

New tricapped thioether derivatives of $\text{Co}_3(\text{CO})_9(\mu\text{-CPh})$

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Abstract

μ -Benzylidyne tricobalt nonacarbonyl, $\text{Co}_3(\text{CO})_9(\mu\text{-CPh})$, reacts readily with sulfur donor ligands. Tridentate ligands 1,3,5-trithia-cyclohexane and tris(thiomethyl)methane both replace three carbonyl groups giving capped derivatives. Dimethylsulfide groups also replace carbonyl groups, forming mono-, di- and trisubstituted derivatives. The capping benzylidyne group is in all cases maintained intact. The crystal structures of the cluster compounds with tridentate sulfur ligands were determined. © 1997 Elsevier Science S.A.

1. Introduction

Triangular cobalt carbonyl clusters with capping alkylidyne ligands, $\text{Co}_3(\text{CO})_9(\mu\text{-CX})$, have been widely studied in recent years because of their catalytic activity in hydroformulation and hydrosilylation reactions [1,2]. The reactions of the μ_3 -alkylidyne carbon atom group in $\text{Co}_3(\text{CO})_9(\mu\text{-CPh})$ have been of particular interest of [3,4].

There has also been continuing interest in the preparation of derivatives of $\text{Co}_3(\text{CO})_9(\mu\text{-CPh})$ through replacement of carbonyl groups of the parent cluster with mono- and bidentate ligands, mainly containing a donor atom of Group 15 (phosphorus, arsenic) [5–9]. In general, bi- and tridentate ligands have been used in cluster chemistry to stabilize the metal frameworks. The phosphine-bridged metal clusters sometimes appear to exhibit novel catalytic activity. For example, some phosphido-bridged ruthenium clusters are active catalysts in hydrogenation of cyclohexanone to cyclohexanol, where as the unsubstituted clusters are inactive [10,11]. Correspondingly $\text{Co}_3(\text{CO})_7(\mu\text{-CMe})(\text{diphosphine})$ is stabilized and activated by the phosphine-bridge in hydroformylation of 1-pentene [12]. It is also proposed that some active catalysts have intermediates with stabilizing bridging ligands.

Tridentate ligands are much more unusual in $\text{Co}_3(\text{CO})_9(\mu\text{-CPh})$ derivatives than are mono- and bidentate ligands. Tridentate phosphorus ligand tris(diphenylphosphine)methane, $\text{CH}(\text{PPh}_2)_3$, has been used to coordinate to tetrahedral clusters [13–16], and it also forms derivatives with $\text{Co}_3(\text{CO})_9(\mu\text{-CPh})$ [17]. Evidently $\text{Co}_3(\text{CO})_9(\mu\text{-CPh})$ has only a few stable derivatives containing sulfur ligands, and all of these ligands are mono- or bidentate. Sulfur- and phosphine-bridged compounds differ significantly. The bidentate sulfur ligands favour axial position, whereas bidentate phosphine ligands usually coordinate to an equatorial position. The sulfur bridge also causes a shortening of the metal–metal bond concerned, while the phosphine bridge leads to an elongation of the metal–metal distance [18].

Earlier we have studied some reactions of aliphatic thioethers with tetrahedral ruthenium, rhodium and cobalt cluster compounds as well as with $\text{Ru}_3(\text{CO})_{12}$ and $\text{Rh}_6(\text{CO})_{16}$ [19–23]. We have also studied the suitability of tridentate compounds as tricapping ligands in clusters. For example, $\text{HRuCo}_3(\text{CO})_{12}$ reacts with 1,3,5-trithiacyclohexane forming the complex $\text{HRuCo}_3(\text{CO})_9(\text{S}_3\text{C}_3\text{H}_6)$ [22]. In the reaction with $\text{HRuCo}_3(\text{CO})_{12}$, the sulfur ligand favours binding to cobalt over ruthenium. In this cluster the ruthenium atom is formally electron deficient, but still the sulfur ligand prefers to bind to the cobalt triangle. Trithiacyclohexane also reacts with $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_{12}$ [23]. In this work we chose the trinuclear cluster

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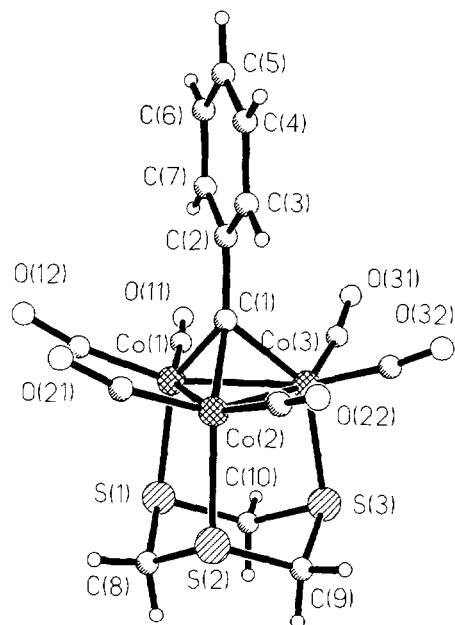


Fig. 1. Structure and numbering scheme for $\text{Co}_3(\text{CO})_6(\mu\text{-CPh})(\text{S}_3\text{C}_3\text{H}_6)$ (1).

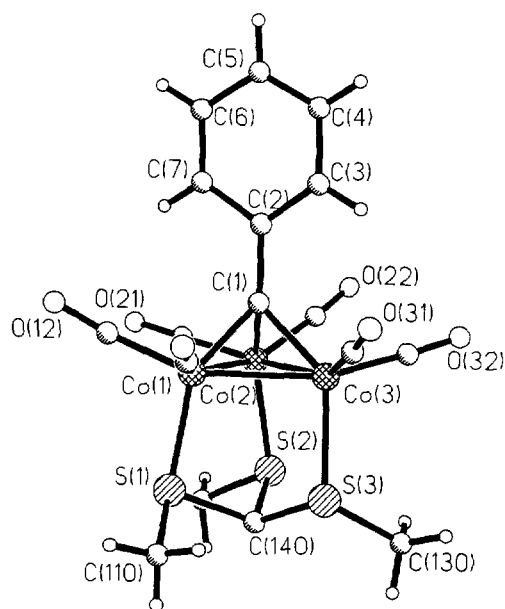


Fig. 2. Structure and numbering scheme for $\text{Co}_3(\text{CO})_6(\mu\text{-CPh})[\text{CH}(\text{SMe})_3]$ (2).

$\text{Co}_3(\text{CO})_9(\mu\text{-CPh})$ for comparison to the $\text{HRuCo}_3(\text{CO})_{12}$. In $\text{HRuCo}_3(\text{CO})_{12}$ the Co–Co bond is approximately 249 pm, while in $\text{Co}_3(\text{CO})_9(\mu\text{-CPh})$ the

Table 1
Selected bond lengths (pm) for $\text{Co}_3(\text{CO})_6(\mu\text{-CPh})(\text{S}_3\text{C}_3\text{H}_6)$ (1)

	Molecule a	Molecule b
Co(1)–Co(2)	246.5 (4)	246.6 (4)
Co(1)–Co(3)	246.6 (4)	247.2 (3)
Co(2)–Co(3)	244.8 (4)	247.4 (3)
Co(1)–S(1)	226.4 (5)	228.4 (6)
Co(2)–S(2)	227.0 (5)	227.0 (6)
Co(3)–S(3)	226.9 (5)	227.8 (6)
Co(1)–C(1)	190.3 (15)	189 (2)
Co(2)–C(1)	189 (2)	187 (2)
Co(3)–C(1)	195 (2)	188 (2)
Co(1)–C(11)	178 (2)	179 (2)
Co(1)–C(12)	177 (3)	178 (2)
Co(2)–C(21)	177 (3)	176 (2)
Co(2)–C(22)	179 (2)	177 (2)
Co(3)–C(31)	173 (2)	180 (3)
Co(3)–C(32)	179 (2)	182 (3)
S(1)–C(8)	180 (2)	180 (2)
S(1)–C(10)	179 (2)	180 (2)
S(2)–C(8)	179 (2)	181 (2)
S(2)–C(9)	179 (3)	180 (2)
S(3)–C(9)	181 (2)	183 (2)
S(3)–C(10)	183 (2)	185 (2)
O(11)–C(11)	112 (2)	112 (2)
O(12)–C(12)	114 (3)	112 (2)
O(21)–C(21)	118 (3)	116 (2)
O(22)–C(22)	114 (2)	117 (2)
O(31)–C(31)	121 (3)	113 (3)
O(32)–C(32)	111 (2)	113 (3)
C(1)–C(2)	146 (2)	151 (2)

Table 2
Selected bond lengths (pm) for $\text{Co}_3(\text{CO})_6(\mu\text{-CPh})[\text{CH}(\text{SMe})_3]$ (2)

Co(1)–Co(2)	246.66 (12)
Co(1)–Co(3)	246.13 (12)
Co(2)–Co(3)	246.50 (13)
Co(1)–S(1)	228.4 (2)
Co(2)–S(2)	228.1 (2)
Co(3)–S(3)	228.2 (2)
Co(1)–C(1)	189.0 (7)
Co(2)–C(1)	189.8 (6)
Co(3)–C(1)	190.7 (6)
Co(1)–C(11)	177.7 (8)
Co(1)–C(12)	176.5 (7)
Co(2)–C(21)	174.8 (8)
Co(2)–C(22)	180.0 (10)
Co(3)–C(31)	177.1 (9)
Co(3)–C(32)	177.6 (9)
S(1)–C(110)	180.1 (8)
S(1)–C(140)	181.8 (7)
S(2)–C(120)	181.3 (8)
S(2)–C(140)	181.9 (7)
S(3)–C(130)	180.5 (8)
S(3)–C(140)	180.7 (8)
O(11)–C(11)	113.4 (9)
C(12)–O(12)	114.6 (9)
O(21)–C(21)	115.0 (10)
O(22)–C(22)	112.1 (11)
C(31)–O(31)	114.6 (10)
O(32)–C(32)	112.4 (11)
C(2)–C(1)	145.3 (9)
C(2)–C(3)	137.2 (11)
C(4)–C(3)	139.2 (12)
C(5)–C(4)	136.6 (15)
C(5)–C(6)	136.9 (14)
C(7)–C(6)	137.8 (11)
C(2)–C(7)	142.0 (10)

Table 3
Bond angles for $\text{Co}_3(\text{CO})_9(\mu\text{-CPh})(\text{S}_3\text{C}_3\text{H}_6)$ (**1**)

	Molecule a	Molecule b
Co(2)–Co(1)–Co(3)	59.54 (10)	60.14 (10)
Co(2)–Co(3)–Co(1)	60.21 (10)	60.03 (10)
Co(3)–Co(2)–Co(1)	60.25 (10)	59.82 (10)
Co(1)–C(1)–Co(3)	79.7 (6)	81.9 (7)
Co(2)–C(1)–Co(1)	81.2 (6)	82.3 (8)
Co(2)–C(1)–Co(3)	79.4 (7)	82.7 (7)
S(1)–Co(1)–Co(2)	96.4 (2)	96.7 (2)
S(1)–Co(1)–Co(3)	98.4 (2)	98.4 (2)
S(2)–Co(2)–Co(1)	97.8 (2)	97.7 (2)
S(2)–Co(2)–Co(3)	97.7 (2)	98.4 (2)
S(3)–Co(3)–Co(1)	96.4 (2)	96.1 (2)
S(3)–Co(3)–Co(2)	97.5 (2)	95.8 (2)
C(1)–Co(1)–Co(2)	49.1 (5)	48.5 (5)
C(1)–Co(1)–Co(3)	51.0 (6)	48.8 (5)
C(1)–Co(2)–Co(1)	49.7 (5)	49.2 (6)
C(1)–Co(2)–Co(3)	51.4 (6)	48.8 (5)
C(1)–Co(3)–Co(1)	49.4 (4)	49.3 (6)
C(1)–Co(3)–Co(2)	49.2 (5)	48.5 (5)
C(1)–Co(1)–S(1)	140.6 (5)	139.0 (5)
C(1)–Co(2)–S(2)	141.7 (5)	140.1 (6)
C(1)–Co(3)–S(3)	139.1 (5)	137.5 (6)
C(11)–Co(1)–Co(2)	155.1 (6)	154.5 (7)
C(12)–Co(1)–Co(2)	99.6 (7)	98.8 (7)
C(11)–Co(1)–Co(3)	97.8 (7)	99.0 (6)
C(12)–Co(1)–Co(3)	149.9 (6)	150.4 (7)
C(21)–Co(2)–Co(1)	97.9 (7)	95.7 (7)
C(22)–Co(2)–Co(1)	154.9 (6)	155.9 (8)
C(21)–Co(2)–Co(3)	151.1 (7)	95.7 (7)
C(22)–Co(2)–Co(3)	98.8 (7)	99.8 (7)
C(31)–Co(3)–Co(1)	99.4 (10)	95.6 (8)
C(32)–Co(3)–Co(1)	152.1 (9)	152.7 (6)
C(31)–Co(3)–Co(2)	153.2 (10)	151.9 (8)
C(32)–Co(3)–Co(2)	97.0 (8)	99.6 (6)
C(11)–Co(1)–C(1)	109.8 (7)	107.4 (8)
C(12)–Co(1)–C(1)	99.3 (8)	101.9 (8)
C(21)–Co(2)–C(1)	100.4 (8)	102.8 (9)
C(22)–Co(2)–C(1)	107.3 (8)	108.5 (10)
C(31)–Co(3)–C(1)	104.8 (10)	105.7 (8)
C(32)–Co(3)–C(1)	104.2 (10)	104.0 (8)
C(11)–Co(1)–S(1)	97.1 (6)	101.1 (6)
C(12)–Co(1)–S(1)	105.7 (6)	105.0 (7)
C(21)–Co(2)–S(2)	104.3 (6)	102.0 (8)
C(22)–Co(2)–S(2)	98.7 (6)	97.9 (8)
C(31)–Co(3)–S(3)	102.3 (7)	100.9 (6)
C(32)–Co(3)–S(3)	102.8 (8)	104.5 (7)
C(12)–Co(1)–C(11)	96.8 (10)	94.1 (9)
C(21)–Co(2)–C(22)	96.2 (9)	98.9 (10)
C(31)–Co(3)–C(32)	96.0 (11)	97.8 (10)
O(11)–C(11)–Co(1)	176.5 (22)	177.9 (17)
O(12)–C(12)–Co(1)	167.5 (18)	174.8 (19)
O(21)–C(21)–Co(2)	168.5 (17)	171.8 (23)
O(22)–C(22)–Co(2)	173.6 (20)	167.8 (23)
O(31)–C(31)–Co(3)	170.1 (22)	174.5 (25)
O(32)–C(32)–Co(3)	173.3 (25)	173.2 (22)
C(8)–S(1)–Co(1)	108.3 (7)	107.6 (6)
C(8)–S(2)–Co(2)	106.7 (7)	106.8 (6)
C(9)–S(2)–Co(2)	106.1 (6)	107.3 (7)
C(9)–S(3)–Co(3)	105.6 (6)	108.6 (6)
C(10)–S(1)–Co(1)	104.7 (6)	106.6 (6)
C(10)–S(3)–Co(3)	106.4 (6)	108.0 (6)
C(10)–S(1)–C(8)	100.5 (10)	99.0 (9)
C(9)–S(2)–C(8)	99.4 (10)	98.4 (9)

Table 3 (continued)

	Molecule a	Molecule b
C(9)–S(3)–C(10)	99.4 (9)	98.4 (10)
S(2)–C(8)–S(1)	114.4 (10)	115.5 (10)
S(2)–C(9)–S(3)	115.7 (12)	113.0 (9)
S(1)–C(10)–S(3)	114.6 (9)	113.0 (10)
C(2)–C(1)–Co(1)	132.6 (12)	126.4 (11)
C(2)–C(1)–Co(2)	133.6 (12)	129.9 (11)
C(2)–C(1)–Co(3)	129.7 (11)	135.0 (12)
C(3)–C(2)–C(1)	120.0 (10)	118.7 (9)
C(7)–C(2)–C(1)	120.0 (10)	121.0 (9)

corresponding bond averages 246.5 pm. The tridentate sulfur ligand is thus expected to fit quite well.

This paper describes the synthesis and spectral and crystallographic characterization of two tridentate thioether derivatives of $\text{Co}_3(\text{CO})_9(\mu\text{-CPh})$.

2. Results and discussion

Although the coordination of polydentate sulfur ligands with metal cluster compounds has not been extensively studied, 1,3,5-trithiacyclohexane ($\text{S}_3\text{C}_3\text{H}_6$) and tris(thiomethyl)methane $\text{CH}(\text{SMe})_3$ should have the right dimensions to coordinate with triangular metal clusters like $\text{Co}_3(\text{CO})_9(\mu\text{-CPh})$ and $\text{Ru}_3(\text{CO})_{12}$.

Benzylidyne tricobalt nonacarbonyl reacts with both 1,3,5-trithiacyclohexane and tris(thiomethyl)methane rapidly precipitating almost quantitatively as compounds **1** and **2** in refluxing heptane. The crystal structures of **1** and **2** are presented in Figs. 1 and 2 respectively. Selected bond lengths are given in Tables 1 and 2 and selected bond angles in Tables 3 and 4. The structure determination of **1** revealed two independent molecules, identical within the limits of determination error. Small differences in bond lengths and angles between the two molecules can best be ascribed to crystal packing effects.

The tridentate ligand displaces the three carbonyl groups in basal position of the parent cluster. In both complexes the ligand is attached in eclipsed configuration and is more or less parallel with the metal triangle (the Co–S bond is 226.4(5)–228.4(6) pm in **1** and 228.1(2)–228.4(2) pm in **2**, and the Co–Co–S angle is 95.8(2)–98.4(2)° for **1** and 90.36(6)–99.63(6)° for **2**).

The average length of the Co–Co bonds in $\text{Co}_3(\text{CO})_9(\mu\text{-CPh})$ is 246.6 pm [24], while the ligand bridged bonds in **1** is 244.8(4)–247.4(3) pm and in **2** 246.13(12)–246.66(12) pm. The average distance Co–C₁ in the parent cluster is 190.6 pm, whereas in **1** it is 189.8 pm and in **2** it is 189.8 pm. Thus, the derivatives with sulfur ligands are not significantly different in structure from the basic cluster. The corresponding bond distances in the comparable compounds with tridentate

Table 4
Selected bond angles for $\text{Co}_3(\text{CO})_6(\mu\text{-CPh})[\text{CH}(\text{SMe})_3]$ (2)

Co(1)–Co(3)–Co(2)	60.09 (3)
Co(3)–Co(1)–Co(2)	60.03 (4)
Co(3)–Co(2)–Co(1)	59.88 (3)
Co(1)–C(1)–Co(2)	81.3 (3)
Co(1)–C(1)–Co(3)	80.8 (3)
Co(2)–C(1)–Co(3)	80.8 (2)
S(1)–Co(1)–Co(2)	90.59 (6)
S(1)–Co(1)–Co(3)	99.23 (6)
S(2)–Co(2)–Co(1)	99.63 (6)
S(2)–Co(2)–Co(3)	90.72 (6)
S(3)–Co(3)–Co(1)	90.36 (6)
S(3)–Co(3)–Co(2)	99.47 (6)
C(1)–Co(1)–Co(2)	49.5 (2)
C(1)–Co(1)–Co(3)	49.9 (2)
C(1)–Co(2)–Co(1)	49.2 (2)
C(1)–Co(2)–Co(3)	49.8 (2)
C(1)–Co(3)–Co(1)	49.3 (2)
C(1)–Co(3)–Co(2)	49.5 (2)
C(1)–Co(1)–S(1)	136.6 (2)
C(1)–Co(2)–S(2)	136.8 (2)
C(1)–Co(3)–S(3)	136.2 (2)
C(11)–Co(1)–Co(2)	150.2 (2)
C(12)–Co(1)–Co(2)	103.1 (3)
C(11)–Co(1)–Co(3)	93.3 (2)
C(12)–Co(1)–Co(3)	153.4 (2)
C(21)–Co(2)–Co(1)	93.1 (3)
C(22)–Co(2)–Co(1)	149.5 (3)
C(21)–Co(2)–Co(3)	151.5 (3)
C(22)–Co(2)–Co(3)	100.6 (3)
C(31)–Co(3)–Co(1)	100.7 (3)
C(32)–Co(3)–Co(1)	152.5 (3)
C(31)–Co(3)–Co(2)	151.8 (3)
C(32)–Co(3)–Co(2)	94.9 (3)
C(11)–Co(1)–C(1)	104.0 (3)
C(12)–Co(1)–C(1)	103.6 (3)
C(21)–Co(2)–C(1)	106.7 (3)
C(22)–Co(2)–C(1)	100.4 (4)
C(31)–Co(3)–C(1)	102.6 (4)
C(32)–Co(3)–C(1)	106.8 (4)
C(11)–Co(1)–S(1)	107.9 (2)
C(12)–Co(1)–S(1)	101.5 (3)
C(21)–Co(2)–S(2)	103.6 (3)
C(22)–Co(2)–S(2)	104.0 (3)
C(31)–Co(3)–S(3)	101.2 (3)
C(32)–Co(3)–S(3)	105.9 (3)
C(12)–Co(1)–C(11)	96.0 (3)
C(21)–Co(2)–C(22)	99.6 (5)
C(31)–Co(3)–C(32)	97.7 (4)
O(11)–C(11)–Co(1)	174.3 (7)
O(12)–C(12)–Co(1)	174.4 (8)
O(21)–C(21)–Co(2)	178.7 (9)
O(22)–C(22)–Co(2)	174.3 (11)
O(31)–C(31)–Co(3)	174.1 (10)
O(32)–C(32)–Co(3)	175.7 (9)
C(110)–S(1)–Co(1)	114.2 (3)
C(120)–S(2)–Co(2)	112.7 (3)
C(130)–S(3)–Co(3)	114.3 (4)
C(140)–S(1)–Co(1)	103.8 (3)
C(140)–S(2)–Co(2)	103.6 (2)
C(140)–S(3)–Co(3)	103.9 (2)
C(110)–S(1)–C(140)	100.6 (4)
C(120)–S(2)–C(140)	100.4 (4)
C(130)–S(3)–C(140)	101.4 (4)
S(1)–C(140)–S(2)	107.5 (3)

Table 4 (continued)

S(3)–C(140)–S(1)	106.6 (4)
S(3)–C(140)–S(2)	108.1 (4)
C(2)–C(1)–Co(1)	131.7 (5)
C(2)–C(1)–Co(2)	131.0 (5)
C(2)–C(1)–Co(3)	131.7 (5)
C(3)–C(2)–C(1)	123.6 (7)
C(2)–C(3)–C(4)	121.8 (9)
C(5)–C(4)–C(3)	120.6 (9)
C(4)–C(5)–C(6)	119.5 (8)
C(5)–C(6)–C(7)	120.4 (8)
C(6)–C(7)–C(2)	121.3 (8)
C(7)–C(2)–C(1)	120.1 (6)
C(3)–C(2)–C(7)	116.4 (7)

phosphorus ligands are slightly longer. For example in $\text{Co}_3(\text{CO})_6(\mu\text{-CPh})[\text{CH}(\text{PPh})_3]$, the Co–Co bond averages 248.4 pm and the Co–C_{ap} bond 190.7 pm [17]. Balavoine et al. explained that the lengthening in metal–metal distances may be caused by an increase in electron density in the σ^* -antibonding orbital when carbonyl groups are replaced by poorer π acceptor phosphorus ligands [12]. With thioether ligands no lengthening occurs in metal–metal bonds.

IR spectra show the symmetry of these structures. The IR-spectrum of the parent cluster has five bands in the terminal carbonyl region, while the trisubstituted derivatives have three bands. The ¹H NMR spectrum of the parent cluster shows the phenyl proton signals as a multiplet at 7.13–7.63 ppm, and the derivatives have the phenyl signals in the same region.

Dimethylsulfide reacts with $\text{Co}_3(\text{CO})_9(\mu\text{-CPh})$ under the same reaction conditions, but the attachment is reversible and the products quickly decompose to the starting compounds unless excess ligand is present. The products do not precipitate in heptane, unlike the derivatives with 1,3,5-trithiacyclohexane and tris(thiomethyl)methane. According to IR characterization, mono- and disubstituted products are formed during the reaction, while the pure trisubstituted product is too unstable to allow purification. The mono- and disubstituted products have similar IR spectra except that the bands of the monodentate compound are at higher wavenumbers. The trisubstituted product did not crystallize even in excess of the ligand. We presume that the tridentate sulfur ligands stabilize the cluster structure enabling the crystallization.

3. Conclusion

1,3,5-Trithiacyclohexane and tris(thiomethyl)methane coordinate easily with $\text{Co}_3(\text{CO})_9(\mu\text{-CPh})$ as tridentate ligand. The aliphatic sulfur compound SMe_2 forms a trisubstituted derivative, but the product is unstable unlike the corresponding tridentate compounds.

4. Experimental

4.1. General comments

The reactions and manipulations of the reagents were carried out under nitrogen with deoxygenated solvents. $\text{Co}_3(\text{CO})_9(\mu\text{-CPh})$ was prepared by a published method [25]. Trithiacyclohexane, tris(thiomethyl)methane and dimethylsulfide were obtained from commercial sources (Aldrich).

FT-IR spectra were recorded on a Nicolet 750 spectrometer in appropriate solvents. The ^1H NMR spectra were recorded on a Bruker AM-250 spectrometer in CDCl_3 with Me_4Si as reference.

4.2. Synthesis of $\text{Co}_3(\text{CO})_6(\mu\text{-CPh})(\text{S}_3\text{C}_3\text{H}_6)$ (1)

$\text{Co}_3(\text{CO})_9(\mu\text{-CPh})$ (72 mg, 0.14 mmol) and trithiacyclohexane (34 mg, 0.25 mmol) were dissolved in 30 ml of heptane. The mixture was refluxed for 30 min and the product was formed almost quantitatively as a brown precipitate while the solution turned clear. The solution was filtered while hot. The precipitate was washed twice with heptane (10 ml). Crystallization from CH_2Cl_2

gave black needle like crystals. The crystals contain CH_2Cl_2 solvent, which upon escape from the crystals causes collapse of the structure. For the purposes of crystallographic determination the crystal was accordingly sealed in a quartz capillary in the presence of the solvent vapour. The sample for elemental analyses was kept in air for several hours to ensure that all solvent was removed from the sample. ^1H NMR: 3.6 and 5.6 ppm (CH_2 , d, $J_{\text{H-H}} = 14$ Hz), 7.2 ppm (Ph, m). IR(CH_2Cl_2): 2034 w, 1996 vs, 1960 w cm^{-1} . Found: C, 33.54%; H, 1.93%; Calculated for $\text{Co}_3\text{S}_3\text{O}_6\text{C}_{16}\text{H}_{11}$ C, 33.58%; H, 1.94%.

4.3. Synthesis of $\text{Co}_3(\text{CO})_6(\mu\text{-CPh})(\text{CH}(\text{SMe})_3)$ (2)

A mixture of $\text{Co}_3(\text{CO})_9(\mu\text{-CPh})$ (100 mg, 0.19 mmol) and $\text{CH}(\text{SMe})_3$ (100 μl , 0.75 mmol) was refluxed in 40 ml of heptane for 30 min. The black product precipitated quantitatively. The solution was filtered at room temperature and the precipitate was washed twice with heptane. IR (CH_2Cl_2): 2031 vw, 1994 vs, 1955 vw. ^1H NMR 2.5 ppm (CH_3 , s), 7.3 ppm (Ph, m) Found: C, 35.02%; H, 2.59%; Calculated for $\text{Co}_3\text{S}_3\text{O}_6\text{C}_{17}\text{H}_{15}$ C, 34.71%; H, 2.57%.

Table 5

Crystal data and collection parameters for $\text{Co}_3(\text{CO})_6(\mu\text{-CPh})(\text{trithiacyclohexane})$ (1) and $\text{Co}_3(\text{CO})_6(\mu\text{-CPh})(\text{CH}(\text{SMe})_3)$ (2)

	1	2
Formula	$\text{Co}_3\text{S}_3\text{C}_{16}\text{O}_6\text{H}_{11}$	$\text{Co}_3\text{S}_3\text{C}_{17}\text{O}_6\text{H}_{15}$
Formula weight (g mol^{-1})	572.22	588.26
Colour, habit	black	black
Crystal size (mm)	$0.1 \times 0.1 \times 0.7$	$0.2 \times 0.3 \times 0.5$
Crystal system	triclinic	orthorhombic
Space group	P-1	$\text{P}2_12_12_1$
a (Å)	8.417 (2)	9.212 (2)
b (Å)	15.749 (3)	15.265 (3)
c (Å)	16.926 (3)	16.066 (3)
α (°)	111.51 (3)	90
β (°)	100.86 (3)	90
λ (°)	97.86 (3)	90
V (Å ³)	1997.3 (9)	2259.2 (8)
Z	4	4
μ (mm^{-1})	2.81	2.48
Calculated density (g cm^{-3})	1.903	1.729
Number of centering reflections	34	30
Centering 2θ (°)	5–23	15–25
Scan range 2θ (°)	4–45	4–45
Scan speed (° min^{-1})	3–30	3–30
h, k, l range	$0 - + 10, - 17 - + 17, - 19 - + 19$	$0 - 10, 0 - 18, 0 - 19$
Number of unique reflections	3090	2229
Number of observed data ($F > 4\sigma(F)$)	1487	1911
Number of parameters	421	262
R	0.0614	0.0396
R_w	0.1695	0.0994
Electron density residuals, max and min ($\text{e}\text{Å}^{-3}$)	0.50; -0.94	0.74; -0.50

$$w = 1/[\sigma^2(F_o^2) + (0.1000 \times p)^2 + 0.00 \times p]$$

$$p = [\max(F_o^{2.0}) + 2 \times F_c^2]/3.$$

4.4. Synthesis of $\text{Co}_3(\text{CO})_6(\mu\text{-CPh})(\text{SMe}_2)_3$ (**3**)

The compound SMe_2 (1 ml, 13.6 mmol) was added to a solution of $\text{Co}_3(\text{CO})_9(\mu\text{-CPh})$ (100 mg, 0.19 mmol) in heptane (40 ml). The solution was refluxed for 2 h. A small amount of insoluble precipitate was formed during the reaction as a result of cluster breakdown. According to IR spectral analysis the solution contained mono-, di- and trisubstituted species. Chromatographic separation on silica also showed several fractions and immediately measured IR spectra of fraction 3 shows the same peaks as **1** and **2**, but after a short time the IR runs showed only parent cluster in all fractions. IR: 2033 vw, 1995 vs, 1957 vw cm^{-1} .

4.5. X-ray crystallography

Data were collected on a Nicolet R3m diffractometer using $\text{Mo-K}\alpha$ radiation ($\lambda = 71.073$ pm). Intensities were corrected for background, polarization and Lorentz factors, profile fitting was applied for both structures. Table 5 presents further crystallographic data. The structures were solved by direct methods using the SHELX 86 program [26] and subsequent least squares refinement by the SHELXL93 program [27]. Anisotropic refinement was carried out for all non-hydrogen atoms. Methyl and phenyl protons were placed in idealized positions with C–H distance of 96 pm and isotropic temperature factors of 0.08 \AA^2 . Phenyls were refined as rigid groups with C–C = 139.5 pm. The test of enantiomorph was made for **1** and the best structure was selected. Absorption correction did not make any improvement to the structures unlike profile fitting.

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