Chemistry of the Paramagnetic $Co_3(CO)_9(\mu_3\text{-}S)$ Cluster. Rational Synthesis of $Co_3(CO)_7(\mu\text{-}X)(\mu_3\text{-}S)$ Complexes

Sándor Vastag,[†] Giuliana Gervasio,*,[‡] Domenica Marabello,[‡]
Gábor Szalontai,[§] and László Markó*,[‡,∥]

Institute of Organic Chemistry and Central Laboratory, University of Veszprém, and Research Group for Petrochemistry of the Hungarian Academy of Sciences, P.O. Box 158, H-8201, Veszprém, Hungary, and Dipartimento di Chimica IFM, Università di Torino, I-10125 Torino, Italy

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The paramagnetic $Co_3(CO)_9(\mu_3{-}S)$ cluster (**1**) reacts with organic compounds containing S−H, S−S, or P−H bonds to give diamagnetic $Co_3(CO)_7(\mu\text{-}X)(\mu_3{-}S)$ (μ-X = (μ-L, μ-(1,2-η)-L, and μ-(1,3-η)-L) complexes. The reaction was used to prepare the derivatives with μ-L = SR (**2a**−**h**; R = Et, *t*-Bu, CH_2Ph, allyl, Ph, C_6F_5, 2-naphthyl, CH_2CH_2OH) and PPh_2 (**7**), μ-(1,2-η)-L = $P(S)Ph_2$ (**8**), and μ-(1,3-η)-L = S_2CR (R = SMe (**4**), OMe (**5**), Ph (**6**)). The reaction results in an increase of the oxidation state of cobalt and may be therefore called an oxidative substitution. It is the first successful and rational way to prepare derivatives of $Co_3(CO)_9(\mu_3\text{-}S)$, a fundamental cluster molecule described in 1961. The crystal structures of the triphenylphosphine-substituted derivative of **2b**, $Co_3(CO)_4(PPh_3)_3(\mu\text{-}S\text{-}t\text{-}Bu)(\mu_3\text{-}S)$ (**3**), and of **4**, **6**, and **8** were determined. A new, high-yield synthesis of **1** is described.

Introduction

The chemistry of the paramagnetic $Co_3(CO)_9(\mu_3\text{-}S)$ cluster (**1**),[1] first prepared 37 years ago, is rather poorly developed. The most obvious reactions in metal carbonyl chemistry, the substitution of the CO ligands by phosphines[2] or isonitriles,[3] result in decomposition. This may be due to the fact that the “surplus” electron of **1** occupies a metal−metal antibonding orbital, and if CO is replaced by a ligand which is a poorer π-acceptor than CO, the effect of this antibonding orbital in decreasing the stability of the cluster becomes more pronounced. Although the removal of one electron from **1** by oxidation results in the electron-precise $[\mathbf{1}]^+$ cation,[4] this complex also proved to be very labile and could be identified only in solution. Attempts to prepare $Co_3(CO)_9(\mu_3\text{-}S)M(CO)_5$ (M = Cr, Mo, W) type complexes failed as well.[2]

Until now only a few reactions of **1** which lead to stable molecules have been described: (a) with S_8 to give the hexanuclear $[Co_3(CO)_7(\mu_3\text{-}S)]_2S_2$,[5] (b) with $PhCH_2SH$ etc. and the corresponding disulfides to give compounds described as “$Co_3(CO)_6(\mu_3\text{-}SR)(\mu_3\text{-}S)$” (R = Et, CH_2Ph) but not unequivocally characterized,[6] (c) with $Na_2[Fe(CO)_4]$ to give $Co_2Fe(CO)_9(\mu_3\text{-}S)$,[7] (d) with $CpW(CO)_3AsMe_2$ to give the unusual tetranuclear cluster $CpW(CO)_3Co_2(\mu_3\text{-}S)(\mu\text{-}AsMe_2)_2Co(CO)_3$,[8] and (e) with Me_3NO and PhC_2H to give $Co_4(CO)_8(\mu\text{-}CO)_2(\mu_4\text{-}S)$ (μ_4-(1,2-η)-HC_2Ph).[9] These reactions, however, appear to have nothing in common, and in addition those mentioned under (d) and (e) involve very complex and stoichiometrically unclear transformations.

This behavior of **1** contrasts sharply with that of the closely related diamagnetic $Co_2Fe(CO)_9(\mu_3\text{-}S)$,[10] which has a rich chemistry, including substitution of the CO ligands by phosphines[11] and isonitriles,[3] reversible oxidation and reduction,[4,12] transformations through metal exchange and addition reactions into other trinuclear[7,8,13] (including chiral) and tetranuclear[14] clusters, and use as a ligand with sulfur as the donor atom.[15]

At the same time a large number of carbonyl clusters are known which contain the Co_3S pyramid as a building block and can be regarded as substituted derivatives of **1** with the general formula $Co_3(CO)_7(\mu$-

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[†] Institute of Organic Chemistry, University of Veszprém.

[‡] Università di Torino.

[§] Central Laboratory, University of Veszprém.

[∥] Research Group for Petrochemistry of the Hungarian Academy of Sciences.

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X)(μ_3-S). All of these complexes have been isolated, however, from complex reaction mixtures obtained by reacting $Co_2(CO)_8$ with different sulfur compounds. They are formed in obviously very complicated reactions, and the reaction paths leading to these compounds are not clear at all. The bridging ligands X in these complexes vary widely and include (1,2-η)-SCSC$Co_3(CO)_9$,[16] (1,3-η)-$S_2CCCo_3(CO)_9$,[17] (1,2-η)-S(Me)-NC_6H_{11},[18] (1,2-η)-SCNMe$_2$,[19] (1,3-η)-$S_2CCo_3(CO)_8$,[20] (1,3-η)-SC(R)NH (R = Me, Ph, *p*-MeOPh),[21] (1,3-η)-S_2COMe,[22] η-PPh$_2$,[23] (1,2-η)-SPMe$_2$,[24] and (1,2,3-η)-(PMe$_2$)$_2$Co-(CO)$_2$.[24] Earlier experiments to prepare at least some of these complexes by starting from **1** failed.[25]

All the above-mentioned complexes containing the $Co_3(CO)_7(\mu\text{-}X)(\mu_3\text{-}S)$ framework proved to be rather stable, and this suggests that a large number of more such compounds may exist. The lack of a rational way to synthesize these clusters, however, prevented a systematic exploration of this field of cobalt carbonyl cluster chemistry. In this paper we now report about a simple reaction which allows the transformation of paramagnetic **1** into its diamagnetic substituted derivatives $Co_3(CO)_7(\mu\text{-}X)(\mu_3\text{-}S)$.

Results and Discussion

Synthesis of $Co_3(CO)_7(\mu\text{-}X)(\mu_3\text{-}S)$ Complexes. The reaction of **1** with thiols and disulfides, which according to an earlier report[6] yields "$Co_3(CO)_6(\mu_3\text{-}SR)(\mu_3\text{-}S)$" type complexes (R = Et, CH$_2$Ph), was chosen as a starting point to find a broadly applicable reaction for the synthesis of substituted derivatives of $Co_3(CO)_9(\mu_3\text{-}S)$. The first object of our work was to prepare a sufficiently stable representative of the $Co_3(CO)_6(\mu_3\text{-}SR)(\mu_3\text{-}S)$ type complexes in order to determine its structure unequivocally by X-ray crystallography.

When **1** was reacted in hexane solution with several different thiols which do not contain other functional groups capable of interacting with cobalt carbonyls, it was found that all of these yield as main products carbonyl complexes having very similar IR spectra in the ν_{CO} region and belong therefore to the same class of compounds. These spectra were completely analogous to those of the previously described $Co_3(CO)_6(\mu_3\text{-}SR)(\mu_3\text{-}S)$ (R = Et, PhCH$_2$) derivatives. Table 1 compiles the IR spectroscopic data of the main products present in the hexane solutions obtained in these reactions.

Among the thiols tested, *t*-BuSH gave the cleanest reaction, and further efforts were concentrated therefore on this thiol and (*t*-BuS)$_2$. When **1** was reacted in hexane solution under Ar with a small excess of *t*-BuSH or (*t*-BuS)$_2$, the starting complex was completely transformed within a few hours and the IR spectra of both solutions showed the bands characteristic of the desired complex. The compound formed was, however, found to be an oil, and therefore it was transformed by excess PPh$_3$ into a substituted derivative which was characterized by X-ray crystallography (vide infra) as $Co_3(CO)_4(PPh_3)_3(\mu\text{-}SBu^t)(\mu_3\text{-}S)$ (**3**).

Table 1. Infrared Spectroscopic Data for $Co_3(CO)_7(\mu\text{-}SR)(\mu_3\text{-}S)$ (Type 2) Complexes in the ν_{CO} Region, in Hexane Solution (cm^{-1})

complex	R	ν_1 (m)	ν_1 (vs)	ν_1 (s)	ν_1 (vw)	ref
2a	Et	2087	2045	2026	2000	6
2b	*t*-Bu	2088	2045	2024	2007	this work
2c	PhCH$_2$	2087	2046	2026	2000	6
2d	allyl	2088	2048	2026	2001	this work
2e	Ph	2090	2047	2028	2010	this work
2f	C$_6$F$_5$	2095	2056	2037	2013	this work
2g	2-naphthyl	2088	2046	2027	2010	this work
2h	HOCH$_2$CH$_2$	2086	2048	2026	2011	this work

This result suggested that the correct formulation of the $Co_3(CO)_6(\mu_3\text{-}SR)(\mu_3\text{-}S)$ complexes is $Co_3(CO)_7(\mu\text{-}SR)(\mu_3\text{-}S)$ (**2**) and that they are formed according to reactions 1 or 2 from **1**.

The evolution of H$_2$ in reaction 1 could be proven by GLC.

$$\underset{\mathbf{1}}{Co_3(CO)_9(\mu_3\text{-}S)} + RSH \rightarrow \underset{\mathbf{2}}{Co_3(CO)_7(\mu\text{-}SR)(\mu_3\text{-}S)} + 2CO + {}^1/_2H_2 \quad (1)$$

$$\underset{\mathbf{1}}{Co_3(CO)_9(\mu_3\text{-}S)} + {}^1/_2(RS)_2 \rightarrow \underset{\mathbf{2}}{Co_3(CO)_7(\mu\text{-}SR)(\mu_3\text{-}S)} + 2CO \quad (2)$$

The evidence for the formation of a complex containing the $Co_3(CO)_7(\mu\text{-}X)(\mu_3\text{-}S)$ framework from $Co_3(CO)_9(\mu_3\text{-}S)$ in a stoichiometrically clean substitution reaction was, however, still not unequivocal. One might argue that the primary product of the reaction between $Co_3(CO)_9(\mu_3\text{-}S)$ and RSH was $Co_3(CO)_6(\mu_3\text{-}SR)(\mu_3\text{-}S)$ and the μ_3-SR ligand was only later transformed into the μ-SR ligand by triphenylphosphine during the formation of **3**.

To prove the formation of $Co_3(CO)_7(\mu\text{-}X)(\mu_3\text{-}S)$ type complexes from $Co_3(CO)_9(\mu_3\text{-}S)$ by reactions such as (1) and (2), a more direct evidence had to be found. When **1** was reacted with bis(methylthio(thiocarbonyl)) disulfide, (MeSCS$_2$)$_2$, the expected $Co_3(CO)_7(\mu\text{-}1,3\text{-}\eta)\text{-}S_2CSMe)(\mu_3\text{-}S)$ (**4**) could be obtained in crystalline form and was characterized by X-ray crystallography (vide infra). The formation of **4** from **1** is described by reaction 3.

$$\mathbf{1} + {}^1/_2(MeSCS_2)_2 \rightarrow \mathbf{4} + 2CO \quad (3)$$

Reactions 1−3 suggest that the reaction of **1** with compounds containing a S−H or a S−S bond (see also the reaction with S$_8$[5]) may be quite general. To further support this assumption, **1** was reacted with dithiocarbonic acid methyl ester, MeOCS$_2$H (liberated in situ from MeOCS$_2$K by acetic acid), and dithiobenzoic acid,

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$PhCS_2H$. In both cases the expected $Co_3(CO)_7(\mu\text{-X})(\mu_3\text{-S})$ type complexes, $Co_3(CO)_7(\mu\text{-}(1,3\text{-}\eta)\text{-}S_2COMe)(\mu_3\text{-S})$[22] (**5**) and $Co_3(CO)_7(\mu\text{-}(1,3\text{-}\eta)\text{-}S_2CPh)(\mu_3\text{-S})$ (**6**), respectively, were the only metal carbonyl derivatives formed as shown by the IR spectra of the reaction mixtures (eqs 4 and 5).

$$\mathbf{1} + MeOCS_2H \rightarrow \mathbf{5} + 2CO + {}^1/_2 \qquad (4)$$

$$\mathbf{1} + PhCS_2H \rightarrow \mathbf{6} + 2CO + {}^1/_2 \qquad (5)$$

Complexes **5** and **6** could be isolated in solid form. Complex **5** has been already described by us earlier[22] and was identified by the identity of its IR spectrum between 400 and 2000 cm^{-1} with the published one. As expected, the yield obtained in reaction 5 (17%) was better than that obtained by the previous method starting from $CoCl_2{\cdot}6H_2O$ (11%, based on Co)[22] and the isolation of **5** did not require chromatographic purification. The structure of **6** was determined by X-ray crystallography (vide infra). The molecular hydrogen evolved in these reactions was detected by GLC.

The successful reactions with compounds containing an SH group prompted us to investigate the possibility of an analogous reaction with compounds containing a P−H bond. In this way we hoped to synthesize $Co_3(CO)_7(\mu\text{-X})(\mu_3\text{-S})$ type complexes having a phosphorus atom as donor in the bridging ligand X, as in the already known $Co_3(CO)_7(\mu\text{-}PPh_2)(\mu_3\text{-S})$[23] and $Co_3(CO)_7(\mu\text{-}1,2\text{-}({}^2\text{-}SPMe_2)(\mu_3\text{-S})$.[24]

In fact, when **1** was reacted with $HPPh_2$ and $HP(S)Ph_2$, the complexes $Co_3(CO)_7(\mu\text{-}PPh_2)(\mu_3\text{-S})$ (**7**) and $Co_3(CO)_7(\mu\text{-}(1,2\text{-}\eta)\text{-}SPPh_2)(\mu_3\text{-S})$ (**8**), respectively, could be obtained in clean reactions. The identity of **7** obtained in this way with that obtained from $Co_2(CO)_8$ and $PhSPPh_2$[23] was shown by its IR and NMR spectrum; the structure of the new complex **8** was determined by X-ray crystallography (vide infra) and found to be similar to that of the dimethyl analogue.[24] Hydrogen was detected in the gases evolved by GLC. Accordingly, the stoichiometries of these reactions (eqs 6 and 7) are like those observed with compounds having S−H bonds that have been discussed above (eqs 4 and 5).

$$\mathbf{1} + HPPh_2 \rightarrow \mathbf{7} + 2CO + {}^1/_2H_2 \qquad (6)$$

$$\mathbf{1} + HP(S)Ph_2 \rightarrow \mathbf{8} + 2CO + {}^1/_2H_2 \qquad (7)$$

The analogy between sulfur and phosphorus compounds in their reactivity against **1** was found to be incomplete. In contrast to compounds with S−S bonds, those having P−P bonds did not react under the conditions used in our experiments.

Reactions 1−7 may be regarded as specific examples of a general reaction of **1** which eliminates the surplus electron of the paramagnetic cluster and transforms it into an electron-precise derivative by substituting two CO ligands with a three-electron-donor ligand. Since in this process the average oxidation state of the three cobalt atoms is increased from +0.33 to +1, it may be called an "oxidative substitution".

The mechanism of these reactions is unclear at present. Experiments to determine the kinetics of the reaction with *t*-BuSH and $(t\text{-BuS})_2$ were not successful: the reaction rates were found to be poorly reproducible and the only unambiguous conclusion was that the reaction is strongly inhibited by CO.

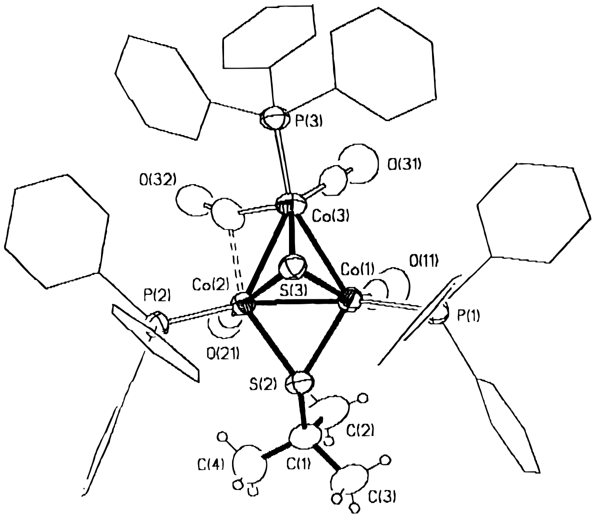

Figure 1. ORTEP plot of $Co_3(CO)_4(PPh_3)_3(\mu\text{-S-}t\text{-Bu})(\mu_3\text{-S})$ (**3**), with atom-labeling scheme.

Preparation of 1. Three methods have been described for the preparation of **1**: from $Co_2(CO)_8$ and elemental sulfur (yield 12%),[1a] from $HCo(CO)_4$ and Na_2SO_3 (yield 18%),[5a] and from $Co_2(CO)_8$ and PhSH (yield 30%).[27] We have now found that **1** can be conveniently prepared in over 60% yield from $Co_2(CO)_8$ and ethylene sulfide under CO in hexane solution at room temperature. Ethylene is evolved in the reaction (eq 8).

$$Co_2(CO)_8 + C_2H_4S \rightarrow \mathbf{1} + C_2H_4 \qquad (8)$$

This desulfurization reaction seems to be quite general. In a qualitative experiment the reaction between 2-phenylthiirane and $Co_2(CO)_8$ was tested and **1** and styrene were identified as the only products. The observation that $Co_2(CO)_8$ is inert against 2-phenylthiirane at room temperature under 27 bar of CO pressure[28] suggests that carbon monoxide strongly inhibits the reaction.

It should be further mentioned that thiiranes and alkyl halides can be carbonylated to β-mercapto acids with $Co_2(CO)_8$ as catalyst in the presence of bases under phase transfer conditions.[29] Due to the very diffferent reaction conditions, however, it is not probable that **1** plays any role in this latter reaction.

Episulfides have been already used for the preparation of $Fe_3(CO)_9(\mu_3\text{-S})_2$ from $Fe_3(CO)_{12}$.[30]

Crystal Structures of Complexes 3, 4, 6, and 8. Figures 1−4 show the molecules of the complexes $Co_3(CO)_4(PPh_3)_3(\mu\text{-S-}t\text{-Bu})(\mu_3\text{-S})$ (**3**), $Co_3(CO)_7(\mu\text{-}(1,3\text{-}\eta)\text{-}S_2CSMe)(\mu_3\text{-S})$ (**4**), $Co_3(CO)_7(\mu\text{-}(1,3\text{-}\eta)\text{-}S_2CPh)(\mu_3\text{-S})$ (**6**), and $Co_3(CO)_7(\mu\text{-}(1,2\text{-}\eta)\text{-}SPPh_2)(\mu_3\text{-S})$ (**8**), respectively. The most relevant distances and angles are listed in Tables 2−5.

The four complexes have a common Co_3S core with a ligand bridging a Co−Co edge and forming three-

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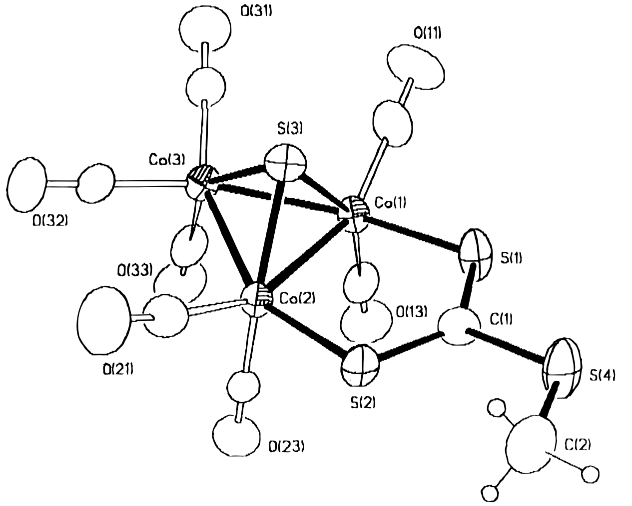

Figure 2. ORTEP plot of $Co_3(CO)_7(\mu\text{-}(1,3\text{-}\eta)\text{-}S_2CSMe)(\mu_3\text{-}S)$ (**4**), with atom-labeling scheme.

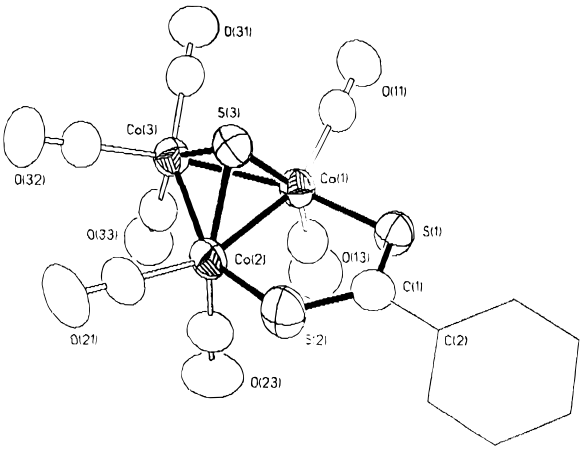

Figure 3. ORTEP plot of $Co_3(CO)_7(\mu\text{-}(1,3\text{-}\eta)\text{-}S_2CPh)(\mu_3\text{-}S)$ (**6**), with atom-labeling scheme.

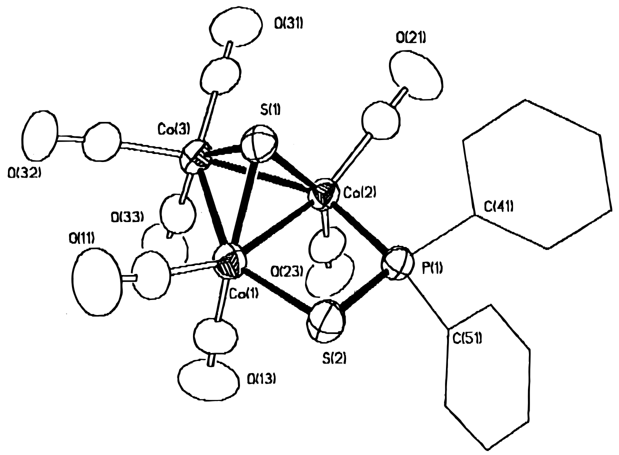

Figure 4. ORTEP plot of $Co_3(CO)_7(\mu\text{-}(1,2\text{-}\eta)\text{-}SPPh_2)(\mu_3\text{-}S)$ (**8**), with atom-labeling scheme.

(complex **3**), four- (complex **8**), or five-membered (complexes **4** and **6**) equatorial rings. The structural features of these 48-electron cores are summarized in Table 6 and compared with the core of $Co_3(CO)_9(\mu_3\text{-}S)$ (49 electrons).

As expected, $Co_3(CO)_9(\mu_3\text{-}S)$ has the biggest cluster; among the other complexes, however, complex **3** shows the greatest average Co−Co and Co−S_{ap} distances, even if two Co−Co bonds are bridged by ligands (S-*t*-Bu and asymmetric CO) and thus a shortening on these bonds is acting. The behavior of complex **3** may be attributed either to the steric hindrance or to the electronic effect of the three PPh_3 ligands; in fact, the PPh_3 ligand is a better σ-donor and a worse π-acceptor than CO and therefore the substitution has a swelling effect on the cluster. The same effect is detectable in the bisubstituted complex $Co_3(CO)_5(PPh_3)_2(\mu_3\text{-}S)(SPMe_2)$[24] (average Co−Co = 2.540(9) Å and average Co−S_{ap} = 2.172(8) Å) and in the monosubstituted $Co_3(CO)_6(PPh_3)(\mu_3\text{-}S)(S_2COSMe)$ (average Co−Co = 2.520(1) Å and average Co−S_{ap} = 2.160(1) Å).[20]

The data of Table 6 show that the least influenced parameter is the Co−S distance as compared to the angle around S_{ap} and to the distance of S_{ap} from the Co_3 plane. Furthermore, the Co−Co bond bridged by the

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 3

Co(1)−Co(2)	2.495(1)	Co(3)−P(3)	2.202(2)
Co(1)−Co(3)	2.603(1)	Co(3)−C(31)	1.746(6)
Co(1)−S(1)	2.183(2)	Co(3)−C(32)	1.779(7)
Co(1)−S(2)	2.254(2)	S(2)−C(1)	1.863(5)
Co(1)−P(1)	2.214(2)	P−C_{av}	1.830(5)
Co(1)−C(11)	1.745(6)	C(1)−C(2)	1.509(8)
Co(2)−Co(3)	2.565(1)	C(1)−C(3)	1.520(8)
Co(2)−S(1)	2.241(2)	C(1)−C(4)	1.498(9)
Co(2)−S(2)	2.280(2)	C(11)−O(11)	1.156(7)
Co(2)−P(2)	2.257(2)	C(21)−O(21)	1.145(7)
Co(2)−C(21)	1.769(5)	C(31)−O(31)	1.153(8)
Co(2)−C(32)	2.285(6)	C(32)−O(32)	1.164(8)
Co(3)−S(1)	2.151(2)		
Co(2)−Co(1)-Co(3)	60.4(1)	S(2)−Co(2)-C(32)	153.3(2)
Co(2)−Co(1)-S(2)	57.1(1)	Co(1)−Co(3)-Co(2)	57.7(1)
Co(3)−Co(1)-S(2)	116.6(1)	Co(2)−Co(3)-C(32)	60.3(2)
S(1)−Co(1)-S(2)	84.5(1)	Co(1)−S(2)-Co(2)	66.8(1)
S(2)−Co(1)-P(1)	107.4(1)	Co(1)−S(2)-C(1)	120.2(2)
S(2)−Co(1)-C(11)	109.5(2)	Co(2)−S(2)-C(1)	120.1(2)
Co(1)−Co(2)-Co(3)	61.9(1)	Co−P−C_{av}	115.8(2)
Co(1)−Co(2)-S(2)	56.1(1)	Co(1)−C(11)-O(11)	177.4(5)
Co(3)−Co(2)-S(2)	117.1(1)	Co(2)−C(21)-O(21)	175.0(5)
S(1)−Co(2)-S(2)	82.5(1)	Co(3)−C(31)-O(31)	177.2(5)
S(2)−Co(2)-P(2)	105.4(1)	Co(2)−C(32)-Co(3)	77.2(2)
S(2)−Co(2)-C(21)	97.7(2)	Co(2)−C(32)-O(32)	128.8(5)
Co(3)−Co(2)-C(32)	42.6(2)	Co(3)−C(32)-O(32)	153.8(5)

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for 4

Co(1)−Co(2)	2.486(2)	Co(3)−C(32)	1.819(9)
Co(1)−Co(3)	2.524(2)	Co(3)−C(33)	1.826(11)
Co(1)−S(1)	2.258(3)	S(1)−C(1)	1.685(9)
Co(1)−S(3)	2.154(3)	S(2)−C(1)	1.680(8)
Co(1)−C(11)	1.815(11)	S(4)−C(1)	1.748(9)
Co(1)−C(13)	1.824(11)	S(4)−C(2)	1.774(11)
Co(2)−Co(3)	2.510(2)	C(11)−O(11)	1.134(14)
Co(2)−S(2)	2.248(3)	C(13)−O(13)	1.089(14)
Co(2)−S(3)	2.152(3)	C(21)−O(21)	1.122(14)
Co(2)−C(21)	1.812(10)	C(23)−O(23)	1.110(13)
Co(2)−C(23)	1.830(10)	C(31)−O(31)	1.138(17)
Co(3)−S(3)	2.173(2)	C(32)−O(32)	1.139(12)
Co(3)−C(31)	1.773(12)	C(33)−O(33)	1.101(14)
Co(2)−Co(1)−Co(3)	60.1(1)	S(1)−C(1)-S(2)	127.7(5)
Co(2)−Co(1)−S(1)	96.2(1)	S(1)−C(1)-S(4)	112.6(5)
Co(1)−Co(2)−Co(3)	60.7(1)	S(2)−C(1)-S(4)	119.7(5)
Co(1)−Co(2)−S(2)	97.4(1)	Co(1)−C(11)-O(11)	177.3(11)
Co(1)−Co(3)−Co(2)	59.2(1)	Co(1)−C(13)-O(13)	179.1(9)
Co(1)−S(1)−C(1)	109.6(3)	Co(2)−C(21)-O(21)	175.1(11)
Co(2)−S(2)−C(1)	109.1(3)	Co(2)−C(23)-O(23)	179.2(10)
Co(1)−S(3)−Co(2)	70.5(1)	Co(3)−C(31)-O(31)	178.0(10)
Co(1)−S(3)−Co(3)	71.4(1)	Co(3)−C(32)-O(32)	179.1(9)
Co(2)−S(3)−Co(3)	70.9(1)	Co(3)−C(33)-O(33)	177.8(9)
C(1)−S(4)−C(2)	104.9		

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) for 6

	molecule A	molecule B		molecule A	molecule B
Co(1)−Co(2)	2.475(1)	2.472(1)	S(2)−C(1)	1.686(4)	1.672(4)
Co(1)−Co(3)	2.543(1)	2.512(1)	C(1)−C(2)	1.488(5)	1.490(6)
Co(1)−S(1)	2.248(1)	2.234(1)	C(2)−C(3)	1.397(6)	1.385(6)
Co(1)−S(3)	2.151(1)	2.152(1)	C(2)−C(7)	1.390(6)	1.388(6)
Co(1)−C(11)	1.814(4)	1.812(4)	C(3)−C(4)	1.382(7)	1.384(8)
Co(1)−C(13)	1.806(4)	1.806(4)	C(4)−C(5)	1.361(9)	1.368(8)
Co(2)−Co(3)	2.523(1)	2.527(1)	C(5)−C(6)	1.382(8)	1.364(8)
Co(2)−S(2)	2.238(1)	2.248(1)	C(6)−C(7)	1.380(7)	1.399(8)
Co(2)−S(3)	2.148(1)	2.158(1)	C(11)−O(11)	1.123(6)	1.132(5)
Co(2)−C(21)	1.794(4)	1.813(5)	C(13)−O(13)	1.117(5)	1.126(5)
Co(2)−C(23)	1.808(5)	1.791(4)	C(21)−O(21)	1.132(5)	1.123(6)
Co(3)−S(3)	2.164(1)	2.176(1)	C(23)−O(23)	1.126(6)	1.141(5)
Co(3)−C(31)	1.823(4)	1.814(4)	C(31)−O(31)	1.124(5)	1.136(5)
Co(3)−C(32)	1.812(5)	1.812(5)	C(32)−O(32)	1.130(6)	1.131(7)
Co(3)−C(33)	1.814(4)	1.801(5)	C(33)−O(33)	1.120(5)	1.142(6)
S(1)−C(1)	1.681(4)	1.686(3)			

	molecule A	molecule B		molecule A	molecule B
Co(2)−Co(1)-Co(3)	60.4(1)	60.9(1)	S(1)−C(1)-S(2)	125.2(2)	126.2(3)
Co(2)−Co(1)-S(1)	95.2(1)	96.9(1)	S(1)−C(1)-C(2)	117.2(3)	115.6(3)
S(1)−Co(1)-C(11)	97.5(1)	95.1(1)	S(2)−C(1)-C(2)	117.6(3)	118.2(3)
S(1)−Co(1)-C(13)	93.0(1)	96.1(1)	Co(1)−C(11)-O(11)	177.2(4)	177.8(4)
Co(1)−Co(2)-Co(3)	61.2(1)	60.3(1)	Co(1)−C(13)-O(13)	178.0(4)	179.0(4)
Co(1)−Co(2)-S(2)	97.5(1)	96.5(1)	Co(2)−C(21)-O(21)	178.4(4)	177.5(4)
S(2)−Co(2)-C(21)	95.5(1)	97.0(2)	Co(2)−C(23)-O(23)	178.3(5)	178.7(4)
S(2)−Co(2)-C(23)	96.3(2)	94.0(2)	Co(3)−C(31)-O(31)	178.8(4)	177.6(4)
Co(1)−Co(3)-Co(2)	58.5(1)	58.7(1)	Co(3)−C(32)-O(32)	178.8(4)	179.7(4)
Co(1)−S(1)-C(1)	111.4(1)	110.2(2)	Co(3)−C(33)-O(33)	177.8(4)	178.5(4)
Co(2)−S(2)-C(1)	109.7(1)	110.2(1)			

Table 5. Selected Bond Lengths (Å) and Bond Angles (deg) for 8

Co(1)−Co(2)	2.470(1)	Co(3)−C(31)	1.820(3)
Co(1)−Co(3)	2.533(1)	Co(3)−C(32)	1.811(3)
Co(1)−S(1)	2.155(1)	Co(3)−C(33)	1.805(3)
Co(1)−S(2)	2.312(1)	P(1)−S(2)	2.033(1)
Co(1)−C(11)	1.797(3)	C(11)−O(11)	1.126(4)
Co(1)−C(13)	1.798(3)	C(13)−O(13)	1.124(4)
Co(2)−Co(3)	2.522(1)	C(21)−O(21)	1.120(4)
Co(2)−P(1)	2.205(1)	C(23)−O(23)	1.133(3)
Co(2)−S(1)	2.157(1)	C(31)−O(31)	1.129(4)
Co(2)−C(21)	1.806(3)	C(32)−O(32)	1.131(3)
Co(2)−C(23)	1.786(2)	C(33)−O(33)	1.127(3)
Co(3)−S(1)	2.167(1)		
Co(2)−Co(1)-Co(3)	60.5(1)	Co(2)−P(1)-S(2)	103.2(1)
Co(2)−Co(1)-S(2)	88.0(1)	Co(1)−S(2)-P(1)	88.0(1)
S(2)−Co(1)-C(11)	98.0(1)	Co(1)−C(11)-O(11)	177.9(3)
S(2)−Co(1)-C(13)	95.8(1)	Co(1)−C(13)-O(13)	178.2(3)
Co(1)−Co(2)-Co(3)	61.0(1)	Co(2)−C(21)-O(21)	177.4(3)
Co(1)−Co(2)-P(1)	80.5(1)	Co(2)−C(23)-O(23)	179.5(2)
P(1)−Co(2)-C(21)	102.0(1)	Co(3)−C(31)-O(31)	177.3(3)
P(1)−Co(2)-C(23)	97.8(1)	Co(3)−C(32)-O(32)	177.0(2)
Co(1)−Co(3)-Co(2)	58.5(1)	Co(3)−C(33)-O(33)	177.7(2)

organic ligand is always shorter than the other two Co−Co bonds. The influences, however, of the three-, four- or five-membered rings on the Co$_3$S core are not systematic because the differences are of the same order of magnitude as the differences between two identical molecules in the same asymmetric unit (complex **6**).

The organic ligands substitute two equatorial CO's, forming roughly planar rings slightly tilted toward S$_{ap}$ (the dihedral angles with the Co$_3$ plane are 11° (complex **3**), 16° (complexes **4** and **6**), and 10° (complex **8**)); in Co$_3$(CO)$_9$(μ_3-S) the tilting angle of the CO$_{eq}$'s is 25°. The situation of the CO ligands is nearly the same for complexes **4**, **6**, and **8** with one axial CO on each cobalt atom and one (on Co(1) and Co(2)) or two equatorial CO's (on Co(3)). Complex **3**, however, shows a quite different scheme, owing to the great bulk of the PPh$_3$ ligand on Co(3) that pushes away an equatorial CO. This ligand thus becomes an asymmetrical bridge below the Co$_3$ plane halfway between an equatorial and an axial CO.

In complex **3** S(2) is an asymmetrical bridge with the longest C(2)−S(2) bond nearly trans (153°) to CO(32) and with the *t*-Bu group below the Co(1)Co(2)S(2) plane (anti with respect to S$_{ap}$). In complexes **4** and **6** the five-membered rings are roughly planar, including S(4) and C(2) for complex **4** (mean deviation 0.04 Å) and atom C(2) for complex **6** (mean deviation 0.06 and 0.02 Å); this planarity is in keeping with a π delocalization over the entire ligand with a more pronounced double-bond character on the C(1)−S(1) and C(1)−S(2) bonds (1.68 Å average).[31] The phenyl ring in complex **6** is not coplanar with the five-membered ring and forms angles of 20 and 38° for molecules A and B, respectively, showing the mobility of this part of the molecule (in the monoclinic form this angle is 56°). In complex **8** the four-membered ring has a mean deviation of 0.04 Å, the coordination around P is tetrahedral, and the P−S distance (2.033(1) Å) corresponds to an elongated double bond. The Co(1)−S(2) bond (2.312(1) Å) is longer than all the other Co−S distances of the other complexes.

Experimental Section

General Methods. All manipulations with air-sensitive compounds were carried out by the standard Schlenk techniques using deoxygenated, dry solvents and gases. Infrared spectra were recorded on a Specord IR 75 (Carl Zeiss, Germany) spectrometer and were calibrated with benzene

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Table 6. Selected Geometric Parameters of the Co_3S Core in Related Complexes

distances and angles	$Co_3(CO)_9S$	**3**	**4**	**6**		**8**
Co(1)−Co(2), Å		2.495(1)	2.486(2)	2.475(1)	2.472(1)	2.470(1)
Co(1)−Co(3), Å		2.603(1)	2.524(2)	2.543(1)	2.512(1)	2.533(1)
Co(2)−Co(3), Å		2.565(1)	2.510(2)	2.523(1)	2.527(1)	2.522(1)
$Co-Co_{av}$, Å	2.637(7)	2.554(1)	2.507(2)	2.514(1)	2.504(1)	2.508(1)
$Co(1)-S_{ap}$, Å		2.183(2)	2.154(3)	2.151(1)	2.152(1)	2.155(1)
$Co(2)-S_{ap}$, Å		2.241(2)	2.152(3)	2.148(1)	2.158(1)	2.157(1)
$Co(3)-S_{ap}$, Å		2.151(2)	2.173(2)	2.164(1)	2.176(1)	2.167(1)
$Co-S_{av}$, Å	2.14(1)	2.192(2)	2.160(3)	2.154(1)	2.162(1)	2.160(1)
$Co_3\cdots S_{ap}$ average	1.50	1.62	1.60	1.59	1.61	1.60
$Co-S_{ap}-Co$ average	76.1(3)	71.3(2)	70.9(1)	71.4(1)	70.8(1)	71.0(1)

(1959.6 cm^{-1}). ^{31}P NMR spectra were obtained on a Varian Unity 300 spectrometer; the spectra were referenced to 85% H_3PO_4. Gas chromatographic analyses were carried out on an HP 5890 chromatograph equipped with a Chrompack 5 Å Molsieve column and a TCD detector (for H_2) or with a Paraplot Q column and an FID detector (for C_2H_4).

Materials. Ethylene sulfide, and the thiols EtSH, $PhCH_2SH$, *t*-BuSH, $CH_2{=}CHCH_2SH$, $HOCH_2CH_2SH$, $C_6H_{11}SH$, PhSH, and 2-$C_{10}H_7SH$, and $(t\text{-BuS})_2$ were commercial products (Aldrich); $Co_2(CO)_8$,[32] Ph_2PH,[33] $Ph_2P(S)H$,[34] $PhCS_2H$,[35] $(MeCS_2)_2$,[36] and $MeOCS_2K$[37] were prepared according to literature methods.

Preparation of $Co_3(CO)_9(\mu_3\text{-}S)$ (1). To 1.71 g (5 mmol) of $Co_2(CO)_8$ dissolved under CO in 40 mL of hexane was added 210 mg (208 μL, 3.5 mmol) of ethylene sulfide and the solution stirred until the IR spectra of samples taken from the reaction mixture indicated that all $Co_2(CO)_8$ has been consumed (about 4 h). The dark brown solution was filtered and the filtrate first kept at 2−4 °C for 1 day and then at −18 °C for 3 days. The black crystals were filtered off and dried under vacuum. Yield: 0.96 g (2.08 mmol), 62.5% based on Co. According to its IR spectrum in hexane the product is contaminated by small amounts (2−3%, estimated) of $Co_4(CO)_{10}S_2$[5a,26] formed as a byproduct. This latter complex is generally rather inert and does not interfere with the reactions described in this paper. Attempts to further purify **1** by recrystallization resulted in a more contaminated product because the tetranuclear complex is the less soluble one. On chromatography on a silica gel column complex **1** decomposes.

Reaction of 1 with Thiols and Disulfides (General Procedure for the Preparation of Complexes 2). A 20−25 mg (∼0.5 mmol) amount of **1** and about 0.6 mmol of the thiol or 0.3 mmol of the disulfide were dissolved in 5 mL of CH_2Cl_2 under Ar and stirred until the reaction was complete (IR monitoring, 2−4 h, depending on the organic reactant). The reaction mixture was then evaporated to dryness in vacuo and dissolved in hexane. The IR data of the hexane solutions obtained are compiled in Table 1.

Synthesis of $Co_3(CO)_4(PPh_3)_3(\mu\text{-}S\text{-}t\text{-}Bu)(\mu_3\text{-}S)$ (3). To 200 mg (0.435 mmol) of **1** dissolved under Ar in 20 mL of hexane were added 40 mg (50 μL, 0.446 mmol) of *t*-BuSH and the reaction mixture was stirred. After the transformation of **1** into **3** was complete (IR monitoring, usually the next day), 690 mg (2.63 mmol) of PPh_3 dissolved in 15 mL of hexane was added and the reaction mixture stored at room temperature for 2 days. The precipitate formed was filtered off and recrystallized from 2 mL of CH_2Cl_2/20 mL of hexane using the slow diffusion method. Yield after 3 days: 210 mg (0.175 mmol) of shiny black crystals, 60%. Anal. Calcd (found) for **3**: Co, 14.77 (14.9); S, 5.36 (5.2); P, 7.76 (7.7). IR (in Nujol): 1981 vs, 1948 s, 1915 m, 1815 w,br cm^{-1}. ^1H NMR (CD_2Cl_2): δ 1.26 (s, Me), 7.25−7.48 (m, Ph). ^{31}P NMR (CD_2Cl_2): δ 37.2 ($\Delta\nu = 460$ Hz) ppm. ^{13}C NMR (CD_2Cl_2) δ 32.8 (s, Me), 43.6 (s, *C*Me_3), 214 (CO) ppm; the signals of the phenyl carbon atoms show the presence of two types of PPh_3 ligands with an intensity ratio of about 1:2 at 128.2 (d, $^1J_{PC} = 8.8$ Hz, C_3), 129.8 (s, C_4), 133.7 (d, $^1J_{PC} = 11.5$ Hz, C_2), 136.3 (d, $^1J_{PC} = 37$ Hz, C_{ipso}) ppm, and 128.4 (d, $^1J_{PC} = 10.4$ Hz, C_3), 129.6 (s, C_4), 134.3 (d, $^1J_{PC} = 9.6$ Hz, C_2), 136.8 (d, $^1J_{PC} = 37$ Hz, C_{ipso}) ppm; the two sets of signals are assigned to the PPh_3 ligand on Co(3) and the two PPh_3 ligands on Co(1) and Co(2), respectively.

Synthesis of $Co_3(CO)_7(\mu\text{-}(1,3\text{-}\eta)\text{-}S_2CSMe)(\mu_3\text{-}S)$ (4). A 230 mg (0.50 mmol) amount of **1** and 56.5 mg (0.25 mmol) of bis(methylthio(thiocarbonyl)) disulfide, $(MeSCS_2)_2$, were dissolved in 20 mL of CH_2Cl_2, and the mixture was stirred under Ar for 3 h. The reaction mixture was evaporated to dryness, dissolved in 15 mL of hexane, and filtered. The IR spectrum of the clear solution showed only the presence of **4**. The solution was stored at 2−4 °C for 1 week. The resulting crystals were recrystallized from hexane. Yield: 51 mg (0.098 mmol) of black cubes, 19.6%. Anal. Calcd (found) for **4**: Co, 33.47 (33.1); S, 24.28 (24.6). IR (in hexane): 2093 s, 2056 vs, 2051 s, 2033 m cm^{-1}. ^1H NMR (CD_2Cl_2): δ 2.66s ppm. ^{13}C NMR (CD_2Cl_2): δ 22.8 (s, Me), 196 (broad, CO), 247.8 (s, S*C*S_2) ppm.

Synthesis of $Co_3(CO)_7(\mu\text{-}(1,3\text{-}\eta)\text{-}S_2COMe)(\mu_3\text{-}S)$ (5). A 184.4 mg (0.40 mmol) amount of **1** and 64.5 mg (0.44 mmol) of $MeOCS_2K$ were dissolved under Ar in 20 mL of CH_2Cl_2, and 25.1 μL (0.44 mmol) of glacial acetic acid was slowly added to the solution with constant stirring. After 2 h the reaction mixture was evaporated to dryness and dissolved in 3 mL of hexane and the hexane solution cooled to −40 °C. Yield: 38.3 mg (0.075 mmol) of shiny black clumps, 17%. ^1H NMR (CD_2Cl_2): δ 4.04 s ppm. ^{13}C NMR (CD_2Cl_2): δ 67.2 (s, Me), 190−210 (very broad, CO), 236.1 (s, O*C*OMe) ppm.

Synthesis of $Co_3(CO)_7(\mu\text{-}(1,3\text{-}\eta)\text{-}S_2CPh)(\mu_3\text{-}S)$ (6). A 170 mg (0.37 mmol) amount of **1** and 63 μL (0.41 mmol) of $PhCS_2H$ were dissolved under Ar in 20 mL of CH_2Cl_2, and the mixture was stirred for 2 h. The reaction mixture was then evaporated to dryness and dissolved in 3 mL of hexane and the hexane solution cooled to −40 °C. Yield: 68 mg (0.12 mmol) of black powder, 33%. Anal. Calcd (found) for **6**: Co, 31.67 (31.3); S, 17.23 (17.4). IR (in hexane): 2092 s, 2055 vs, 2050 s, 2033 m, 2015 vw cm^{-1}. ^{13}C NMR (CD_2Cl_2): δ 196 (broad, CO), 250.0 (s, S_2*C*Ph); the signals of the phenyl carbon atoms are at 126.1 (C_2), 128.5 (C_3), 132.2 (C_4), 148.7 (C_{ipso}) ppm. Crystals suitable for X-ray determination were obtained by cooling a toluene solution of the complex.

Synthesis of $Co_3(CO)_7(\mu\text{-}PPh_2)(\mu_3\text{-}S)$ (7). To 184 mg (0.40 mmol) of **1** dissolved under Ar in 15 mL of hexane was added 80 mg (75 μL, 0.43 mmol) of Ph_2PH and the reaction monitored by IR spectroscopy as described for the preparation of **1**. After the transformation of **1** into **7** was complete (6−8 h), the reaction mixture was separated by chromatography on a silica gel column. Using a hexane/CH_2Cl_2 (4/1) solvent mixture as eluent gave **7** as the first fraction which was evaporated to dryness under vacuum, dissolved in 5 mL of hexane, and cooled

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Table 7. Crystal Data, Data Collection, and Refinement Parameters for 3, 4, 6, and 8

	3	**4**	**6**	**8**
empirical formula	$C_{62}H_{54}Co_3O_4P_3S_2$	$C_9H_3Co_3O_7S_4$	$C_{14}H_5Co_3O_7S_3$	$C_{19}H_{10}Co_3O_7PS_2$
fw	1196.9	528.1	558.2	622.2
crys size, mm; color	0.22 × 0.40 × 0.60; brown	0.12 × 0.26 × 0.54; black	0.10 × 0.18 × 0.56; black	0.26 × 0.30 × 0.50; black
cryst syst, space group	monoclinic, $P2_1/n$	monoclinic, $C2/c$	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$
unit cell dimens				
a, Å	12.952(3)	13.755(3)	8.178(2)	7.755(2)
b, Å	31.530(4)	8.007(2)	14.825(3)	9.189(2)
c, Å	14.128(6)	30.739(5)	16.612(3)	16.475(3)
α, deg			82.71(3)	88.40(2)
β, deg	90.37(2)	91.90(2)	77.01(3)	87.72(2)
γ, deg			85.56(3)	86.76(2)
V Å^3; Z	5755(3); 4	3375(1); 8	1944(1); 4	1170.9(4); 2
density (calcd), g/cm^3	1.381	2.079	1.907	1.765
abs coeff, mm^{-1}	1.057	3.435	2.884	2.384
2θ range for data collection, deg	2.0−50.0	2.0−55.0	2.0−55.0	2.0−65.0
scan type	ω	ω	$\theta-2\theta$	$\theta-2\theta$
scan speed (variable), deg/min	4.00−20.0	4.00−20.0	4.00−20.0	4.00−20.0
scan range, deg	1.60	1.80	2.20	2.00
no. of rflns collected	10 376	3375	9327	9157
no. of indep rflns	9955 (R(int) = 0.0254)	2782 (R(int) = 0.0282)	8949 (R(int) = 0.0236)	8427 (R(int) = 0.0157)
no. of obsd rflns	5845 ($F > 4.0\sigma(F)$)	2114 ($F > 4.0\sigma(F)$)	6494 ($F > 4.0\sigma(F)$)	6049 ($F > 4.0\sigma(F)$)
abs cor	semiempirical from ψ scans	semiempirical from ψ scans	semiempirical from ψ scans	semiempirical from ψ scans
max and min transmissn	0.2119, 0.2616	0.0884, 1.0000	0.0132, 0.0454	0.0683, 0.1160
refinement method	full-matrix least squares	full-matrix least squares	full-matrix least squares	full-matrix least squares
quantity minimized	$\sum w(F_o - F_c)^2$	$\sum w(F_o - F_c)^2$	$\sum w(F_o - F_c)^2$	$\sum w(F_o - F_c)^2$
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0002F^2$	$w^{-1} = \sigma^2(F) + 0.0020F^2$	$w^{-1} = \sigma^2(F) + 0.0015F^2$	$w^{-1} = \sigma^2(F) + 0.0012F^2$
no. of params refined	667	208	487	289
goodness of fit[a]	1.21	1.38	1.03	0.94
final R indices (obsd data): R1, wR2[a]	0.0464, 0.0401	0.0614, 0.0799	0.0382, 0.0504	0.0305, 0.0431
R indices (all data)	0.0974, 0.2933	0.0807, 0.1072	0.0554, 0.1019	0.0491, 0.1820
largest and mean Δ/σ	0.007, 0.001	0.018, 0.001	0.034, 0.005	0.002, 0.000
largest diff peak and hole, e/Å^3	0.42, −0.39	0.99, −0.94	0.55, −0.57	0.42, −0.25

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)]^2]^{1/2}$; goodness of fit = $[\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$.

to −78 °C. Yield: 98 mg of small black crystals (0.166 mmol), 42%. IR (in hexane): 2077 m, 2034 s, 2015 m (lit.[23] IR 2076 m, 2033 s, 2014 m) cm $^{-1}$. ^{31}P NMR (CD_2Cl_2): δ 213.1 (s, (μ-PPh_2) (lit.[23] NMR 71.9 with $P(OMe)_3$ as reference equal to 212.9) ppm.

Synthesis of $Co_3(CO)_7(\mu\text{-}(1,2\text{-}\eta)\text{-}SPPh_2)(\mu_3\text{-}S)$ (8). To 184 mg (0.40 mmol) of **1** dissolved under Ar in 15 mL of CH_2Cl_2 was added 90 mg (0.40 mmol) of $Ph_2P(S)H$ and the reaction monitored by IR spectroscopy as described for the preparation of **1**. After the transformation of **1** into **8** was complete (2−3 h), the reaction mixture was evaporated to dryness in vacuo and the residue dissolved in 10 mL of hexane. Chromatography on silica gel using a hexane/CH_2Cl_2 (4/1) solvent mixture as eluent gave **8** as the main fraction. This was concentrated to 5 mL in vacuo and stored first in a refrigerator and then at −78 °C. Yield: 107 mg of black crystals (0.172 mmol), 43%. Anal. Calcd (found) for **8**: Co, 28.41 (28.3); S, 10.30 (10.5); P, 4.98 (4.9). IR (in hexane): 2086 s, 2046 vs, 2043 s, 2027 m cm^{-1}. ^{13}C NMR ($CDCl_3$): δ 197 (broad, CO), the signals of the phenyl carbon atoms are at 128.6 and 128.75 (C_3), 133.6 and 136.5 (C_4), 131.0 and 131.8 (C_2), 136.1 and 138.2 (C_{ipso}) ppm. ^{31}P NMR ($CDCl_3$): δ 47 (s, μ-P(S)Ph_2) ppm.

X-ray Analysis of Complexes 3, 4, 6, and 8. Crystal data and parameters of data collections and of refinements are collected in Table 7. The data were collected at 20 °C on a Siemens P4 diffractometer graphite-monochromatized with Mo Kα radiation (λ = 0.710 73 Å). Two standard reflections measured every 50 reflections showed no decay. The absorption correction was applied using the method of ref 38. The structures were solved by direct methods using the Siemens SHELXTL IRIS package,[39] used also for refinement. The non-hydrogen atoms were anisotropically refined. The last Fourier difference maps showed peaks corresponding to some H atoms; the H atoms of the methyls and of the phenyl rings were, however, calculated and refined riding on the corresponding carbon atoms with $U_{iso} = 0.080$ Å^2. The fractional coordinates of complexes **3**, **4**, **6**, and **8** are listed in the Supporting Information.

Complex **6** crystallizes in two modifications in the triclinic and monoclinic systems; the data reported in the present work refer to the triclinic form.

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Supporting Information Available: Tables giving all bond angles for **3** and anisotropic thermal parameters for non-hydrogen atoms, calculated coordinates for H atoms, and atomic coordination for non-H atoms for **3**, **4**, **6**, and **8** (20 pages). Ordering information is given on any current masthead page.

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