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Formation of the Salt-like Complexes $[Co\{S_2CC(PPh_3)_2\}_3][Co(CO)_4]_3$ and $[(CO)_4Mn\{S_2CC(PPh_3)_2\}][Mn(CO)_5]$ from the Reaction of the Related Carbonyl Compounds with $S_2CC(PPh_3)_2$

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Abstract. The betain-like compound $S_2CC(PPh_3)_2$ (**1**), which is obtained from CS_2 and the double ylide $C(PPh_3)_2$, reacts with $[Co_2(CO)_8]$ and $[Mn_2(CO)_{10}]$ in THF to afford the salt-like complexes $[Co\{S_2CC(PPh_3)_2\}_3][Co(CO)_4]_3$ (**2**) and $[(CO)_4Mn\{S_2CC(PPh_3)_2\}][Mn(CO)_5]$ (**3**), respectively, in good yields. At both d^6 cations **1** acts as a chelating ligand. Disproportionation reactions from formal Co^0 into Co^{III} and Co^{-I} and from Mn^0 into Mn^I and Mn^{-I} occurred with the removal of four or one carbonyl groups, respectively. The crystal structures of **2**·5.5THF and **3**·2THF are reported, which show a shortening of the C−C bond in the ligand upon complex formation. The compounds are further characterized by ^{31}P NMR and IR spectroscopy.

Keywords: Carbodiphosphorane CS_2 adduct; Chelating ligand; Crystal structures; Manganese complex; Cobalt(III) complex

1 Introduction

The betain-like compound $S_2CC(PPh_3)_2$ (**1**) is easily obtained as a bright orange precipitate by adding CS_2 to a toluene solution of the carbodiphosphorane $Ph_3P{=}C{=}PPh_3$. Although this adduct has been known since more than 40 years, the chemistry was only sparingly explored. At elevated temperature or even upon stirring in organic solvents at room temperature **1** slowly splits into $SPPh_3$ and the ylide-like heterocumulene $S{=}C{=}CPPh_3$ [1]. Recently, we have solved the crystal structure of **1**, which shows a short carbon carbon bond distance and a small dihedral angle between the CS_2 and the CP_2 plane of about 20° indicating some double bond character between the carbon atoms [2]. DFT calculations demonstrated that $Ph_3P{=}C{=}PPh_3$ mainly acts as a σ-donor via the sp^2 carbon atom but a weak additional π-interaction between the filled p orbital of the ylidic carbon atom and the empty p orbital of the CS_2 moiety is operative [2]. This electron flow should also influence the electron density at the sulfur atoms with result of enhanced nucleophilic properties relative to those of similar $S_2C{\leftarrow}D$ compounds, in which D acts only as a σ-donor. Further we could show that **1** can act as a bidentate ligand towards group 6 carbonyl compounds to produce the related $[(CO)_4M\{S_2CC(PPh_3)_2\}]$ complexes [2]. With silver salts, containing weakly coordinating anions, interesting coordination compounds with $[Ag^+]_4$ and $[Ag^+]_6$ cores could be obtained [3]. These results prompted us to study the coordination chemistry of **1** more intensively in particular to look at reactions with other transition metal carbonyl compounds. In this contribution we present the results of the reaction of **1** with the dinuclear carbonyl complexes $[Co_2(CO)_8]$ and $[Mn_2(CO)_{10}]$.

2 Results and Discussion

The reactions of **1** with the carbonyl compounds were carried out as heterogeneous reactions in THF, in which **1** is insoluble. In halogenated hydrocarbons **1** is soluble, but side reactions with the solvent may occur. If a slight excess $[Co_2(CO)_8]$ was slowly added to a suspension of **1** in THF immediately CO evolution was observed with formation of a dark red brown solution. After about 10 min CO evolution had ceased and all material was dissolved. The ^{31}P NMR spectrum of the solution showed one signal at 16.10 ppm. From the THF solution dark red crystals separated after several days, which were identified as the salt-like complex $[Co\{S_2CC(PPh_3)_2\}_3][Co(CO)_4]_3{\cdot}5.5THF$ (**2**·5.5THF). The ligand had induced a disproportionation reaction from formal Co^0 in $[Co_2(CO)_8]$ into Co^{III} and Co^{-I} in cation and anion, respectively, according to equ. (1). During the related reaction of a 1 : 2 mixture of **1** with $[Mn_2(CO)_{10}]$ in THF no visible CO evolution was observed. But after about 10 to 15 h at room temperature all of the starting betain **1** had dissolved to produce an orange solution from which the salt-like complex **3** could be isolated (equ. (2)). The ^{31}P NMR spectrum of the solution gave a

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signal at 16.6 ppm, which was accompanied by two low intense signals at 42.1 and −10.2 ppm belonging to $SPPh_3$ and the heterocummulene $S{=}C{=}C{=}PPh_3$, respectively, according to a slow decomposition of **1** in solution. Experiments with a 2 : 1 mixture of **1** with $[Mn_2(CO)_{10}]$ in THF gave similar results, but the signals of the decomposition products of **1** increased. Similar to the formation of **2** a dismutation occurred starting from Mn^0 into Mn^I and Mn^{-I} as shown in equ. (2). Parallel to the formation of **3**, in all cases a slow decomposition of **1** is operative according to equ. (3).

$$2\,[Co_2(CO)_8] + 3\,S_2CC(PPh_3)_2 \rightarrow \underset{\mathbf{2}}{[Co\{S_2CC(PPh_3)_2\}_3][Co(CO)_4]_3} + 4\,CO \quad (1)$$

$$[Mn_2(CO)_{10}] + S_2CC(PPh_3)_2 \rightarrow \underset{\mathbf{3}}{[(CO)_4Mn\{S_2CC(PPh_3)_2\}][Mn(CO)_5]} + CO \quad (2)$$

$$S_2CC(PPh_3)_2 \rightarrow SPPh_3 + S{=}C{=}C{=}PPh_3 \quad (3)$$

The cation of **3** is isoelectronic to the neutral compounds $[(CO)_4M\{S_2CC(PPh_3)_2\}]$ (M = Cr, Mo, W) published earlier and, similar to these complexes, the cations of **2** and **3** have low spin d^6 electron configurations. The replacement of CO groups by the chelating ligand **1** at one Co atom caused a heterolytic splitting of the Co−Co bond [4] with formation of the stable $[Co(CO)_4]^-$ anion and concentration of the ligand at the other cobalt atom, a route which is typical for the interaction of $[Co_2(CO)_8]$ with various Lewis bases. However, the formation of a Co^{III} cation is very unusual and disproportionation of $[Co_2(CO)_8]$ with soft Lewis bases normally proceeds with the formation of $[Co^I][Co(CO)_4]$ compounds while hard O and N donors favor disproportionation into paramagnetic $[Co^{II}][Co(CO)_4]_2$ complexes [5]. To our knowledge, no further reactions of $[Co_2(CO)_8]$ with chelating neutral sulfur containing ligands like **1** are described.

The σ-donor/π-acceptor ratio of **1** is greater than that of CO as shown from IR data of the $[(CO)_4M\{S_2CC(PPh_3)_2\}]$ complexes (M = Cr, Mo, W) [2], and the ligand favors disproportion over formation of a bridging ligand in a Co_2 moiety. To our knowledge, the salt **2** is the first compound containing a highly charged cation with a CoS_6 core and is also the first one in which more than one of the betain-like ligand **1** is coordinated at a transition metal atom. Other Co^{III} complexes with six sulfur atoms in an octahedral environment are known with negatively charged dithiocarboxylato [6], dithiocarbamato [7], thioxanthato [8], or xanthato [9] ligands to produce neutral complexes in all cases, and starting materials were Co^{II} or Co^{III} complexes. A heterolytic splitting of the metal metal bond is also operative with $[Mn_2(CO)_{10}]$ to produce the d^8 anion $[Mn(CO)_5]^-$ and the d^6 cation $[Mn(CO)_5]^+$, and the latter is stabilized by replacement of only one CO ligand by the chelating ligand **1**.

The IR spectrum of **2** exhibits a strong band at 1882 cm^{-1} according to the IR active F_2 ν(CO) vibration of the $[Co(CO)_4]^-$ anion [10, 11]. Further strong bands at 1063 and 1098 belong to the vibration of the CS_2 group; similar bands were recorded in all known complexes with **1** as ligand, and no dependence of the position from charge and number of the ligands is detectable. The IR spectrum of **3** in the ν(CO) region is composed of the vibrations of the terminal CO groups of anion and cation, but which are clearly separated. For the cation three bands were recorded at 2086, 2009 (broad with a shoulder), and 1943 cm^{-1} consistent with a local C_{2v} symmetry (2 A_1, B_1, B_2), and this band pattern is closely related to that of the neutral complexes $[(CO)_4M\{S_2CC(PPh_3)_2\}]$, however, according to the positive charge, the bands are shifted by about 100 to 145 wave numbers to higher frequencies. Thus, the positive charge overcompensates the normal low frequency shift of the chelating ligand, which shows a greater σ-donor/π-acceptor ratio than CO and which should induce enhanced back bonding into CO π* orbitals. A similar band pattern is recorded in the cation $[(CO)_4Mn\{S_2CP(C_6H_{11})_3\}]^+$ [12]. The low frequency bands at 1852, 1884, and 1900 can be assigned to the CO groups of the anion (A_2'', E') and are identical with those in other complexes containing the $[Mn(CO)_5]^-$ anion [13]; the presence of three CO bands represents the deviation from the ideal D_{3h} symmetry. Two medium to strong bands at 1066 and 1099 cm^{-1} can be assigned to the vibration of the CS_2 moiety. **3** does not react with PPh_3 at room temperature even under ultrasonic irradiation; the ^{31}P NMR spectrum of the reaction mixture shows the unchanged signals of the starting materials.

3 Crystal Structures

In order to get a deeper inside into the properties of **2** and **3**, the molecular structures were determined by single crystal X-ray diffraction measurements. Dark red crystals of $[Co\{S_2CC(PPh_3)_2\}_3][Co(CO)_4]_3\cdot5.5THF$ (**2**·5.5THF) were obtained on standing a THF solution at room temperature for several days. One anion is disordered in two positions (0.8:0.2). Orange crystals of $[(CO)_4Mn\{S_2CC(PPh_3)_2\}][Mn(CO)_5]\cdot2THF$ (**3**·2THF) formed from a THF solution by layering with n-pentane. The THF molecules are disordered and could be refined in two split positions (0.6:0.4). An ORTEP view of the cation of **2**·5.5THF is shown in Figure 1; the $Co(S_2CCP_2)_3$ core is separately depicted in Figure 2. The cation of **3**·2THF is shown in Figure 3. Details of the structure determination are summarized in Table 1; bond distances and angles of the cations are given in Table 2 and 3. Molecular structures of similar compounds with the CoS_6 core with negatively charged ligands have been determined earlier [7−9].

3.1 Molecular structure of 2·5.5THF

The structure shows separated cations and anions with no remarkable interionic contacts. In the cation the cobalt atom is surrounded by six sulfur atoms in a distorted octahedral environment. The structure of the cation is depicted

Table 1 Crystal data and structural refinement details

	2·5.5THF	**3**·2THF
formula	$C_{148}H_{134}Co_4O_{17.5}P_6S_6$	$C_{55}H_{46}Mn_2O_{11}P_2S$
mw/g·mol^{-1}	2806.59	1118.90
a/pm	1417.7(1)	1061.6(1)
b/pm	4255.7(2)	1193.9(1)
c/pm	2369.3(1)	2174.2(2)
α /°	90	76.11(1)
β /°	102.94(1)	84.17(1)
γ /°	90	85.44(1)
crystal size/mm	0.23×0.2×0.19	0.26×0.25×0.16
volume/pm^3·10^6	13932(1)	2656.9(4)
Z	4	2
d_{calc} /g·cm^{-3}	1.338	1.399
crystal system	monoclinic	triclinic
space group	$P2_1/c$ (Nr. 14)	$P\bar{1}$ (Nr. 2)
diffractometer	IPDS II (Stoe)	IPDS II (Stoe)
Radiation	Mo-K_α	Mo-K_α
temperature/K	193	193
μ /cm^{-1}	6.9	6.7
$2\theta_{max}$ /°	52.41	52.49
index range	$-17 \le h \le 17$ $-51 \le k \le 52$ $-26 \le l \le 29$	$-13 \le h \le 13$ $-14 \le k \le 14$ $-26 \le l \le 26$
number of rflns collected	70156	38734
number of indep. rflns (R_{int})	24844 (0.0597)	10639 (0.0607)
number of observed rflns with $F_0 > 4\sigma(F_0)$	14207	6421
parameters	1561	615
absorption correction	numerical	numerical
structure solution	direct methods SHELXS-97 [22]	Patterson method SHELXTL-Plus [23]
refinement against F^2	SHELXH-97 [24]	SHELXL-97 [25]
H atoms	calculated positions with common displacement parameter	calculated positions with common displacement parameter
R_1	0.0597	0.0451
wR_2 (all data)	0.171	0.1156
max. electron density left/ (e·pm^{-3})·10^{-6}	0.75	0.61

in Figure 1; the $Co(S_2CCP_2)_3$ core is shown in Figure 2. Relative to the starting ligand **1** the dihedral angles S_2C/P_2C have increased from 20° up to values of 28°, 30°, and 32°; the slightly different angles are probably due to packing effects. Another important change in going from the free ligand to the complex is the shortening of the C−C distance from 147 pm to about 144.5 pm, indicating a further increase of the double bond character. Both trends, C−C bond shortening and increase of the dihedral angle, were also recorded in the corresponding $[(CO)_4M\{S_2CC(PPh_3)_2\}]$ complexes (M = Cr, Mo, W) and the latter effect interpreted in terms of an increased steric interaction of phenyl groups with the sulfur atoms upon C−C bond shortening, pushing the sulfur atoms further out of the favored planar arrangement [2]. The P−C distance which amounts to 163.1(3) pm in the carbodiphosphorane $C(PPh_3)_2$ [14] according to a p-σ* interaction increased in going to **1** (175.1(2) pm) and shows a mean value of 175.4(5) pm in the cobalt complex; the average C−S bond length amounts to 170.3(4) pm and is slightly longer than in the free ligand. The small CS_2 bite angle of 108° of the ligand (125° in the free ligand) leads to three small (average 75.9°) SCoS angles; within each of the three planes of the octahedron, spanned by four S atoms and the Co atom, the sum of SCoS angles amounts to 361.2°, indicating only a small deviation from planarity. Similarly, the three four-membered CoSCS rings are planar. The PCP angles were not influenced on complex formation. The Co−S distances (average 226.4(1) pm) do not differ from those containing Co^{III} and negatively charged $[S_2CNR_2]^-$ ligands [15]. The parameters of the three $[Co(CO)_4]^-$ anions are normal and do not deviate markedly from a tetrahedral arrangement of the carbonyl groups.

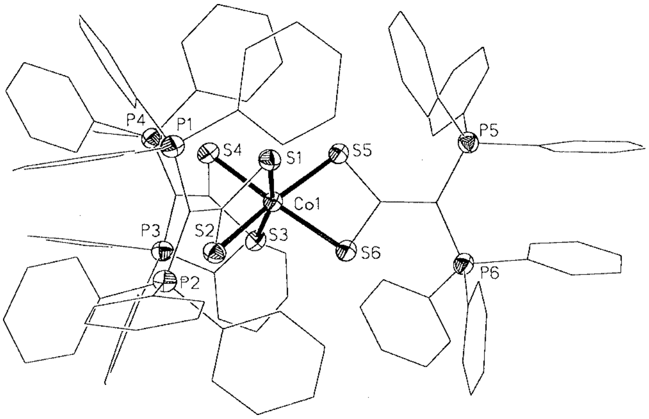

Fig. 1 Molecular structure of the cation of $[Co\{S_2CC(PPh_3)_2\}_3][Co(CO)_4]_3$·5.5THF (**2**·5.5THF) showing the atom numbering scheme. The ellipsoids are drawn at a 40% probability level; the H atoms at the phenyl groups are omitted for clarity.

Table 2 Selected bond lengths/pm and angles/° in the cation of **2**

Co(1)−S(1)	227.6(1)	Co(1)−S(2)	225.0(1)
Co(1)−S(3)	227.4(1)	Co(1)−S(4)	226.5(1)
Co(1)−S(5)	225.4(1)	Co(1)−S(6)	226.4(1)
S(1)−C(2)	171.7(4)	S(2)−C(2)	168.9(5)
S(3)−C(40)	171.0(4)	S(4)−C(40)	169.6(5)
S(5)−C(78)	170.0(4)	S(6)−C(78)	170.6(4)
P(1)−C(1)	174.7(5)	P(3)−C(39)	175.2(5)
P(2)−C(1)	176.1(5)	P(4)−C(39)	176.0(5)
P(5)−C(77)	175.7(5)	P(6)−C(77)	174.8(4)
C(1)−C(2)	144.8(6)	C(39)−C(40)	144.0(7)
C(77)−C(78)	145.0(5)		
S(1)−Co(1)−S(2)	75.83(5)	S(1)−Co(1)−S(3)	166.54(4)
S(1)−Co(1)−S(4)	95.10(5)	S(1)−Co(1)−S(5)	95.99(5)
S(1)−Co(1)−S(6)	95.11(5)	S(2)−Co(1)−S(3)	94.66(5)
S(2)−Co(1)−S(4)	93.31(4)	S(2)−Co(1)−S(5)	168.32(5)
S(2)−Co(1)−S(6)	96.09(5)	S(3)−Co(1)−S(4)	75.70(5)
S(3)−Co(1)−S(5)	94.71(5)	S(3)−Co(1)−S(6)	95.36(5)
S(4)−Co(1)−S(5)	95.75(5)	S(4)−Co(1)−S(6)	167.54(5)
S(5)−Co(1)−S(6)	76.10(4)	Co(1)−S(1)−C(2)	86.6(2)
Co(1)−S(2)−C(2)	88.1(2)	Co(1)−S(3)−C(40)	86.9(2)
Co(1)−S(4)−C(40)	87.6(2)	Co(1)−S(5)−C(78)	87.3(2)
Co(1)−S(6)−C(78)	86.9(2)	P(1)−C(1)−P(2)	126.7(2)
P(1)−C(1)−C(2)	118.0(3)	P(2)−C(1)−C(2)	115.1(3)
S(1)−C(2)−S(2)	109.5(2)	S(1)−C(2)−C(1)	125.2(4)
S(2)−C(2)−C(1)	125.3(3)	P(3)−C(39)−P(4)	124.6(3)
S(3)−C(40)−C(39)	118.0(3)	P(4)−C(39)−C(40)	117.4(4)
S(3)−C(40)−S(4)	109.7(3)	S(3)−C(40)−C(39)	124.5(4)
S(4)−C(40)−C(39)	125.7(3)	P(5)−C(77)−P(6)	126.8(2)
P(5)−C(77)−C(78)	116.7(3)	P(6)−C(77)−C(78)	116.4(3)
S(5)−C(78)−S(6)	109.7(2)	S(5)−C(78)−C(77)	125.3(3)
S(6)−C(78)−C(77)	125.0(3)		

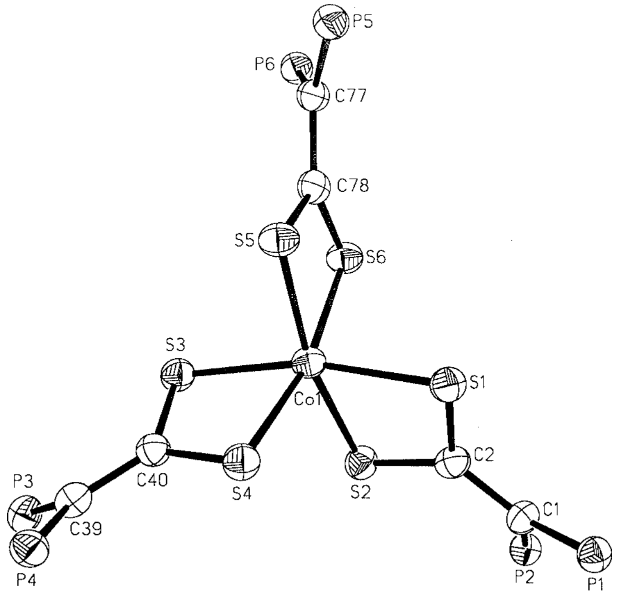

Fig. 2 View of the $Co(S_2CCP_2)_3$ core of **2**·5.5THF showing the atom numbering scheme. The ellipsoids are drawn at a 40 % probability level.

Table 3 Selected bond lengths/pm and angles/° in the cation of **3**

Mn(1)−S(1)	236.5(1)	Mn(1)−S(2)	238.5(1)
Mn(1)−C(1)	181.2(4)	Mn(1)−C(2)	182.2(4)
Mn(1)−C(3)	185.4(4)	Mn(1)−C(4)	186.5(4)
S(1)−C(6)	170.9(3)	S(2)−C(6)	170.4(3)
P(1)−C(5)	176.2(3)	P(1)−C(12)	180.4(3)
P(1)−C(18)	180.9(3)	P(1)−C(24)	181.1(3)
P(2)−C(5)	176.0(3)	P(2)−C(30)	180.4(3)
P(2)−C(36)	180.6(3)	P(2)−C(42)	180.2(3)
O(1)−C(1)	114.7(4)	O(2)−C(2)	113.8(4)
O(3)−C(3)	113.8(4)	O(4)−C(4)	113.4(4)
C(5)−C(6)	143.1(4)		
S(1)−Mn(1)−S(2)	72.59(3)	S(1)−Mn(1)−C(1)	95.5(1)
S(1)−Mn(1)−C(2)	169.4(1)	S(1)−Mn(1)−C(3)	88.2(1)
S(1)−Mn(1)−C(4)	88.1(1)	S(2)−Mn(1)−C(1)	168.1(1)
S(2)−Mn(1)−C(2)	96.9(1)	S(2)−Mn(1)−C(3)	89.1(1)
S(2)−Mn(1)−C(4)	88.4(1)	C(1)−Mn(1)−C(2)	95.1(1)
C(1)−Mn(1)−C(3)	90.1(2)	C(1)−Mn(1)−C(4)	91.3(2)
C(2)−Mn(1)−C(3)	92.1(2)	Mn(1)−S(1)−C(6)	88.5(1)
C(3)−Mn(1)−C(4)	176.0(2)	Mn(1)−C(1)−O(1)	178.3(4)
Mn(1)−S(2)−C(6)	88.0(1)	Mn(1)−C(3)−O(3)	179.1(3)
Mn(1)−C(2)−O(2)	179.6(4)	P(1)−C(5)−P(2)	126.4(2)
Mn(1)−C(4)−O(4)	179.2(3)	P(2)−C(5)−C(6)	116.2(2)
P(1)−C(5)−C(6)	117.3(2)	S(1)−C(6)−C(5)	123.9(2)
S(1)−C(6)−S(2)	110.9(2)	S(2)−C(6)−C(5)	125.1(2)

3.2 Molecular structure of 3·2THF

No nearer contacts between cation and anion exist. The structure of the cation is closely related to the structures of the neutral derivatives of the group 6 transition metal carbonyl compounds $[(CO)_4M\{S_2CC(PPh_3)_2\}]$ and is shown in Figure 3. The two sulfur atoms of the ligand **1** and four CO groups form a distorted octahedral environment of the Mn^I atom. The positive charge has no dramatic influence on the parameters of the ligand, which are close together within the group 6 metal complexes. Only the C−C distance decreased by about 2 pm to 143.1(4) pm, while the C−P distances increased by about 1 pm to 176.2(2) pm relative to the neutral species, indicative for a shift of the electron density away from P to the S atoms upon complex formation. The SCS angle is slightly more acute, while the SMnS angle is larger than the related SMS angles (M = Cr, Mo, W). The dihedral angle between the S_2C and the P_2C planes amounts to 29°, which is identical with the related angles in the neutral group 6 derivatives. The anion has a distorted trigonal bipyramidal structure with C-Mn-C angles in the equatorial plane of 124.3(2)°, 120.7(2)° and 115.0(2)°; the axial CO groups form an angle of 174.9(2)°. The other C-M-C angles are in the range between 86.6(2)° and 92.5(2)°. The parameters are similar as in $[C(NMe_2)_3][Mn(CO)_5]$ reported earlier [13].

4 Concluding Remarks

Towards various transition metal complexes the betain **1** acts as a chelating ligand rather than as a monodentate one. The cobalt complex **2** represents the first compound with a

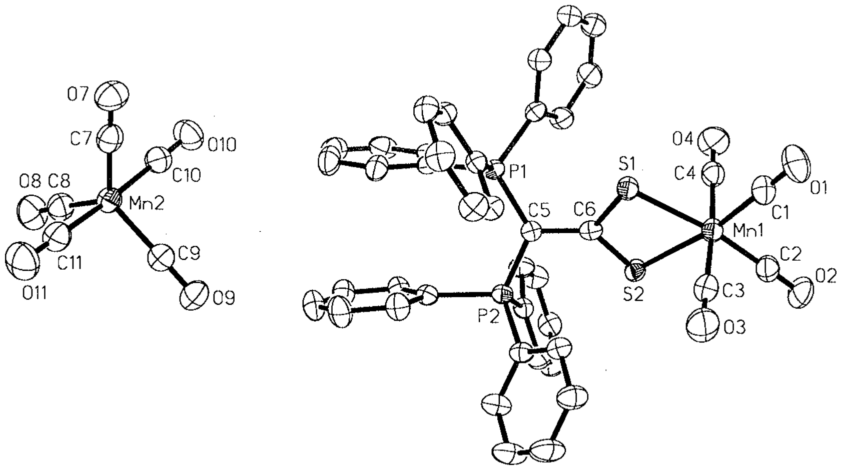

Fig. 3 Molecular structure of the cation of **3**·2THF showing the atom numbering scheme. The ellipsoids are drawn at a 40 % probability level; the H atoms at the phenyl rings are omitted for clarity.

cationic CoS_6 core with a charge of +III and, to our knowledge, **3** is one of the rare examples of a cationic carbonyl species with the $[(CO)_4MnS_2]^+$ core characterized by X-ray analysis. Only two further examples were published containing either the S_2CPCy_3 group [16] or two tetramethylthiourea molecules [17], respectively. The structures of various neutral species are also reported containing different ligands such as dithioacetato, thiolato, disulfido or phosphinodithiolato ligands, and in all cases a *cis* arrangement is realized [18]. Also a variety of structures with neutral $[X(CO)_3Mn(S_2C{-}D)]$ compounds were published [12, 19, 20]. As yet, the group 6 carbonyls and **2** and **3** are the only carbonyl derivatives containing **1** as chelating ligand. Our attempts to obtain similar complexes from group 8 transition metal carbonyls have failed and the reaction with $[Ni(CO)_4]$ produced only an oily material which could not be crystallized as yet. Further studies about the complex ability of **1** and related compounds are in progress.

5 Experimental Section

General Considerations. All operations were carried out under an argon atmosphere in dried and degassed solvents using Schlenk techniques. The solvents were thoroughly dried and freshly distilled prior to use. The IR spectra (in Nujol) were run on a Nicolet 510 spectrometer. The ^{31}P NMR spectra were run on a Bruker ARX 200 spectrometer and referenced to external H_3PO_4. $S_2CC(PPh_3)_2$ (**1**) was obtained according to a modified literature procedure [1] by adding CS_2 to a solution of $C(PPh_3)_2$ in toluene at room temperature. Commercially available $[Mn_2(CO)_{10}]$ was sublimed before use, and $[Co_2(CO)_8]$ was prepared according to the procedure described in [21].

Preparation of $[Co\{S_2CC(PPh_3)_2\}_3][Co(CO)_4]_3$ (2): To a solution of 0.27 g $[Co_2(CO)_8]$ (0.79 mmol) in about 50 ml THF was added 0.48 g of **1** (0.78 mmol), which dissolved with evolution of CO. The mixture was stirred for about 10 h and filtered. The ^{31}P NMR spectrum of the solution showed a main band at 16.1 and minor intense signals at 15.5 and 15.1 ppm. On standing of the solution for two days, followed by layering with n-pentane, dark red crystals of $[Co\{S_2CC(PPh_3)_2\}_3][Co(CO)_4]_3\cdot5.5THF$ (**2**·5.5THF) formed. Yield 0.45 g (47 % rel. to **1**). ^{31}P NMR: 16.1 ppm in THF and 14.8 ppm in CH_2Cl_2. IR (Nujol mull, cm^{-1}): 1880 vs, br (CO), 1481 m, 1439 s, 1397 w, 1212 s, 1189 s, 1162 w, 1089 s, 1063 s, 1027 w, 999 w, 908 w, 811 w, 747 m, 720 m, 688 m, 555 vs, 522 s, 506 m, 495 m, 410 w.

Preparation of $[(CO)_4Mn\{S_2CC(PPh_3)_2\}][Mn(CO)_5]$ (3): A suspension of 0.44 g $[Mn_2(CO)_{10}]$ (1.13 mmol) and 0.34 g **1** (0.56 mmol) in about 30 ml THF was stirred at room temperature for about 12 h until a nearly clear orange solution was obtained. The ^{31}P NMR spectrum of the solution showed three singlets at 42.1, 16.6, and −10.2 ppm in a 0.07:1:0.07 ratio, respectively. The main signal was assigned to **3** and the low intense signals to the decomposition products of **1**, $SPPh_3$ and $SCCPPh_3$. The solution was filtered and layered with n-pentane. At first an orange yellow microcristalline precipitate of **3** was obtained; additional layering with n-pentane produced orange crystals of **3**·2THF. Yield: 0.39 g (70 %, rel. to **1**). IR (Nujol mull, cm^{-1}): 2086 s, 2009 vs, 1943 vs, (CO groups of the cation); 1900 vs, 1884 vs, 1852 vs (CO groups of the anion); 1481 m, 1439 s, 1217 vs, 1190 m, 1164 m, 1099 m, 999 w, 913 w, 805 w, 746 m, 720 m, 683 s, 658 s, 626 m, 619 m, 583 w, 556 w, 524 w, 503 w, 497 w, 463 w, 439 w, 412 w.

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ. Copies of the data can be obtained on quoting the depository numbers CCDC 601918 (**2**·5.5THF), CCDC 601919 (**3**·2THF), (Fax: (+44)1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

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