated A-frame complexes are mostly between 178 and 170°, exceptions are $[(SCN)Ni(\mu\text{-}dppm)_2(\mu\text{-}C{=}CH_2)Ni(NCS)]$,[2] $[Rh_2(CO)_2(\mu\text{-}CCHPh)(dppm)_2]$[27] and $[Rh_2(CO)_2(\mu\text{-}H)(\mu\text{-}CO)(dppm)_2][p\text{-}C_6H_4SO_3]$[28] with angles of about 155°. On the other hand *cis*-co-ordinated cradle complexes show P–M–P angles of 100–110°.[26,27,29] Complex **4** lies in between these, although with a P–Co–P angle of 146° it can be regarded as more *trans* than *cis* co-ordinated. The P–Co–P angles of the complex $[Co_2(CO)_2(\mu\text{-}CO)(\mu\text{-}I)(dppm)(dmpm)]I$[16] [dmpm = bis(dimethylphosphino)methane] are 168° with the P atoms bent towards the I bridge, and we think the P–Co–P angles should diminish by substituting the iodine ligand by the smaller sulfur ligand. In $[Ir_2(CO)_2(\mu\text{-}CO)(\mu\text{-}S)(dppm)_2]$[25] the phosphorus atoms are also bent towards the S bridge and not towards the CO bridge (P–Ir–P = 167°). The other two CO groups are terminal and in *trans* position to the sulfur bridge. Complex **4** is isostructural to $[Ir_2(CO)_2(\mu\text{-}CO)(\mu\text{-}S)(dppm)_2]$[25] and can be viewed as two nearly square-pyramidal co-ordinated cobalt atoms with the bridging carbon monoxide ligand in the apical position. The largest deviation of the basal atoms from the respective basal square co-ordination planes containing S, P(1), P(2), C(2) and S, P(3), P(4), C(3) is 0.13 Å, and the Co atoms are displaced 0.487(2) and 0.490(2) Å from these planes. Due to the shorter separation of the metal atoms in **4** the dihedral angle of 90.0(2)° between the two planes containing S, P(1), P(2), C(2) and S, P(3), P(4), C(3) is about 10° narrower than found in $[Ir_2(CO)_2(\mu\text{-}CO)(\mu\text{-}S)(dppm)_2]$.[25] The P atoms do not deviate by more than 0.05 Å from their least-square plane, which is nearly perpendicular to the plane containing the Co atoms, S and bridging CO group. The bond distances in **4** lie in the normal range. The Co–Co separation [2.559(3) Å] is comparable with the value found in $[Co_2(CO)_8]$ (2.524 Å)[30] and indicates a metal–metal bond, which completes the stable configuration of 18 electrons for each Co atom. The Co–S bond lengths of 2.262(6) and 2.275(5) Å are nearly identical and about 0.2 Å shorter than in $[Ir_2(CO)_2(\mu\text{-}CO)(\mu\text{-}S)(dppm)_2]$. The angle Co(1)–S–Co(2) of 68.7(1)° can be compared with Ir–S–Ir of 70.5(1)°. The Co–P distances between 2.179(4) and 2.200(4) Å are slightly shorter than in $[Co_2(CO)_2(\mu\text{-}CO)(\mu\text{-}I)(dppm)(dmpm)]I$,[16] and the Co–C and C–O bond lengths are in the region expected for cobalt complexes containing terminal and bridging CO groups.[30]

The crystal structure of **6** consists of well separated $[Co_2(CO)_2(\mu\text{-}S)(\mu\text{-}SO_2)(dppm)_2]$ complexes and CH_2Cl_2 solvate molecules. A perspective view of **6** is given in Fig. 2. The structure of **6** with bridging sulfur, SO_2 and dppm ligands closely resembles that of **4**. Important distances and angles of the structure are listed in Table 3.

The distance between the Co atoms of 2.685(2) Å in **6** is about 0.1 Å longer than the Co–Co distance in **4**. Therefore the Co(1)–S(1)–Co(2) bond angle increases from 68.7(1)° in **4** to 73.18(9)°, while the Co–S(1) bond lengths of 2.253(3) and 2.251(3) Å are not changed within experimental error. The bridging SO_2 ligand is symmetrically co-ordinated to the Co centres [Co(1)–S(2) ≈ Co(2)–S(2) = 2.177(4) (av.) Å]. The S–O bond lengths of 1.461(8) and 1.483(8) Å and the O–S–O bond angle of 111.9(5)° are typical for $\mu\text{-}SO_2$ complexes.[3,7] The Co–P and Co–C vectors as well as the P–Co–P angles are comparable with the values found in **4**.

Table 3 Interatomic distances (Å) and angles (°) in $[Co_2(CO)_2(\mu\text{-}S)(\mu\text{-}SO_2)(dppm)_2]$ **6**

Co(1)–Co(2)	2.685(2)	O(2)–C(2)	1.16(1)
Co(1)–S(1)	2.253(3)	P(1)–C(11)	1.87(2)
Co(1)–S(2)	2.174(4)	P(1)–C(111)	1.86(2)
Co(1)–P(1)	2.200(3)	P(1)–C(121)	1.82(1)
Co(1)–P(2)	2.212(3)	P(2)–C(12)	1.84(2)
Co(1)–C(1)	1.74(2)	P(2)–C(211)	1.82(2)
Co(2)–S(1)	2.251(3)	P(2)–C(221)	1.86(1)
Co(2)–S(2)	2.180(3)	P(3)–C(12)	1.85(1)
Co(2)–P(3)	2.206(3)	P(3)–C(311)	1.83(1)
Co(2)–P(4)	2.210(3)	P(3)–C(321)	1.85(2)
Co(2)–C(2)	1.73(1)	P(4)–C(11)	1.86(1)
S(2)–O(3)	1.461(8)	P(4)–C(411)	1.83(2)
S(2)–O(4)	1.483(8)	P(4)–C(421)	1.85(1)
O(1)–C(1)	1.16(1)		
S(1)–Co(1)–S(2)	105.4(2)	S(1)–Co(2)–C(2)	155.2(4)
S(1)–Co(1)–P(1)	79.4(1)	S(2)–Co(2)–P(3)	103.5(2)
S(1)–Co(1)–P(2)	82.9(1)	S(2)–Co(2)–P(4)	106.1(1)
S(1)–Co(1)–C(1)	158.1(4)	S(2)–Co(2)–C(2)	99.5(4)
S(2)–Co(1)–P(1)	109.8(1)	P(3)–Co(2)–P(4)	148.8(2)
S(2)–Co(1)–P(2)	103.0(1)	P(3)–Co(2)–C(2)	93.1(4)
S(2)–Co(1)–C(1)	96.4(4)	P(4)–Co(2)–C(2)	91.4(4)
P(1)–Co(1)–P(2)	145.8(1)	O(3)–S(2)–O(4)	111.9(5)
P(1)–Co(1)–C(1)	91.6(4)	Co(1)–S(1)–Co(2)	73.18(9)
P(2)–Co(1)–C(1)	94.2(4)	Co(1)–S(2)–Co(2)	76.1(1)
S(1)–Co(2)–S(2)	105.3(2)	P(1)–C(11)–P(4)	114.3(6)
S(1)–Co(2)–P(3)	80.1(2)	P(2)–C(12)–P(3)	116.9(5)
S(1)–Co(2)–P(4)	83.1(2)		

Experimental

The cobalt complexes $[Co_2(CO)_2(\mu\text{-}CO)(\mu\text{-}I)(dppm)_2]I$ [16] and $[Co_2(CO)_2(\mu\text{-}CO)(dppm)_2]$ **1** [16] and C_2H_4SO [31] were prepared

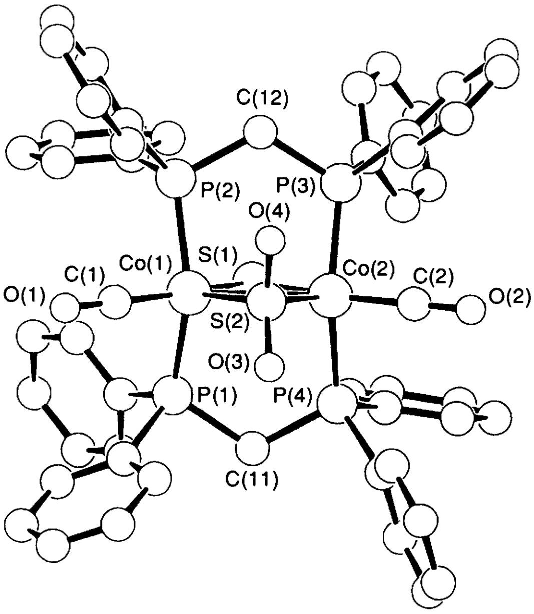


Fig. 2 Perspective view of $[Co_2(CO)_2(\mu\text{-}S)(\mu\text{-}SO_2)(dppm)_2]$ **6**

Table 4 Atomic coordinates for $[Co_2(CO)_2(\mu\text{-}CO)(\mu\text{-}S)(dppm)_2]\cdot 1.5Me_2CO$ with e.s.d.s in parentheses. Atoms marked with * were refined isotropically

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Co(1)	0.346 3(1)	0.157 77(7)	0.438 0(1)	C(212)	0.411(1)	0.262 9(6)	0.314(1)
Co(2)	0.202 1(1)	0.153 71(8)	0.508 2(1)	C(213)	0.449(1)	0.306 9(7)	0.282(1)
S(1)	0.271 9(4)	0.229 2(2)	0.476 9(3)	C(214)	0.410(1)	0.330 7(6)	0.208(1)
P(1)	0.439 7(3)	0.176 5(2)	0.554 9(2)	C(215)	0.332(1)	0.309 4(6)	0.163(1)
P(2)	0.283 0(3)	0.183 3(2)	0.311 0(2)	C(216)	0.293(1)	0.265 8(6)	0.193(1)
P(3)	0.107 0(3)	0.176 5(2)	0.394 0(2)	C(221)	0.286(1)	0.135 5(5)	0.225 5(8)
P(4)	0.262 8(3)	0.177 6(2)	0.637 4(2)	C(222)	0.228(1)	0.092 4(7)	0.220(1)
O(2)	0.482 7(7)	0.103 1(4)	0.361 1(6)	C(223)	0.235(2)	0.052 4(8)	0.160(1)
O(3)	0.075 1(8)	0.088 3(5)	0.581 6(7)	C(224)	0.297(2)	0.058 8(8)	0.104(1)
O(1)	0.274 3(8)	0.054 1(4)	0.459 4(8)	C(225)	0.349(2)	0.101 1(8)	0.107(1)
O(4)*	0.764(1)	0.128 5(6)	0.471(1)	C(226)	0.345(1)	0.138 3(7)	0.168(1)
O(5)*	0.280(2)	0.442(1)	0.518(2)	C(311)	0.028(1)	0.230 0(6)	0.410 2(9)
C(1)	0.274(1)	0.098 6(5)	0.466(1)	C(312)	0.037(1)	0.278 9(7)	0.381(1)
C(2)	0.428 1(9)	0.123 4(5)	0.393 3(8)	C(313)	−0.027(2)	0.318 6(7)	0.399(1)
C(3)	0.127(1)	0.113 7(6)	0.549 9(9)	C(314)	−0.095(1)	0.306(1)	0.442(1)
C(4)*	0.770(1)	0.080 3(7)	0.467(1)	C(315)	−0.101(1)	0.258(1)	0.471(1)
C(5)*	0.267(3)	0.396(2)	0.496(2)	C(316)	−0.040(1)	0.218 7(8)	0.455(1)
C(11)	0.160(1)	0.199 6(6)	0.300 4(9)	C(321)	0.026(1)	0.127 7(7)	0.342 9(9)
C(12)	0.385(1)	0.195 9(6)	0.649 8(9)	C(322)	0.043(1)	0.075 3(7)	0.361(1)
C(41)*	0.850(2)	0.053 8(9)	0.518(1)	C(323)	−0.015(1)	0.034 4(8)	0.320(1)
C(42)*	0.706(2)	0.050(1)	0.406(1)	C(324)	−0.089(2)	0.052 8(9)	0.262(1)
C(51)*	0.287(3)	0.377(2)	0.424(3)	C(325)	−0.105(1)	0.104 0(9)	0.247(1)
C(52)*	0.207(3)	0.375(2)	0.534(3)	C(326)	−0.047(1)	0.141 5(8)	0.284(1)
C(111)	0.519(1)	0.125 4(5)	0.600 1(8)	C(411)	0.214(1)	0.234 6(6)	0.682 6(9)
C(112)	0.500(1)	0.073 8(7)	0.579(1)	C(412)	0.256(1)	0.259 6(7)	0.756(1)
C(113)	0.556(1)	0.034 3(7)	0.614(1)	C(413)	0.212(1)	0.301 9(7)	0.787(1)
C(114)	0.653(2)	0.097 1(8)	0.693(1)	C(414)	0.133(1)	0.320 2(8)	0.749(1)
C(115)	0.636(1)	0.046 5(7)	0.672(1)	C(415)	0.091(1)	0.295 3(9)	0.677(1)
C(116)	0.595(1)	0.137 6(7)	0.660(1)	C(416)	0.133(1)	0.252 7(8)	0.644(1)
C(121)	0.514 3(9)	0.231 6(6)	0.544 8(8)	C(421)	0.260(1)	0.128 0(6)	0.723 3(8)
C(122)	0.501(1)	0.282 3(5)	0.573(1)	C(422)	0.200(1)	0.130 4(7)	0.781(1)
C(123)	0.559(2)	0.322 3(6)	0.558(1)	C(423)	0.196(2)	0.092 2(8)	0.841(1)
C(124)	0.627(1)	0.314 7(8)	0.512(1)	C(424)	0.252(2)	0.050 9(8)	0.846(1)
C(125)	0.640(1)	0.265 5(8)	0.484(1)	C(425)	0.311(2)	0.047 1(8)	0.789(1)
C(126)	0.585(1)	0.222 4(7)	0.499(1)	C(426)	0.313(1)	0.086 1(8)	0.725(1)
C(211)	0.333(1)	0.242 1(6)	0.269 0(8)				

Table 5 Atomic coordinates for $[Co_2(CO)_2(\mu\text{-}S)(\mu\text{-}SO_2)(dppm)_2]\cdot CH_2Cl_2$ with e.s.d.s in parentheses. Atoms marked with * were refined isotropically

Atom	*x*	*y*	*z*
Co(1)	0.200 7(1)	0.156 87(5)	0.599 49(8)
Co(2)	0.292 2(1)	0.166 41(5)	0.455 11(8)
S(1)	0.126 5(2)	0.185 90(9)	0.479 0(1)
S(2)	0.362 0(2)	0.141 8(1)	0.574 8(2)
P(1)	0.101 0(2)	0.095 60(9)	0.559 0(2)
P(2)	0.205 1(2)	0.234 01(9)	0.634 4(2)
P(3)	0.306 6(2)	0.245 59(9)	0.462 9(2)
P(4)	0.217 4(2)	0.102 50(9)	0.394 8(2)
O(1)	0.213 8(8)	0.121 9(3)	0.768 8(5)
O(2)	0.468 8(6)	0.157 6(3)	0.353 4(5)
O(3)	0.396 6(6)	0.091 6(3)	0.581 0(5)
O(4)	0.439 4(6)	0.175 2(3)	0.615 8(5)
C(1)	0.208 9(9)	0.136 5(4)	0.701 8(6)
C(2)	0.399 3(9)	0.160 8(4)	0.395 6(7)
C(11)	0.119 1(9)	0.070 2(4)	0.454 0(6)
C(12)	0.285 2(8)	0.270 3(4)	0.567 3(6)
C(111)	0.117 9(9)	0.040 8(4)	0.624 8(6)
C(112)	0.213(1)	0.019 2(5)	0.628 1(8)
C(113)	0.233(1)	−0.022 0(5)	0.681 2(9)
C(114)	0.157(1)	−0.037 7(5)	0.727 9(9)
C(115)	0.062(1)	−0.015 9(5)	0.726 0(9)
C(116)	0.042(1)	0.023 9(4)	0.673 2(8)
C(121)	−0.038 8(9)	0.106 4(4)	0.559 3(6)
C(122)	−0.113 0(9)	0.077 1(5)	0.515 4(7)
C(123)	−0.219 3(9)	0.085 4(5)	0.519 9(8)
C(124)	−0.254(1)	0.122 2(5)	0.569 4(9)
C(125)	−0.182(1)	0.151 7(5)	0.613(1)
C(126)	−0.075 5(9)	0.143 5(5)	0.607 9(8)
C(211)	0.074 6(8)	0.260 2(4)	0.632 5(6)
C(212)	0.016 3(8)	0.250 5(4)	0.701 5(7)
C(213)	−0.089(1)	0.265 6(5)	0.696 9(9)
C(214)	−0.135(1)	0.288 9(5)	0.629 0(9)
C(215)	−0.076(1)	0.298 0(5)	0.564 2(8)
C(216)	0.029 3(9)	0.285 1(4)	0.563 1(7)
C(221)	0.261 6(8)	0.254 8(4)	0.736 9(6)
C(222)	0.226(1)	0.295 7(5)	0.773 9(7)
C(223)	0.274(1)	0.312 5(5)	0.850 2(7)
C(224)	0.356 5(9)	0.287 7(5)	0.888 4(6)
C(225)	0.395 8(9)	0.246 9(5)	0.850 8(7)
C(226)	0.347 0(9)	0.229 7(4)	0.774 8(7)
C(311)	0.222 3(8)	0.280 1(4)	0.388 7(6)
C(312)	0.182 2(8)	0.257 6(4)	0.315 7(6)
C(313)	0.123 5(9)	0.284 9(4)	0.254 8(6)
C(314)	0.105 4(9)	0.332 7(5)	0.267 5(8)
C(315)	0.143(1)	0.355 6(5)	0.341 2(8)
C(316)	0.203 3(8)	0.329 1(4)	0.401 2(7)
C(321)	0.436 6(8)	0.271 7(4)	0.447 9(6)
C(322)	0.453 2(9)	0.311 5(5)	0.399 0(7)
C(323)	0.552 2(9)	0.329 0(5)	0.389 1(9)
C(324)	0.636(1)	0.306 4(5)	0.427 4(9)
C(325)	0.623 5(9)	0.267 2(5)	0.475 8(7)
C(326)	0.525 4(9)	0.249 2(5)	0.486 9(7)
C(411)	0.297 7(8)	0.051 2(4)	0.365 8(6)
C(412)	0.253(1)	0.015 6(4)	0.310 9(8)
C(413)	0.311(1)	−0.025 4(4)	0.294 4(9)
C(414)	0.411(1)	−0.031 4(5)	0.331 9(8)
C(415)	0.454(1)	0.002 9(4)	0.385 5(7)
C(416)	0.396 7(9)	0.044 2(4)	0.403 0(7)
C(421)	0.145 5(8)	0.117 9(4)	0.295 0(6)
C(422)	0.042 5(9)	0.134 6(4)	0.292 7(7)
C(423)	−0.007(1)	0.150 2(4)	0.218 1(7)
C(424)	0.043(1)	0.147 4(5)	0.144 9(8)
C(425)	0.145(1)	0.130 0(5)	0.147 2(7)
C(426)	0.197 1(9)	0.115 7(4)	0.222 7(7)
Cl(1)*	0.451(5)	0.057(2)	0.152(4)
Cl(2)*	0.652(1)	0.097 9(6)	0.118(1)
Cl(3)*	0.362(2)	0.090(1)	0.103(2)
Cl(4)*	0.767(2)	0.437 7(9)	0.447(1)
C(3)*	0.533(5)	0.092(2)	0.184(4)

according to published procedures. Thiirane (Fluka) and SO_2 were used as supplied. All operations were carried out under a pure argon atmosphere, using Schlenk techniques. All solvents were dried, distilled and degassed before use.

Proton (250 MHz) and $^{13}C\text{-}\{^1H\}$ (62.7 MHz) NMR spectra were recorded at room temperature (25 °C) using a Bruker WP-250 instrument; $^{31}P\text{-}\{^1H\}$ (32.9 MHz) NMR spectra were recorded at −30 °C using a Bruker WP-80 with chemical shifts given relative to external 85% H_3PO_4–$(CD_3)_2CO$. IR spectra were recorded as KBr pellets on a Bruker IFS 48 with Aspect 1000. Mass spectra were recorded on a Varian MAT 711A. Elemental analysis were performed on a Carlo-Erba 1104 analyser.

Preparations.—$[Co_2(CO)_2(\mu\text{-}SO_2)_2(dppm)_2]$ **2**. At −30 °C a moderate stream of SO_2 was bubbled for 1 min through a suspension of **1** (200 mg, 0.206 mmol) in toluene (10 cm^3); the resultant red solution was then stirred for 1 h at −30 °C. Addition of hexane (30 cm^3) to the red solution gave a dark red solid which was collected by filtration, washed with hexane and dried *in vacuo*; 198 mg (90%) (Found: C, 57.40; H, 3.50; S, 6.20. Calc. for $C_{52}H_{44}Co_{52}O_6P_4S_2$: C, 58.30; H, 4.10; S, 6.00%).

$[Co_2(CO)_2(\mu\text{-}CO)_2(dppm)_2]$ **3**. Carbon monoxide was bubbled for 15 min through a solution of **1** (200 mg, 0.206 mmol) in acetone (10 cm^3) at 0 °C. The solution became red brown and was stirred for a further 30 min under a CO atmosphere. The acetone was then removed by evaporation and the resultant yellow-brown solid was dried *in vacuo*; 195 mg (95%) (Found: C, 64.30; H, 4.15. Calc. for $C_{54}H_{44}Co_2O_4P_4$: C, 64.95; H, 4.40%).

$[Co_2(CO)_2(\mu\text{-}CO)(\mu\text{-}S)(dppm)_2]$ **4**. Thiirane (0.1 cm^3, 1.67 mmol) was added to a slurry of **1** (200 mg, 0.206 mmol) in toluene (10 cm^3) and stirred for 1 h at 25 °C. The resultant solution changed from dark green to dark brown. Then hexane (30 cm^3) was added and the resultant brown solid collected by filtration and dried *in vacuo*; 185 mg (90%) (Found: C, 63.30; H, 4.15; S, 3.40. Calc. for $C_{52}H_{44}Co_2O_6P_4S_2$: C, 63.45; H, 4.40; S, 3.20%).

$[Co_2(CO)_2(\mu\text{-}CO)(\mu\text{-}SO_2)(dppm)_2]$ **5**. A suspension of **3** (100 mg, 0.1 mmol) in toluene (10 cm^3) was treated for 10 min with a slow stream of SO_2 at −30 °C. It was stirred for a further 15 min while its colour changed from dark brown to orange-brown. Addition of hexane (30 cm^3) at −30 °C afforded an orange solid which was dried *in vacuo*; 73 mg (70%) (Found: C, 60.75; H, 4.00; S, 6.55. Calc. for $C_{53}H_{44}Co_2O_5P_4S$: C, 61.50; H, 4.25; S, 3.10%).

$[Co_2(CO)_2(\mu\text{-}S)(\mu\text{-}SO_2)(dppm)_2]$ **6**. Sulfur dioxide was bubbled for 30 min through acetone (10 cm^3) containing 100 mg (0.1 mmol) of **4**. After stirring for a further 30 min the acetone was removed by evaporation and the resulting violet solid was dried *in vacuo*; 103 mg (100%) (Found: C, 59.75; H, 4.00; S, 6.55. Calc. for $C_{52}H_{44}Co_2O_4P_4S_2$: C, 60.15; H, 4.25; S, 6.15%).

X-Ray Studies.—$[Co_2(CO)_2(\mu\text{-}CO)(\mu\text{-}S)(dppm)_2]\cdot 1.5Me_2CO$: Suitable crystals for X-ray diffraction experiments were obtained from acetone as dark red platelets. As the crystals of **4**$\cdot$1.5Me$_2$CO disintegrate rapidly with the loss of the solvent molecules, all diffraction experiments were carried out at 200 K on an automated Enraf-Nonius CAD4 single-crystal diffractometer.

Crystal data. $C_{115}H_{106}Co_4O_9P_8S_2$, $M = 2179.8$, monoclinic, space group $P2_1/n$ (no. 14), $a = 14.950(5)$, $b = 25.480(5)$, $c = 15.682(4)$ Å, $\beta = 98.18(2)°$, $U = 5911.7$ Å^3, $Z = 2$, $D_c = 1.224$ g cm^{-3}, crystal dimensions 0.5 × 0.3 × 0.1 mm, graphite-monochromated Mo-Kα radiation (λ = 0.710 89 Å), μ(Mo-Kα) = 7.405 cm^{-1}, F(000) = 2256.

Data collection and processing. CAD4 diffractometer, ω-scan technique, with θ 3–26°, 200 K. 9963 Reflections were measured, and after Lorentz and polarization corrections, 3692 symmetrically independent observations having $I > 3\sigma(I)$ were retained. The unit-cell dimensions were calculated from 25 accurately centred reflections of high θ values.

Structure analysis and refinement. The position of the Co and P atoms and of the S atom was derived from direct methods.[32] The positions of the remaining non-hydrogen atoms of **4** and of the solvent molecules were found by successive difference Fourier calculations and least-square refinements.[33] The R value at this point was 0.143. An empirical absorption correction[34] and the introduction of anisotropic thermal parameters for the non-hydrogen atoms of **4** improved R to 0.079. The positions of the hydrogen atoms of **4** were calculated (C–H 0.95 Å) and included in the structure factor calculation with fixed thermal parameters to give a final R value of 0.074, R' = 0.089 [$w = 1/\sigma^2(I)$]. Atomic coordinates are given in Table 4.

$[Co_2(CO)_2(\mu\text{-}S)(\mu\text{-}SO_2)(dppm)_2]\cdot CH_2Cl_2$.—Crystals of **6** were found to rapidly lose solvent upon removal from CH_2Cl_2–$(C_3H_7)_2O$ solution. Therefore the crystal used for data collection was coated with a viscous high-molecular-weight hydrocarbon and secured to the end of a glass fibre by cooling to 205 K.

Crystal data. $C_{53}H_{46}Cl_2CoO_4P_4S_2$, M = 1123.8, monoclinic, space group $P2_1/n$ (no. 14), a = 12.850(5), b = 27.660(4), c = 16.056(5) Å, β = 93.85(3)°, U = 5693.9 Å^3, Z = 4, D_c = 1.306 g cm^{-3}, crystal dimensions 0.8 × 0.4 × 0.15 mm, graphite-monochromated Mo-Kα radiation (λ = 0.710 89 Å), μ(Mo-Kα) = 8.928 cm^{-1}, F(000) = 2304.

Data collection and processing. CAD4 diffractometer, ω-scan technique, with θ 5–25°, 205 K. 8926 Reflections were measured, and after Lorentz and polarization corrections and merging, a sufficient number of 4324 independent observations having $I > 4\sigma(I)$ was retained. The unit-cell dimensions were calculated from 25 accurately centred reflections of high θ values.

Structure analysis and refinement. The structure was solved by direct methods[32] and refined as described above. Refinement of **6** with isotropic thermal parameters converged at R = 0.104 and, after introduction of anisotropic thermal parameters R fell to 0.08. The solvent molecules were found to be disordered over two positions and could be refined with an occupancy factor of 0.5. The final model converged with R = 0.065. An absorption correction was not applied. Atomic coordinates are given in Table 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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