2968 *Inorg. Chem.* **1980**, *19*, 2968–2975

Contribution from the Istituto di Chimica Generale e Inorganica,
Università, Laboratorio CNR, Florence, Italy

Mono- and Dinuclear CS_2 Metal Complexes with 1,1,1-Tris((diphenylphosphino)methyl)ethane

C. BIANCHINI, C. MEALLI, A. MELI, A. ORLANDINI, and L. SACCONI*

Received February 20, 1980

The tris(tertiary phosphine) 1,1,1-tris((diphenylphosphino)methyl)ethane, triphos, forms stable mononuclear and dinuclear CS_2 metal complexes with formulas $[(\text{triphos})Co(\pi\text{-}CS_2)]$ (**1**), $[(\text{triphos})Co(\mu\text{-}CS_2)Cr(CO)_5]\cdot 0.25CH_2Cl_2$ (**2**), $[(\text{triphos})Co(\mu\text{-}CS_2)Mn(\eta^5\text{-}C_5H_5)(CO)_2]$ (**3**), and $[(\text{triphos})Co(\mu\text{-}CS_2)Co(\text{triphos})](BPh_4)_2\cdot 2(CH_3)_2CO$ (**4**), respectively. The X-ray structures of compounds **1**, **2**, and **4** have been determined. Crystal data for **1** are space group $Pn2_1a$, $a = 21.035$ (9) Å, $b = 17.090$ (8) Å, $c = 10.283$ (5) Å, and $Z = 8$. The cobalt atom is coordinated by the three phosphorus atoms of the triphos ligand and by the π-bonded CS_2 molecule through a C═S linkage. Crystal data for **2** are space group $P2_1/n$, $a = 25.23$ (2) Å, $b = 18.43$ (1) Å, $c = 22.19$ (2) Å, $\beta = 114.8$ (3)°, and $Z = 8$. The cobalt atom is bonded to the three phosphorus atoms of the triphos ligand and π bonded to a C═S linkage; the other sulfur atom of the CS_2 unit is σ bonded to the chromium atom, which is thus hexacoordinated in a distorted octahedral geometry. Crystal data for **4** are space group $P\bar{1}$, $a = 18.120$ (4) Å, $b = 14.074$ (4) Å, $c = 12.705$ (3) Å, $\alpha = 91.3$ (2)°, $\beta = 106.1$ (3)°, $\gamma = 111.8$ (3)°, and $Z = 1$. The bridging CS_2 unit is π bonded to one cobalt atom through a C═S linkage and σ bonded to the other metal through the two terminal sulfur atoms. The $CoCS_2Co$ fragment is strictly planar. The electronic nature of the bound CS_2 ligand is discussed in the light of structural and spectroscopic parameters.

Introduction

Since the synthesis of the first CS_2 metal complex $[Pt(CS_2)(PPh_3)_2]$ by Wilkinson et al.,[1] several CS_2 complexes with transition metals have been isolated. However, many of the compounds obtained are not completely characterized; in particular, their stereochemistry and structure have not been adequately established.[2]

Indeed, X-ray diffraction studies are limited to a few cases of monomeric complexes where CS_2 is η^2 bonded to the metal[3] and to a dinuclear CS_2-bridged platinum complex containing a metal dithioformato fragment bonded through the two sulfur atoms to the second metal.[4] Owing to the scarcity of structural information, the bonding mode of CS_2 in transition-metal complexes is still an object of intense speculation.

In previous work from this laboratory it has been shown that the metal–ligand moiety formed by some transition metals, particularly cobalt, and the tripodlike triphosphine 1,1,1-tris((diphenylphosphino)methyl)ethane, triphos, is capable of forming stable mononuclear and dinuclear complexes with a variety of σ- and π-donor groups.[5,6] It therefore seemed that it would be interesting to investigate the reactivity of CS_2 toward the (triphos)Co moiety.

We have succeeded in preparing the mononuclear compound $[(\text{triphos})Co(\pi\text{-}CS_2)]$ (**1**) and the dinuclear compound $[(\text{triphos})Co(\mu\text{-}CS_2)Co(\text{triphos})]\ (BPh_4)_2\cdot 2(CH_3)_2CO$ (**4**). The reactivity of compound **1**, as a ligand, has also been investigated; in particular the heterodinuclear compounds $[(\text{triphos})Co(\mu\text{-}CS_2)Cr(CO)_5]\cdot 0.25CH_2Cl_2$ (**2**) and $[(\text{triphos})Co(\mu\text{-}CS_2)Mn(\eta^5\text{-}C_5H_5)(CO)_2]$ (**3**) have been obtained. All complexes have been characterized by appropriate physical methods.

Complete X-ray structure determinations on compounds **1**, **2**, and **4** have provided the structural parameters needed to elucidate the different bonding modes and electronic nature of the bonded CS_2 group in such complexes.

A preliminary account of part of this work has already been published.[7,8]

Experimental Section

Reagents. Cobalt tetrafluoroborate, sodium tetraphenylborate, sodium borohydride, ethanol, 1-butanol, acetone, butyl ether, methylene chloride, ethyl ether, and petroleum ether were of reagent grade and were used without further purification. Tetrahydrofuran and carbon disulfide were purified by distillation over $LiAlH_4$ and over molecular sieves (3-Å), respectively. $Co_2(CO)_8$ was purchased from Strem Chemicals Inc., Danvers, Mass. The ligand 1,1,1-tris((diphenylphosphino)methyl)ethane was prepared as previously described.[9]

Physical Measurements. The methods used for the magnetic and molar conductance measurements and the recording of infrared and UV–visible spectra have been described previously.[10]

Preparation of the Complexes. All operations were performed under N_2 and with oxygen-free solvents. The solid complexes were collected on a sintered-glass frit and dried in a stream of nitrogen.

$[(\text{triphos})Co(\pi\text{-}CS_2)]$ (1). Method I. A 10-mL portion of carbon disulfide was added to a mixture of $Co_2(CO)_8$ (0.5 mmol) and triphos (1 mmol) in tetrahydrofuran (50 mL). After dilution with ethanol and concentration by gentle heating, garnet red crystals precipitated which were separated by filtration and washed with ethanol and petroleum ether. They were recrystallized from methylene chloride/ethanol.

Method II. A solution of sodium naphthalenide, prepared by shaking naphthalene (1.20 mmol) with an excess of sodium chips in tetrahydrofuran (30 mL), was added dropwise to a suspension of **4** (0.50 mmol) in tetrahydrofuran (50 mL). The suspended compound slowly dissolved to give a red-brown solution. After the solvent was removed under reduced pressure, the residue was washed with ethyl ether and then extracted with methylene chloride (20 mL). By addition of ethanol (30 mL) followed by slow evaporation of the solvent, crystals of **1** precipitated.

---

(1) Baird, M. C.; Wilkinson, G. *Chem. Commun.* **1966**, 514.

(2) Yaneff, P. V. *Coord. Chem. Rev.* **1977**, *23*, 183.

(3) (a) Mason, R.; Rae, A. I. M. *J. Chem. Soc. A* **1970**, 1767. (b) Drew, M. G. B.; Sun Pu, L. *Acta Crystallogr., Sect. B* **1977**, *33*, 1207. (c) Le Bozec, H.; Dixneuf, P. H.; Carty, A. J.; Taylor, N. J. *Inorg. Chem.* **1978**, *17*, 2568. (d) Werner, H.; Leonhard, K.; Burschka, Ch. *J. Organomet. Chem.* **1978**, *160*, 291. Fachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1979**, 1612.

(4) Lisy, J. M.; Dobrzynsky, E. D.; Angelici, R. J.; Clardy, J. *J. Am. Chem. Soc.* **1975**, *97*, 656.

(5) (a) Mealli, C.; Midollini, S.; Sacconi, L. *Inorg. Chem.* **1975**, *14*, 2513. (b) Dapporto, P.; Midollini, S.; Orlandini, A.; Sacconi, L. *Ibid.* **1976**, *15*, 2768. (c) Benelli, C.; Di Vaira, M.; Noccioli, G.; Sacconi, L. *Ibid.* **1977**, *16*, 182.

(6) (a) Di Vaira, M.; Midollini, S.; Sacconi, L. *J. Am. Chem. Soc.* **1979**, *101*, 1757. (b) Bianchini, C.; Dapporto, P.; Meli, A.; Sacconi, L. *J. Organomet. Chem.*, in press.

(7) Bianchini, C.; Meli, A.; Orlandini, A.; Sacconi, L. *Inorg. Chim Acta* **1979**, *35*, L375.

(8) Bianchini, C.; Mealli, C.; Meli, A.; Orlandini, A.; Sacconi, L. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 673.

(9) Hewertson, W.; Watson, H. R. *J. Chem. Soc.* **1962**, 1490.

(10) (a) Sacconi, L.; Morassi, R. *J. Chem. Soc. A* **1968**, 2997. (b) Sacconi, L.; Bertini, I.; Mani, F. *Inorg. Chem.* **1968**, *7*, 1417.

Table I. Analytical and Physical Data of the Complexes

compd	% calcd C	% calcd H	% calcd Co	% calcd S	% found C	% found H	% found Co	% found S	μ_{eff} (293 K), μ_B
[(triphos)Co(CS_2)]	66.39	5.17	7.75	8.44	66.04	5.24	7.63	8.22	1.91
[(triphos)Co(CS_2)Cr$(CO)_5$]·0.25CH_2Cl_2 [a]	58.32	4.09	6.05	6.59	57.47	4.12	5.85	6.38	1.95
[(triphos)Co(CS_2)Mn(C_5H_5)$(CO)_2$] [b]	62.89	4.74	6.30	6.85	62.75	5.17	6.10	6.65	2.18
[(triphos)Co(CS_2)Co(triphos)]$(BPh_4)_2$·2$(CH_3)_2$CO [c]	74.86	5.96	5.36	2.92	75.01	6.06	5.25	2.92	

[a] Calcd: Cr, 5.34. Found: Cr, 5.00. [b] Calcd: Mn, 5.87. Found: Mn, 5.52. [c] Molar conductance value for a ca. 10^{-3} M nitroethane solution: 94 $cm^2\ \Omega^{-1}\ mol^{-1}$.

Table II. Maxima and Extinction Coefficients for the Electronic Spectra of the Complexes

compd	state [a]	abs max, μm^{-1} (ϵ_M for soln)
[(triphos)Co(CS_2)]	a	0.88, 1.28, 1.96 sh, 2.44 sh
	b	0.91 (270), 1.30 (431), 1.96 (915)
[(triphos)Co(CS_2)Cr$(CO)_5$]·0.25CH_2Cl_2	a	0.90, 1.33, 1.94 sh, 2.50 sh
	b	0.90 (298), 1.31 (680), 1.77 (848)
[(triphos)Co(CS_2)Mn(C_5H_5)$(CO)_2$]	a	0.90, 1.15, 1.72 sh, 2.10 sh
	b	0.92 (275), 1.17 (435), 1.74 sh
[(triphos)Co(CS_2)Co(triphos)]$(BPh_4)_2$·2$(CH_3)_2$CO	a [b]	
	c	1.28 (7100), 1.59 (4110), 1.96 (5079)

[a] Key: a, solid at room temperature; b, methylene chloride solution; c, 1,2-dichloroethane solution. [b] Unresolved absorption between 1.00 and 2.50 μm^{-1}.

Method III. $NaBH_4$ (2.5 mmol) in ethanol (30 mL) was added at room temperature to a mixture of **4** (1 mmol) in acetone (40 mL) in the presence of an excess of carbon disulfide. The resulting solution was concentrated in a stream of nitrogen until crystals of **1** appeared.

If carbon disulfide is not added to the above reaction mixture, red crystals having the formula [(triphos)Co(CS_2)]·[(triphos)Co(BH_4)] (**5**) are obtained.

[(triphos)Co(μ-CS_2)Cr$(CO)_5$]·0.25CH_2Cl_2 (2). A solution of [Cr$(CO)_5$(THF)] formed in situ by UV irradiation of the corresponding hexacarbonyl complex[11] (0.87 mmol) in tetrahydrofuran (60 mL) was added under nitrogen to a solution of **1** (0.66 mmol) in tetrahydrofuran (250 mL) which had been stored at −10 °C. The reaction mixture was kept for 6 h at room temperature. The solvent was removed under vacuum and the resulting residue extracted with methylene chloride (40 mL). On addition of ethanol (30 mL) followed by slow evaporation of the solvent, black crystals appeared which were separated by filtration and washed with a 1:1 butyl ether–ethanol mixture and petroleum ether. They were recrystallized from methylene chloride/ethanol.

[(triphos)Co(μ-CS_2)Mn(η^5-C_5H_5)$(CO)_2$] (3). This compound was obtained by a procedure analogous to the one above except for the substitution of [(η^5-C_5H_5)Mn$(CO)_2$(THF)] for the chromium derivative. The red-brown crystals so obtained were recrystallized from acetone/isopropyl alcohol.

[(triphos)Co(μ-CS_2)Co(triphos)]$(BPh_4)_2$·2$(CH_3)_2$CO (4). Method I. Carbon disulfide vapors were bubbled for 5 min into a hot mixture of triphos (1 mmol) in acetone (40 mL) and Co$(BF_4)_2$·6H_2O (1 mmol) in butanol (30 mL). On addition of $NaBPh_4$ (1 mmol) in ethanol (20 mL) and slow evaporation of the solvent, dark brown crystals were formed which were separated by filtration and washed with butanol and petroleum ether. They were recrystallized from acetone/ethanol.

Method II. A solution of **1** (1 mmol) in methylene chloride (20 mL) was allowed to react with a mixture of Co$(BF_4)_2$·6H_2O (1 mmol) in butanol (20 mL) and of triphos (1 mmol) in methylene chloride (20 mL). $NaBPh_4$ (2 mmol) in ethanol (20 mL) was added. Following concentration, crystals of **4** precipitated and were washed as above. They were recrystallized from acetone/ethanol. Analytical and spectroscopic data are reported in Tables I and II.

Collection and Reduction of X-ray Intensity Data. All three compounds were studied on a Philips fully automatic computer-controlled diffractometer, using Mo Kα radiation, monochromatized with a flat graphite crystal. The crystals of compounds **2** and **4** used for X-ray analysis were coated in paraffin to prevent the decomposition which would result from contact with the air. The unit cell parameters were obtained and refined from the information gathered by using the "peak-hunting" procedure after suitable crystals of each compound had been positioned in a random orientation in the center of the instrument. Details of the crystal data and data collection for the three compounds are given in Table III. After correction for background, the standard deviations $\sigma(I)$ of the intensities I were calculated as described elsewhere,[12] with use of values for the instability factor k of 0.03, 0.04, and 0.03 for complexes **1**, **2**, and **4**, respectively. The data were corrected for Lorentz–polarization effects and an absorption correction was applied to F_o values for complexes **1** and **4**. The transmission factors are in the ranges 0.95–0.86 and 0.90–0.85 for **1** and **4**, respectively. No absorption correction could be applied to complex **2** due to difficulties in indexing the crystal faces.

Solution and Refinement of the Structures. The calculations were carried out by using the XRY72 and the SHELX76 crystallographic programs, either on the CII 10070 or on the CDC 7600 computer. Atomic scattering factors and dispersion corrections, as well as absorption corrections, were taken from ref 13 for crystals **1** and **4**, while they were taken from ref 14 for crystal **2**. The refinement was based on F_o, the function minimized being $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$. The agreement factors are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum(w|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

[(triphos)Co(π-CS_2)] (1). The structure determination was carried out starting from the atomic positions of the isomorphous structure of [Ni(triphos)(SO_2)].[5b] A difference Fourier synthesis revealed the positions of the atoms of the CS_2 group. Full-matrix least-squares refinement was undertaken with two isotropic cycles on all nonhydrogen atoms; then further refinement was carried out with the assignment of anisotropic temperature factors to cobalt, sulfur, and phosphorus atoms. Throughout the refinement, the phenyl rings were treated as rigid groups of D_{6h} symmetry. At this point the hydrogen atoms were introduced at their calculated positions but were not refined. Due to the polar nature of the $Pn2_1a$ space group, two possible orientations of the structure (x, y, z and $x, \bar{y}, z$) were considered and the absolute configuration was determined by applying the anomalous dispersion corrections. A final least-squares cycle led to convergence at the discrepancy indices $R = 0.051$ and $R_w = 0.055$ for x, y, z and $R = 0.053$ and $R_w = 0.057$ for $x, \bar{y}, z$ respectively.

[(triphos)Co(μ-CS_2)Cr$(CO)_5$]·0.25CH_2Cl_2 (2). The structure analysis, which required the determination of two independent molecules of [(triphos)Co(μ-CS_2)Cr$(CO)_5$] for the asymmetric unit, was solved by the heavy-atom method. A three-dimensional Patterson synthesis revealed the positions of the two cobalt atoms of the asymmetric unit. Successive Fourier maps yielded the positions of all nonhydrogen atoms. Atoms belonging to a methylene chloride molecule were detected at this stage. According to the results of elemental analysis, the atoms of the solvent molecule were allotted

---

(11) Fisher, E. O.; Herberhold, M. *Experientia, Suppl.* **1964**, *No. 9*, 259.

(12) Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197.

(13) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV: (a) p 99; (b) p 61.

(14) (a) Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104. (b) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175. (c) Cromer, D. T. *Acta Crystallogr.* **1965**, *18*, 17.

Table III. Crystal Data and Data Collection Details

	[(triphos)Co(π-CS_2)]	[(triphos)Co(μ-CS_2)Cr$(CO)_5$]·$0.25CH_2Cl_2$	[(triphos)Co(μ-CS_2)Co(triphos)]-$(BPh_4)_2$·$2(CH_3)_2CO$
mol formula	$C_{42}H_{39}CoP_3S_2$	$C_{47.25}H_{39.5}Cl_{0.5}CoCrO_5P_3S_2$	$C_{137}H_{110}Co_2B_2O_2P_6S_2$
mol wt	759.76	1946.08	2198.02
a, b, c, Å	21.035 (9), 17.090 (8), 10.283 (5)	25.23 (2), 18.43 (1), 22.19 (2)	18.120 (4), 14.074 (4), 12.705 (3)
α, β, γ, deg	90, 90, 90	90, 114.8 (3), 90	91.3 (2), 106.1 (3), 111.8 (3)
d_{obsd} (flot), g cm^{-3}	1.36	1.37	1.27
d_{calcd}, g cm^{-3}	1.365	1.380	1.275
V, $Å^3$	3696.62	9363.91	2860.64
Z	8	8	1
space group	$Pn2_1a$	$P2_1/n$	$P\bar{1}$
abs coeff, μ(Mo Kα), cm^{-1}	7.27	8.37	4.58
color	garnet red	black	dark brown
habit	parallelepiped	irregular prism	prism
dimens, mm	0.2 × 0.2 × 0.3	0.15 × 0.5 × 0.3	0.12 × 0.18 × 0.28
λ(Mo Kα)	0.7107	0.7107	0.7107
monochromator	flat graphite crystal	flat graphite crystal	flat graphite crystal
attenuator	not used	not used	not used
takeoff angle, deg	3	3	3
method	ω-2θ scan	ω-2θ scan	ω-2θ scan
scan speed, deg/s	0.08	0.07	0.07
scan width, deg	0.8	(0.7 + 0.69 to θ)	0.7
bkgd time	half the scan time	half the scan time	half the scan time
stds	3 every 120 min	3 every 120 min	3 every 120 min
max dev stand, %	7	15	10
2θ limits, deg	$6 \leqslant 2\theta \leqslant 40$	$5 \leqslant 2\theta \leqslant 40$	$6 \leqslant 2\theta$ 40
no. of data used ($I \geqslant 3\sigma(I)$)	2205	3614	4187

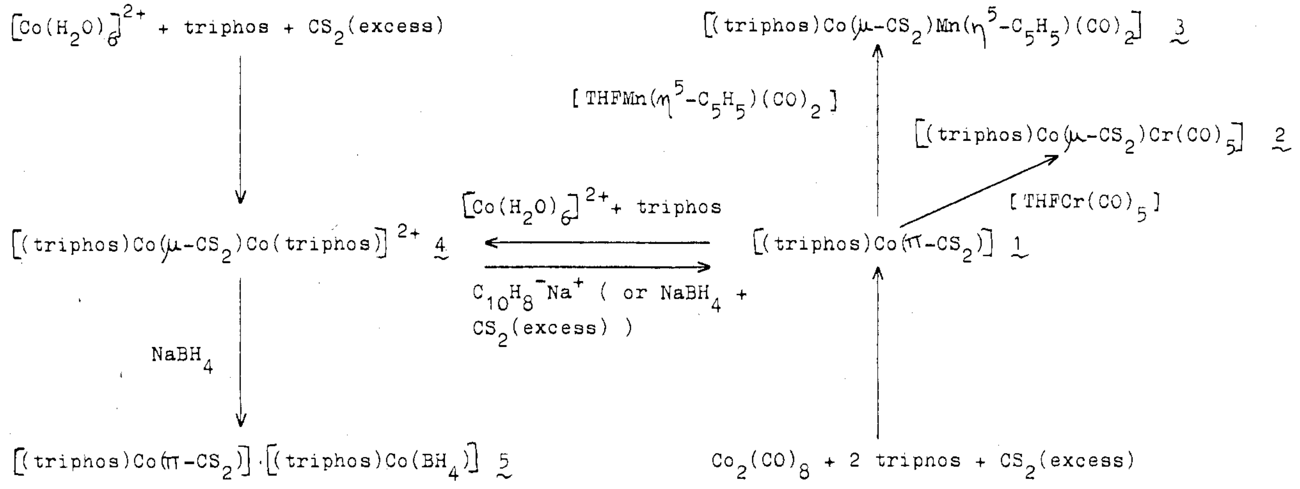

Figure 1. Flow diagram illustrating the preparations and the reactions of the complexes described.

a population parameter of 0.5, which was not varied. Owing to the large number of parameters to be refined, the refinement was carried out by blocking the least-squares matrix and constraining the phenyl rings as rigid bodies of D_{6h} symmetry. Hydrogen atoms were introduced in their calculated positions and not varied. Cobalt, chromium, phosphorus, and sulfur atoms were assigned anisotropic temperature vibrations. At convergence, the final residuals *R* and R_w were 0.079 and 0.088, respectively.

[(triphos)Co(μ-CS_2)Co(triphos)]$(BPh_4)_2$·$2(CH_3)_2CO$ (4). The cobalt atom was located from an inspection of a three-dimensional Patterson function, and all the other nonhydrogen atoms were found from successive Fourier syntheses. The process of structure solution and refinement was successfully carried out in the triclinic space group $P\bar{1}$, even though the ratio CS_2 fragment/Co(triphos)BPh_4 equal to $^1/_2$ was hardly consistent with the assumed presence of a center of inversion. In fact at the final stage of refinement this problem came out imperatively and was solved by rationalizing the arrangement of the CS_2 fragment with respect to the center of inversion. An attempt to operate in the acentric space group *P*1 was unsuccessfull due to the high correlation coefficients between most atomic parameters since a center of symmetry actually operates between all the non-CS_2 atoms. Thus, all of these atoms were satisfactorily refined by using the usual least-squares methods in space group $P\bar{1}$ down to an *R* factor of about 0.12. F_o and ΔF Fouriers calculated at this stage showed a zigzag chain of four peaks astride the center of symmetry. These peaks had approximately the same height and the two inner ones were 1.8 Å apart. This pattern was misleading and even the formation of a new CSSC or SCCS fragment could not be ruled out in principle. As one can infer, the problem of disorder in this region can have more than one solution. We have found that the most rational one from both the crystallographic and chemical point of view is the following. We have assumed that a CS_2 molecule is bonded to the two metal atoms in two different modes (see Discussion). Therefore the two metals in each individual dimer are not equivalent, but they are equivalent when all the dimers in the crystal are considered. From a crystallographic point of view this was obtained by assigning a 0.5 population parameter to each atom of the CS_2 unit and by allowing the center of inversion to be operative over these atoms. By use of this treatment the refinement produced a further lowering of the *R* and R_w factors down to 0.076 and 0.084, respectively. The correctness of this treatment was further demonstrated by the chemical significance of the bond distances and angles within the Co(CS_2)Co skeleton. Through the refinement, anisotropic temperature factors were assigned to cobalt, sulfur, and phosphorus atoms. Hydrogen atoms, introduced in the geometrical positions, were not refined. The phenyl rings of the ligand and of the tetraphenylborate ion were treated as rigid bodies

Table IV. Atomic[a] Parameters (×10^4) for the Structure of [(triphos)Co(π-CS_2)]

atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co	−645 (1)	−1321[b]	664 (1)	359 (6)	353 (6)	332 (6)	8 (8)	−12 (6)	−48 (7)
P1	381 (1)	−1267 (2)	1268 (2)	351 (12)	357 (12)	365 (12)	18 (15)	3 (10)	−25 (14)
P2	−547 (1)	−131 (2)	−209 (3)	378 (13)	350 (14)	340 (13)	5 (12)	−5 (11)	−3 (12)
P3	−965 (1)	−835 (2)	2558 (2)	347 (12)	384 (12)	299 (11)	23 (11)	10 (11)	−45 (12)
S1	−780 (2)	−2474 (3)	−259 (4)	787 (22)	433 (17)	730 (22)	−154 (17)	−195 (19)	−10 (16)
S2	−2135 (2)	−1868 (3)	−166 (4)	538 (20)	1297 (38)	1201 (33)	−355 (31)	−170 (23)	−274 (23)

atom	x/a	y/b	z/c	U, Å^2	atom	x/a	y/b	z/c	U, Å^2
C1	364 (5)	970 (6)	2918 (10)	483 (27)	C4	−338 (4)	580 (6)	1094 (9)	354 (22)
C2	63 (4)	249 (6)	2225 (9)	366 (22)	C5	−339 (4)	−181 (6)	3237 (9)	362 (22)
C3	619 (4)	−272 (6)	1766 (9)	391 (23)	C	−1374 (5)	−1846 (7)	60 (10)	531 (28)

[a] The form of the ellipsoid is $\exp(-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + \ldots))$. [b] This value was chosen to have accordance with the y coordinate of the [Ni(triphos)SO_2] complex.[5b]

Table V. Thermal and Derived Positional Parameters (×10^4) of Group Atoms for the Structure of [(triphos)Co(π-CS_2)]

atom	x/a	y/b	z/c	U, Å^2
C1,1	570 (3)	−1893 (3)	2693 (6)	370 (22)
C2,1	1098 (3)	−1768 (3)	3488 (6)	491 (27)
C3,1	1236 (3)	−2292 (3)	4488 (6)	631 (29)
C4,1	847 (3)	−2942 (3)	4694 (6)	598 (24)
C5,1	319 (3)	−3066 (3)	3898 (6)	577 (25)
C6,1	181 (3)	−2542 (3)	2898 (6)	489 (26)
C1,2	1023 (3)	−1545 (4)	141 (6)	435 (25)
C2,2	1633 (3)	−1230 (4)	246 (6)	549 (27)
C3,2	2112 (3)	−1474 (4)	−599 (6)	654 (33)
C4,2	1981 (3)	−2034 (4)	−1550 (6)	734 (37)
C5,2	1372 (3)	−2349 (4)	−1655 (6)	729 (38)
C6,2	893 (3)	−2105 (4)	−810 (6)	556 (28)
C1,3	93 (4)	−47 (4)	−1437 (7)	375 (22)
C2,3	507 (4)	589 (4)	−1516 (7)	640 (34)
C3,3	977 (4)	606 (4)	−2472 (7)	851 (38)
C4,3	1033 (4)	−13 (4)	−3349 (7)	818 (41)
C5,3	619 (4)	−649 (4)	−3270 (7)	752 (38)
C6,3	149 (4)	−666 (4)	−2314 (7)	600 (31)
C1,4	−1194 (3)	379 (4)	−1083 (6)	401 (22)
C2,4	−1268 (3)	1189 (4)	−1022 (6)	530 (28)
C3,4	−1760 (3)	1551 (4)	−1704 (6)	604 (32)
C4,4	−2178 (3)	1102 (4)	−2447 (6)	566 (30)
C5,4	−2104 (3)	292 (4)	−2508 (6)	672 (34)
C6,4	−1612 (3)	−70 (4)	−1826 (6)	539 (27)
C1,5	−1129 (3)	−1533 (4)	3878 (6)	348 (22)
C2,5	−919 (3)	−1426 (4)	5152 (6)	545 (28)
C3,5	−1067 (3)	−1977 (4)	6105 (6)	674 (34)
C4,5	−1426 (3)	−2636 (4)	5785 (6)	583 (30)
C5,5	−1636 (3)	−2744 (4)	4511 (6)	620 (33)
C6,5	−1488 (3)	−2192 (4)	3558 (6)	509 (28)
C1,6	−1678 (3)	−200 (4)	2693 (5)	538 (27)
C2,6	−1814 (3)	187 (4)	3855 (5)	513 (28)
C3,6	−2339 (3)	683 (4)	3933 (5)	672 (34)
C4,6	−2728 (3)	793 (4)	2849 (5)	738 (37)
C5,6	−2592 (3)	407 (4)	1687 (5)	721 (37)
C6,6	−2067 (3)	−90 (4)	1609 (5)	538 (27)

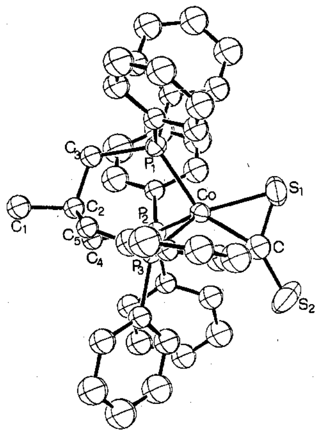

Figure 2. Perspective view of the complex molecule [(triphos)Co(π-CS_2)]. ORTEP diagram showing 30% probability ellipoids.

of D_{6h} symmetry. An acetone molecule, detected from a difference Fourier map, was refined as a rigid group.

Tables IV–X report final atomic parameters for all the compounds. Listings of F_o and F_c are available as supplementary material.

Results and Discussion

The preparations and the reactions of the complexes described in this paper are reported in Figure 1.

The sections below discuss, in turn, the relevant chemical and spectroscopic properties of all complexes and the structural results of **1**, **2**, and **4**. Figures 2 and 4 report the perspective views of the complexes **1** and **4**, respectively. Figure 3 shows the two independent complex molecules A and B of complex **2**. Tables XI–XIII give selected bond lengths and bond angles for complexes **1**, **2**, and **4**, respectively.

[(triphos)Co(π-CS_2)] (1). This garnet red complex is quite air stable in the solid state but rather unstable in solution. It

Table VI. Atomic[a] Parameters (×10^4) for the Structure [(triphos)Co(μ-CS_2)Cr(CO)$_5$]·0.2CH_2Cl_2

atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co1	3016 (1)	2527 (2)	3182 (2)	378 (17)	478 (19)	438 (23)	17 (19)	157 (17)	−15 (16)
Co2	1536 (1)	2011 (2)	7111 (2)	456 (18)	512 (21)	509 (24)	55 (20)	244 (18)	54 (16)
Cr1	908 (1)	1721 (2)	1480 (2)	464 (23)	733 (29)	676 (32)	28 (26)	99 (23)	−3 (20)
Cr2	440 (2)	3441 (2)	4897 (2)	713 (27)	738 (29)	667 (33)	66 (28)	228 (25)	105 (23)
S1	2318 (3)	1855 (4)	3214 (3)	785 (48)	1300 (66)	596 (55)	118 (51)	197 (44)	−467 (47)
S2	1886 (2)	2165 (4)	1732 (3)	526 (40)	941 (52)	491 (48)	−32 (45)	130 (37)	−147 (37)
S3	819 (3)	2821 (3)	6730 (3)	815 (48)	813 (51)	934 (61)	347 (48)	576 (47)	347 (40)
S4	1337 (3)	2875 (4)	5712 (3)	634 (41)	969 (55)	701 (53)	278 (47)	384 (40)	268 (40)
P1	3570 (2)	2757 (3)	4249 (3)	434 (35)	437 (41)	450 (47)	−3 (38)	171 (35)	6 (31)
P2	3001 (2)	3689 (3)	2950 (3)	407 (35)	482 (40)	445 (48)	18 (38)	168 (35)	3 (31)
P3	3788 (2)	2281 (3)	2976 (3)	417 (34)	545 (44)	501 (47)	−45 (40)	228 (35)	−44 (32)
P4	1392 (3)	1332 (3)	7857 (3)	667 (43)	456 (43)	612 (52)	35 (41)	348 (41)	36 (36)
P5	2459 (2)	2240 (3)	7824 (3)	560 (37)	384 (41)	581 (51)	85 (39)	281 (38)	12 (32)
P6	1756 (2)	1034 (3)	6699 (3)	516 (38)	516 (42)	511 (49)	31 (40)	258 (38)	53 (33)

[a] The form of the thermal ellipsoid is $\exp(-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + \ldots))$.

Table VII. Atomic Parameters for the Structure of [(triphos)Co(μ-CS_2)Cr$(CO)_5$]·0.25CH_2Cl_2 (All Quantities ×10^4)

atom	*x/a*	*y/b*	*z/c*	*U*, Å^2
O6	1020 (8)	650 (11)	512 (10)	1159 (72)
O7	773 (9)	2799 (12)	2438 (11)	1448 (85)
O8	1331 (7)	617 (10)	2578 (9)	890 (62)
O9	512 (8)	2931 (11)	459 (10)	1087 (72)
O10	−283 (8)	1149 (10)	1135 (9)	997 (65)
O17	1089 (8)	4714 (11)	4695 (10)	1179 (75)
O18	−279 (9)	2252 (12)	5087 (11)	1408 (84)
O19	212 (9)	4362 (12)	5880 (11)	1282 (85)
O20	600 (13)	2548 (17)	3864 (15)	2152 (136)
O21	−657 (9)	4032 (11)	3900 (10)	1197 (74)
C1	4809 (9)	4074 (11)	4000 (11)	592 (69)
C2	4260 (8)	3582 (12)	3738 (11)	430 (67)
C3	4252 (8)	3237 (11)	4376 (10)	466 (64)
C4	3732 (8)	4107 (11)	3380 (10)	486 (64)
C5	4319 (8)	3022 (11)	3267 (11)	545 (68)
C6	975 (11)	1057 (15)	889 (14)	818 (94)
C7	821 (12)	2357 (16)	2086 (15)	1033 (103)
C8	1181 (10)	1028 (14)	2172 (14)	769 (87)
C9	637 (11)	2468 (15)	799 (14)	741 (91)
C10	171 (12)	1407 (15)	1274 (14)	894 (94)
C11	2322 (8)	2178 (11)	2521 (10)	482 (67)
C12	2921 (9)	101 (12)	8464 (11)	677 (75)
C13	2493 (10)	695 (13)	8047 (13)	633 (81)
C14	1913 (9)	584 (11)	8136 (11)	582 (71)
C15	2755 (9)	1461 (12)	8352 (11)	629 (71)
C16	2400 (8)	620 (11)	7331 (11)	492 (69)
C17	856 (11)	4208 (16)	4755 (14)	912 (95)
C18	10 (14)	2686 (17)	4987 (16)	1095 (108)
C19	320 (12)	4028 (17)	5521 (16)	1093 (111)
C20	552 (15)	2884 (20)	4276 (19)	1710 (150)
C21	−194 (14)	3784 (17)	4309 (16)	1124 (117)
C22	1280 (9)	2637 (12)	6385 (11)	523 (71)
C23	−23 (19)	4906 (25)	7350 (23)	708 (141)
Cl1	587 (7)	4427 (9)	7771 (8)	1114 (59)
Cl2	−24 (7)	5721 (9)	7326 (8)	1131 (58)

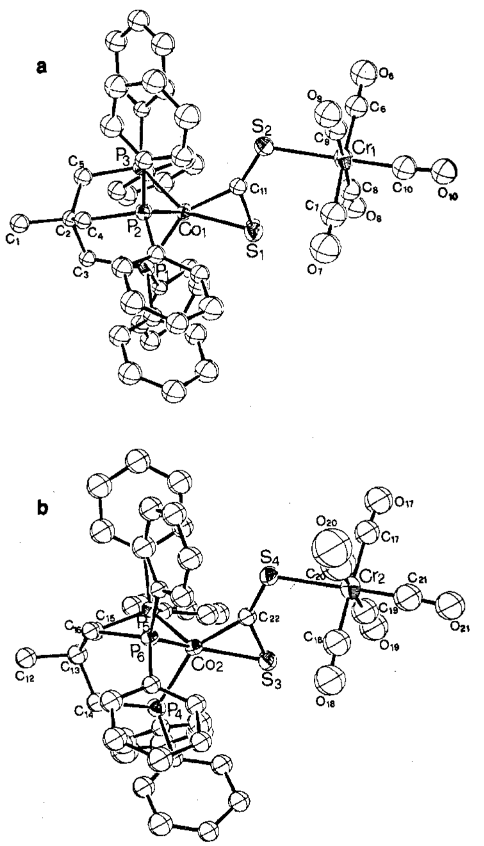

Figure 3. (a) Perspective view of the complex molecule A of [(triphos)Co(μ-CS_2)Cr$(CO)_5$]. (b) Perspective view of the complex molecule B of [(triphos)Co(μ-CS_2)Cr$(CO)_5$].

Table VIII. Thermal and Derived Positional Parameters of Group Atoms for the Structure of [(triphos)Co(μ-CS_2)Cr$(CO)_5$]·0.25CH_2Cl_2 (×10^4)

atom	*x/a*	*y/b*	*z/c*	*U*, Å^2
C1,1	3810 (6)	2017 (8)	4822 (17)	403 (61)
C2,1	4098 (6)	2187 (8)	5493 (7)	609 (75)
C3,1	4271 (6)	1637 (8)	5966 (7)	761 (78)
C4,1	4157 (6)	915 (8)	5768 (7)	780 (79)
C5,1	3870 (6)	745 (8)	5096 (7)	815 (87)
C6,1	3697 (6)	1295 (8)	4623 (7)	639 (72)
C1,2	3215 (6)	3332 (8)	4638 (8)	576 (72)
C2,2	2747 (6)	3001 (9)	4706 (8)	749 (82)
C3,2	2413 (6)	3393 (9)	4957 (8)	887 (91)
C4,2	2547 (6)	4115 (9)	5141 (8)	883 (86)
C5,2	3015 (6)	4446 (9)	5073 (8)	846 (89)
C6,2	3349 (6)	4054 (9)	4821 (8)	738 (78)
C1,3	2769 (7)	3933 (7)	2067 (6)	515 (70)
C2,3	2167 (7)	3968 (7)	1696 (6)	728 (76)
C3,3	1941 (7)	4139 (7)	1023 (6)	966 (92)
C4,3	2316 (7)	4275 (7)	722 (6)	866 (85)
C5,3	2918 (7)	4240 (7)	1094 (6)	838 (81)
C6,3	3144 (7)	4069 (7)	1766 (6)	820 (79)
C1,4	2536 (5)	4267 (8)	3180 (7)	503 (68)
C2,4	2640 (5)	5010 (8)	3269 (7)	659 (72)
C3,4	2279 (5)	5445 (8)	3449 (7)	848 (85)
C4,4	1815 (5)	5138 (8)	3541 (7)	692 (79)
C5,4	1710 (5)	4395 (8)	3451 (7)	883 (87)
C6,4	2071 (5)	3960 (8)	3271 (7)	520 (67)
C1,5	3759 (6)	2148 (7)	2153 (7)	450 (64)
C2,5	3260 (6)	2328 (7)	1590 (7)	695 (75)
C3,5	3256 (6)	2262 (7)	963 (7)	894 (88)
C4,5	3752 (6)	2016 (7)	900 (7)	787 (81)
C5,5	4251 (6)	1835 (7)	1464 (7)	792 (85)
C6,5	4255 (6)	1901 (7)	2090 (7)	728 (75)
C1,6	4160 (6)	1464 (7)	3397 (7)	501 (65)
C2,5	4698 (6)	1457 (7)	3946 (7)	666 (75)
C3,6	4933 (6)	804 (7)	4260 (7)	882 (81)
C4,6	4630 (6)	158 (7)	4025 (7)	824 (81)
C5,6	4091 (6)	166 (7)	3476 (7)	796 (78)
C6,6	3856 (6)	818 (7)	3162 (7)	591 (68)
C1,7	683 (5)	908 (9)	7599 (6)	464 (65)
C2,7	199 (5)	1336 (9)	7233 (6)	661 (72)
C3,7	−356 (5)	1029 (9)	6959 (6)	680 (75)
C4,7	−428 (5)	295 (9)	7052 (6)	625 (75)
C5,7	56 (5)	−133 (9)	7419 (6)	876 (87)
C6,7	611 (5)	174 (9)	7692 (6)	737 (81)
C1,8	1408 (6)	1782 (10)	8614 (7)	530 (65)
C2,8	1709 (6)	1452 (10)	9229 (7)	1201 (88)
C3,8	1792 (6)	1821 (10)	9809 (7)	1417 (105)
C4,8	1573 (6)	2521 (10)	9774 (7)	1123 (90)
C5,8	1272 (6)	2851 (10)	9160 (7)	1210 (100)
C6,8	1189 (6)	2482 (10)	8579 (7)	999 (80)
C1,9	2575 (8)	2954 (8)	8418 (8)	500 (70)
C2,9	3051 (8)	2945 (8)	9036 (8)	722 (79)
C3,9	3146 (8)	3525 (8)	9471 (8)	959 (91)
C4,9	2765 (8)	4113 (8)	9288 (8)	897 (91)
C5,9	2289 (8)	4122 (8)	8670 (8)	903 (88)
C6,9	2194 (8)	3542 (8)	8235 (8)	789 (84)
C1,10	3001 (7)	2513 (9)	7516 (7)	453 (63)
C2,10	3550 (7)	2189 (9)	7744 (7)	984 (93)
C3,10	3945 (7)	2407 (9)	7492 (7)	989 (99)
C4,10	3791 (7)	2948 (9)	7011 (7)	954 (98)
C5,10	3243 (7)	3272 (9)	6782 (7)	938 (94)
C6,10	2848 (7)	3054 (9)	7035 (7)	702 (78)
C1,11	1177 (6)	353 (8)	6419 (6)	501 (69)
C2,11	609 (6)	611 (8)	6088 (6)	580 (71)
C3,11	143 (6)	126 (8)	5847 (6)	623 (74)
C4,11	246 (6)	−617 (8)	5935 (6)	889 (85)
C5,11	814 (6)	−875 (8)	6266 (6)	782 (84)
C6,11	1280 (6)	−390 (8)	6508 (6)	701 (76)
C1,12	1927 (7)	1087 (8)	5976 (7)	437 (64)
C2,12	2472 (7)	1329 (8)	6041 (7)	787 (82)
C3,12	2593 (7)	1367 (8)	5485 (7)	834 (84)
C4,12	2171 (7)	1164 (8)	4865 (7)	785 (81)
C5,12	1627 (7)	923 (8)	4800 (7)	791 (81)
C6,12	1505 (7)	885 (8)	5356 (7)	737 (80)

Table IX. Atomic[a] Parameters (× 10^4) for the Structure of [(triphos)Co(μ-CS_2)Co(triphos)]$(BPh_4)_2 \cdot 2CH_3$

atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co1	−1020 (1)	−1201 (1)	−1111 (1)	400 (7)	376 (7)	382 (7)	7 (5)	44 (5)	154 (5)
P1	−1515 (1)	−1530 (2)	−2953 (2)	568 (15)	443 (14)	386 (14)	35 (11)	126 (12)	115 (12)
P2	−2281 (1)	−1522 (2)	−1027 (2)	414 (14)	440 (14)	453 (14)	52 (11)	100 (11)	163 (11)
P3	−1151 (1)	−2823 (2)	−939 (2)	484 (14)	406 (13)	416 (14)	35 (11)	47 (11)	196 (11)
S1	−277 (4)	−116 (5)	507 (5)	415 (32)	583 (35)	344 (35)	9 (27)	129 (27)	95 (26)
S2	210 (3)	−207 (4)	−1452 (4)	504 (28)	678 (31)	439 (31)	−52 (26)	130 (24)	85 (24)

atom	x/a	y/b	z/c	U, Å^2	atom	x/a	y/b	z/c	U, Å^2
C1	−3562 (5)	−4321 (7)	−3242 (7)	614 (25)	C	484 (19)	432 (23)	−147 (25)	816 (75)
C2	−2778 (5)	−3347 (6)	−2593 (6)	435 (21)	O	−2661 (6)	3757 (8)	−929 (8)	1739 (38)
C3	−2502 (5)	−2663 (6)	−3460 (7)	509 (23)	C6	−3325 (6)	3304 (10)	−735 (9)	1357 (44)
C4	−3040 (5)	−2799 (6)	−1808 (7)	507 (22)	C7	−4141 (7)	3325 (16)	−1502 (13)	2335 (64)
C5	−2095 (5)	−3738 (6)	−1981 (7)	496 (22)	C8	−3333 (9)	2747 (11)	294 (10)	1625 (51)

[a] The form of the ellipsoid is $\exp(-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + \ldots))$.

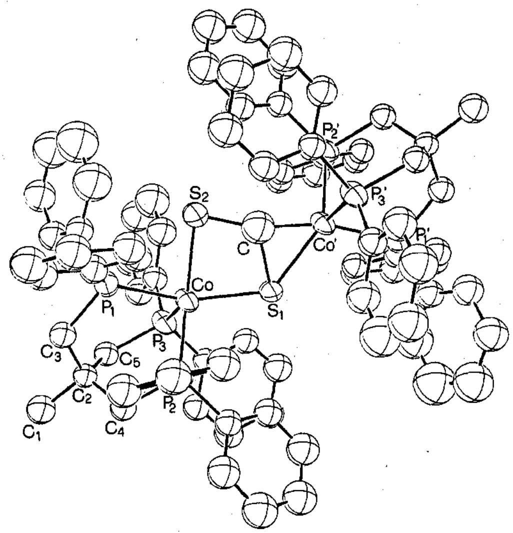

Figure 4. Perspective view of the complex cation [(triphos)Co(μ-CS_2)Co(triphos)]$^{2+}$.

has a low solubility in benzene and THF but dissolves fairly readily in methylene chloride and 1,2-dichloroethane in which it is nonconducting. The room-temperature μ_{eff} is equal to 1.91 μ_B (χ_M = 1536 × 10^{-6}), as expected for a d^9 configuration of the metal and 17 valence electrons.

The crystal and molecular structure consists of individual [(triphos)Co(π-CS_2)] molecules. The cobalt atom is five-coordinated by the three phosphorus atoms of the triphos ligand and by a CS_2 molecule through a C=S linkage. No bonding interaction between the cobalt atom and the second sulfur atom is envisaged. The overall geometry of the "planar" Co–CS_2 fragment resembles that found in other metal complexes, containing a terminally π-bonded CS_2 group.[3] In particular the C–S(1) and C–S(2) bond lengths (1.68 (1) and 1.62 (1) Å), although somewhat longer than the corresponding lengths found in the free CS_2 molecule (1.554 Å, average),[15] agree very well with those of the iron derivative (1.68 and 1.62 Å). The lenghthening of both the C–S(1) and C–S(2) distances with respect to the free molecule suggests that the π coordination of CS_2 reduces the bond order of both C–S bonds. This may result either from a charge transfer from the ligand to the metal or from an electron transfer from the metal to antibonding orbitals of the ligand. It is noteworthy that the S–C–S angle and the averaged value of the C–S bond lengths are very close to the values found for the free CS_2 molecule in the $^3A_2$ excited state (135.8° and 1.64 Å).[16]

Complex **1** is isomorphous with the metal complexes of general formula [(triphos)MX], where M = Co, Ni, or Cu and X = halogen, SO_2, BH_4, NO, SO_4, SeO_4, etc., whose crystal structures have already been determined.[5] The isomorphism of all such compounds clearly shows that the steric requirements of the (triphos)M moiety determine both the structure and the packing of these complexes, regardless of the chemical nature and size of the ancillary ligands. This is confirmed by the existence of the red paramagnetic product **5** obtained by reaction of **4** with $NaBH_4$. Elemental analysis and X-ray diffraction studies[17] carried out on this product showed that it is a solid solution of the two complexes [(triphos)Co(π-CS_2)] and [(triphos)Co(BH_4)], in the ratio of about 1:1.

The electronic spectrum of **1** is practically identical both in the solid state and in solution and has two bands at 0.88 and 1.28 μm^{-1}, respectively, and two shoulders at 1.96 and 2.44 μm^{-1}. The IR spectrum, as a Nujol mull, shows two bands at 1120 and 625 cm^{-1}. The higher frequency band is assigned to the out-of-ring ν(C=S) stretching vibration while the lower frequency band is assigned to the in-ring ν(C=S) stretching vibration. These data are comparable to those found for other π-CS_2 complexes.[18]

It is well-known that on complexation with the metal, the CS_2 molecule becomes more electron rich particularly at the sulfur atoms, and thus highly activated toward electrophilic reagents. In support of this we have found that **1** reacts with the cobalt(II) aquo cation in the presence of the triphos ligand giving the complex **4** and that the uncoordinated sulfur atom of **1**, behaving as a strong nucleophile, displaces the weakly coordinated tetrahydrofuran ligand from [Cr$(CO)_5$(THF)] and [(η^5-C_5H_5)Mn$(CO)_2$(THF)] leading to the complexes **2** and **3**.

[(triphos)Co(μ-CS_2)Cr$(CO)_5$]·0.25CH_2Cl_2 (2) and [(triphos)Co(μ-CS_2)Mn$(CO)_2$(η^5-C_5H_5)] (3). These complexes are black and red-brown, respectively, quite air stable in the solid state, and soluble in common organic solvents in which they are nonelectrolytes. The crystal and molecular structure of compound **2** consists of dinuclear complex molecules of [(triphos)Co(μ-CS_2)Cr$(CO)_5$] with methylene chloride molecules interspersed in the lattice. The CS_2 group has been found to bridge the (triphos)Co and the Cr$(CO)_5$ fragments. The cobalt atom is five-coordinated by the three phosphorus atoms of the triphos ligand and by the CS_2 molecule through a C=S linkage. The chromium atom shows a distorted octahedral geometry, being linked to five carbonyl groups and to the second sulfur atom of the CS_2 molecule, through a σ bond.

---

(15) Guenther, A. H. *J. Chem. Phys.* **1959**, *31*, 1095.

(16) Kleman, B. *Can. J. Phys.* **1963**, *41*, 2034.

(17) Bianchini, C.; Mealli, C.; Meli, A.; Orlandini, A.; Sacconi, L., unpublished results.

(18) Butler, I. S.; Fenster, A. E. *J. Organomet. Chem.* **1974**, *66*, 161.

Table X. Thermal and Derived Positional Parameters (×10^4) of Group Atoms for the Structure of [(triphos)Co(μ-CS$_2$)Co(triphos)](BPh$_4$)$_2$·2(CH$_3$)$_2$CO

atom	*x/a*	*y/b*	*z/c*	*U*, Å^2
C1,1	−832 (3)	−1773 (4)	−3642 (5)	574 (24)
C2,1	−905 (3)	−2771 (4)	−3942 (5)	670 (27)
C3,1	−311 (3)	−2916 (4)	−4355 (5)	809 (30)
C4,1	355 (3)	−2062 (4)	−4469 (5)	1118 (38)
C5,1	428 (3)	−1064 (4)	−4169 (5)	1393 (44)
C6,1	−166 (3)	−920 (4)	−3755 (5)	1126 (38)
C1,2	−1729 (3)	−486 (4)	−3636 (4)	531 (23)
C2,2	−1405 (3)	503 (4)	−3048 (4)	552 (23)
C3,2	−1613 (3)	1282 (4)	−3543 (4)	631 (26)
C4,2	−2145 (3)	1072 (4)	−4627 (4)	747 (28)
C5,2	−2468 (3)	82 (4)	−5216 (4)	817 (30)
C6,2	−2261 (3)	−697 (4)	−4720 (4)	726 (27)
C1,3	−2515 (3)	−1580 (4)	275 (5)	535 (23)
C2,3	−1939 (3)	−1557 (4)	1276 (5)	617 (25)
C3,3	−2162 (3)	−1628 (4)	2246 (5)	824 (30)
C4,3	−2962 (3)	−1722 (4)	2216 (5)	837 (31)
C5,3	−3539 (3)	−1746 (4)	1215 (5)	898 (32)
C6,3	−3315 (3)	−1675 (4)	244 (5)	777 (28)
C1,4	−2648 (3)	−530 (4)	−1567 (4)	460 (21)
C2,4	−2244 (3)	441 (4)	−924 (4)	576 (24)
C3,4	−2444 (3)	1265 (4)	−1297 (4)	683 (26)
C4,4	−3048 (3)	1119 (4)	−2315 (4)	713 (27)
C5,4	−3451 (3)	148 (4)	−2959 (4)	648 (26)
C6,4	−3251 (3)	−676 (4)	−2585 (4)	533 (23)
C1,5	−1246 (3)	−3248 (4)	383 (4)	486 (22)
C2,5	−2003 (3)	−3897 (4)	514 (4)	618 (25)
C3,5	−2044 (3)	−4139 (4)	1561 (4)	758 (29)
C4,5	−1328 (3)	−3731 (4)	2477 (4)	783 (30)
C5,5	−571 (3)	−3081 (4)	2345 (4)	729 (28)
C6,5	−530 (3)	−2840 (4)	1299 (4)	591 (24)
C1,6	−338 (4)	−3223 (4)	−1106 (5)	532 (23)
C2,6	372 (4)	−2515 (4)	−1304 (5)	736 (28)
C3,6	971 (4)	−2841 (4)	−1485 (5)	1049 (36)
C4,6	859 (4)	−3875 (4)	−1470 (5)	932 (33)
C5,6	150 (4)	−4584 (4)	−1272 (5)	887 (32)
C6,6	−449 (4)	−4257 (4)	−1091 (5)	710 (27)
C1,7	6141 (4)	3931 (4)	3060 (5)	532 (22)
C2,7	5554 (4)	3691 (4)	2011 (5)	761 (29)
C3,7	5380 (4)	4473 (4)	1477 (5)	1077 (36)
C4,7	5793 (4)	5497 (4)	1991 (5)	997 (35)
C5,7	6380 (4)	5737 (4)	3040 (5)	944 (33)
C6,7	6554 (4)	4955 (4)	3574 (5)	722 (27)
C1,8	5655 (3)	2640 (4)	4539 (5)	507 (22)
C2,8	5251 (3)	3258 (4)	4760 (5)	613 (25)
C3,8	4737 (3)	2957 (4)	5435 (5)	789 (29)
C4,8	4627 (3)	2039 (4)	5888 (5)	794 (29)
C5,8	5031 (3)	1422 (4)	5667 (5)	773 (29)
C6,8	5545 (3)	1722 (4)	4992 (5)	628 (26)
C1,9	7293 (4)	3491 (4)	4589 (4)	534 (23)
C2,9	7925 (4)	3865 (4)	4095 (4)	617 (25)
C3,9	8761 (4)	4247 (4)	4745 (4)	754 (29)
C4,9	8965 (4)	4255 (5)	5888 (4)	864 (31)
C5,9	8333 (4)	3881 (4)	6383 (4)	762 (29)
C6,9	7497 (4)	3499 (4)	5733 (4)	614 (25)
C1,10	6106 (3)	1943 (5)	2918 (5)	529 (23)
C2,10	5269 (3)	1338 (5)	2358 (5)	688 (26)
C3,10	5059 (3)	466 (5)	1613 (5)	908 (32)
C4,10	5685 (3)	199 (5)	1430 (5)	890 (32)
C5,10	6523 (3)	804 (5)	1990 (5)	833 (30)
C6,10	6733 (3)	1676 (5)	2734 (5)	612 (25)

The two independent but chemically equivalent complex molecules A and B show bond distances and angles very close to each other so that the structure will be discussed in terms of averaged values. The difference between A and B molecules is due to the different orientation of the triphos ligand with respect to the CS$_2$Cr(CO)$_5$ moiety, as evident just by looking at Figure 3.

The (triphos)Co(CS$_2$) moiety is essentially unchanged with respect to the mononuclear complex [(triphos)Co(π-CS$_2$)], the differences in bond lengths and angles being not significant.

Table XI. Selected Bond Lengths (Å) and Angles (Deg) for the Structure of [(triphos)Co(π-CS$_2$)]

Co–P1	2.247 (3)	P2–C4	1.86 (1)
Co–P2	2.232 (3)	P2–C1,3	1.85 (1)
Co–P3	2.222 (3)	P2–C1,4	1.85 (1)
Co–S1	2.206 (4)	P3–C5	1.86 (1)
Co–C	1.88 (1)	P3–C1,5	1.84 (1)
C–S1	1.68 (1)	P3–C1,6	1.86 (1)
C–S2	1.62 (1)	C1–C2	1.56 (1)
P1–C3	1.84 (1)	C2–C3	1.54 (1)
P1–C1,1	1.86 (1)	C2–C4	1.54 (1)
P1–C1,2	1.84 (1)	C2–C5	1.53 (1)
P1–Co–P2	89.2 (1)	P1–Co–C	153.3 (4)
P1–Co–P3	91.9 (1)	P2–Co–C	112.1 (4)
P2–Co–P3	92.3 (1)	P3–Co–C	102.7 (4)
P1–Co–S1	106.2 (1)	S1–Co–C	47.7 (4)
P2–Co–S1	130.7 (1)	S1–C–S2	133.8 (8)
P3–Co–S1	132.2 (1)	Co–C–S2	149.9 (8)

The Cr–S bond distance, averaging 2.444 (7) Å, although somewhat longer than the sum of the covalent radii, falls within the range of values reported for such kinds of bonds.[19] The values of both cis and trans Cr–C bond distances agree well with other known Cr–C distances.[20] The Cr–C bond distances for CO trans to sulfur atom is shorter than that of the CO cis. It is known that competition between the CO and the sulfur atom trans to it can take place with the formation of partial multiple bonding to the metal atom. Nevertheless the high disorder found in the region of the carbonyl groups does not allow here a deeper analysis.

The room-temperature magnetic moments of 1.95 and 2.18 μ_B (χ_M = 1576 and 2030 × 10^{-6}) for **2** and **3**, respectively, corresponding to doublet ground states, are in agreement with the existence of 17 valency electrons, supplied by the d^9 cobalt atom, the three phosphorus atoms of the triphos ligand, and the double bond of the CS$_2$ molecule. The reflectance spectra of complexes **2** and **3** are very similar to each other and to that of **1** showing absorptions in the region 0.80–2.50 μm^{-1} (Table II). The solution spectra are essentially identical with the reflectance spectra. The IR spectra of both compounds show a band at 1110 cm^{-1} attributable to the C=S stretch which agrees well with that found in other complexes containing the same kind of CS$_2$ bridge.[21] The absorption bands in the ν(CO) stretching region at 2055, 1982, 1930, and 1887 cm^{-1} and at 1915 and 1850 cm^{-1} for **2** and **3** are comparable respectively with those found in LCr(CO)$_5$ and LMn(CO)$_2$(η^5-C$_5$H$_5$) complexes.[22]

[(triphos)Co(μ-CS$_2$)Co(triphos)](BPh$_4$)$_2$·2(CH$_3$)$_2$CO (4). This dark brown compound is reasonably air stable in the solid state but decomposes rapidly in common organic solvents unless air is excluded. In this case it behaves as a 1:2 electrolyte (see Table I). It is diamagnetic and exhibits similar solution and reflectance spectra, which consist of a main absorption band in the region 1.00–2.50 μm^{-1}, split into three components (Table II).

The crystal and molecular structure consists of dimeric complex cations of [(triphos)Co(μ-CS$_2$)Co(triphos)]$^{2+}$, BPh$_4^-$ anions, and some amount of acetone molecules in the lattice. Two moieties of (triphos)Co are linked together by a CS$_2$ molecule, which coordinates a cobalt atom through a π C=S, linkage and the other cobalt atom through two σ bonds originating from the two sulfur atoms. The CoSC$_2$Co fragment is strictly planar.

---

(19) (a) Raubenheimer, H. G.; Boeyens, J. C. A.; Lotz, S. *J. Organomet. Chem.* **1976**, *112*, 145. (b) Baker, E. N.; Larsen, N. G. *J. Chem. Soc.* **1976**, 1769.

(20) Ghilardi, C. A.; Midollini, S.; Orlandini, A.; Sacconi, L. *Inorg. Chem.*, in press, and references therein.

(21) (a) Oehmichen, U.; Southern, T. G.; Le Bozec, H.; Dixneuf, P. *J. Organomet. Chem.* **1978**, *156*, C29. (b) Herberhold, M.; Suss-Fink, M. *Chem. Ber.* **1978**, *111*, 2273.

(22) (a) Dobson, G. R.; Stoltz, I. W.; Sheline, R. K. *Adv. Inorg. Chem. Radiochem.* **1966**, *8*, 1. (b) Strohmeir, W.; Guttenberger, J. F.; Hellman, M. *Z. Naturforsch., B* **1964**, *19*, 353.

Table XII. Selected Bond Lengths (Å) and Angles (Deg) for the Structure of $[(triphos)Co(\mu\text{-}CS_2)Cr(CO)_5]\cdot 0.25CH_2Cl_2$

molecule A		molecule B	
Co1–P1	2.228 (6)	Co2–P4	2.224 (8)
Co1–P2	2.200 (6)	Co2–P5	2.236 (5)
Co1–P3	2.226 (7)	Co2–P6	2.193 (7)
Co1–S1	2.180 (8)	Co2–S3	2.220 (7)
Co1–C11	1.87 (2)	Co2–C22	1.86 (2)
Cr1–S2	2.430 (7)	Cr2–S4	2.458 (6)
Cr1–C6	1.85 (3)	Cr2–C17	1.87 (3)
Cr1–C7	1.87 (3)	Cr2–C18	1.82 (3)
Cr1–C8	1.89 (3)	Cr2–C19	1.88 (4)
Cr1–C9	1.94 (3)	Cr2–C20	1.83 (4)
Cr1–C10	1.81 (3)	Cr2–C21	1.70 (3)
S1–C11	1.65 (3)	S3–C22	1.67 (3)
S2–C11	1.63 (2)	S4–C22	1.62 (3)
P1–C3	1.85 (2)	P4–C14	1.82 (2)
P1–C1,1	1.79 (2)	P4–C1,7	1.81 (1)
P1–C1,2	1.82 (2)	P4–C1,8	1.86 (2)
P2–C4	1.85 (2)	P5–C15	1.80 (2)
P2–C1,3	1.85 (1)	P5–C1,9	1.80 (2)
P2–C1,4	1.81 (2)	P5–C1,10	1.84 (2)
P3–C5	1.83 (2)	P6–C16	1.81 (2)
P3–C1,5	1.81 (2)	P6–C1,11	1.83 (2)
P3–C1,6	1.81 (1)	P6–C1,12	1.83 (2)
C1–C2	1.55 (3)	C12–C13	1.54 (3)
C2–C3	1.56 (3)	C13–C14	1.57 (4)
C2–C4	1.57 (3)	C13–C15	1.58 (3)
C2–C5	1.52 (3)	C13–C16	1.51 (4)
C6–O6	1.16 (4)	C17–O17	1.14 (4)
C7–O7	1.17 (4)	C18–O18	1.17 (4)
C8–O8	1.11 (3)	C19–O19	1.13 (4)
C9–O9	1.10 (3)	C20–O20	1.15 (6)
C10–O10	1.16 (3)	C21–O21	1.23 (3)
P1–Co1–P2	90.3 (2)	P4–Co2–P5	91.5 (2)
P1–Co1–P3	92.6 (2)	P4–Co2–P6	89.8 (3)
P1–Co1–S1	103.2 (3)	P4–Co2–S3	107.5 (3)
P1–Co1–C11	149.8 (8)	P4–Co2–C22	152.4 (8)
P2–Co1–P3	94.7 (3)	P5–Co2–P6	94.6 (2)
P2–Co1–S1	128.7 (3)	P5–Co2–S3	125.6 (2)
P2–Co1–C11	103.4 (6)	P5–Co2–C22	112.1 (6)
P3–Co1–S1	132.9 (3)	P6–Co2–S3	134.5 (3)
P3–Co1–C11	112.5 (8)	P6–Co2–C22	101.7 (8)
S1–Co1–C11	47.5 (8)	S3–Co2–C22	47.4 (8)
S2–Cr1–C6	90.0 (9)	S4–Cr2–C17	92.1 (8)
S2–Cr1–C7	92.1 (9)	S4–Cr2–C18	90.1 (9)
S2–Cr1–C8	93.0 (8)	S4–Cr2–C19	94.9 (8)
S2–Cr1–C9	86.1 (8)	S4–Cr2–C20	86.0 (1.0)
S2–Cr1–C10	178.4 (1.0)	S4–Cr2–C21	176.6 (1.1)
C6–Cr1–C7	177.3 (1.4)	C17–Cr2–C18	176.9 (1.2)
C6–Cr1–C8	91.1 (1.3)	C17–Cr2–C19	88.0 (1.4)
C6–Cr1–C9	91.4 (1.3)	C17–Cr2–C20	91.3 (1.6)
C6–Cr1–C10	90.0 (1.3)	C17–Cr2–C21	90.2 (1.4)
C7–Cr1–C8	87.2 (1.3)	C18–Cr2–C19	94.1 (1.6)
C7–Cr1–C9	90.3 (1.3)	C18–Cr2–C20	86.6 (1.7)
C7–Cr1–C10	87.9 (1.3)	C18–Cr2–C21	87.5 (1.5)
C8–Cr1–C9	177.4 (1.2)	C19–Cr2–C20	178.8 (1.6)
C8–Cr1–C10	88.5 (1.2)	C19–Cr2–C21	87.7 (1.5)
C9–Cr1–C10	92.3 (1.1)	C20–Cr2–C21	91.4 (1.6)
Cr1–S2–C11	114.4 (9)	Cr2–S4–C22	112.4 (8)
S1–C11–S2	136.8 (1.4)	S3–C22–S4	135.6 (1.3)

Table XIII. Selected Bond Lengths (Å) and Angles (Deg) for the Structure of $[(triphos)Co(\mu\text{-}CS_2)Co(triphos)](BPh_4)_2\cdot 2(CH_3)_2CO$

Co–P1	2.231 (6)	P2–C1,3	1.82 (2)
Co–P2	2.191 (6)	P2–C1,4	1.83 (1)
Co–P3	2.228 (6)	P3–C5	1.83 (2)
Co–S1	2.27 (1)	P3–C1,5	1.83 (1)
Co–S2	2.31 (1)	P3–C1,6	1.82 (2)
Co′–S1	2.29 (1)	C1–C2	1.56 (3)
Co′–C	1.72 (5)	C2–C3	1.54 (3)
C–S1	1.75 (7)	C2–C4	1.52 (3)
C–S2	1.72 (7)	C2–C5	1.56 (3)
P1–C3	1.83 (2)	B–C1,7	1.67 (3)
P1–C1,1	1.82 (2)	B–C1,8	1.68 (3)
P1–C1,2	1.83 (1)	B–C1,9	1.68 (3)
P2–C4	1.85 (2)	B–C1,10	1.68 (3)
P1–Co–P2	90.2 (2)	S1–Co–S2	77.7 (5)
P1–Co–P3	93.0 (2)	P1′–Co′–S2	112.1 (4)
P2–Co–P3	92.7 (2)	P2′–Co′–S2	138.1 (4)
P1–Co–S1	152.6 (4)	P3′–Co′–S2	119.6 (4)
P2–Co–S1	98.6 (4)	P1′–Co′–C	155.4 (1.8)
P3–Co–S1	112.4 (4)	P2′–Co′–C	97.0 (1.8)
P1–Co–S2	83.0 (3)	P3′–Co′–C	110.0 (1.8)
P2–Co–S2	153.9 (4)	S1–Co′–C	49.3 (2.2)
P3–Co–S2	112.7 (4)	S1–C–S2	112.2 (3.7)

While the bond lengths and bond angles involving the phosphine ligand are very similar to those of the monomeric compound **1** as well as to those of the dinuclear derivative **2**, the bond distance and angles within the Co–CS_2 groups are somewhat different. Indeed the S–C–S angle, 112.2 (3.7)°, is smaller than that found in complexes **1** and **2**, 133.8 (8) and 136.2 (1.4)° (average), respectively. The C–S(1) and C–S(2) distances are close to each other (1.75 (7) and 1.72 (7) Å) and longer than those found in complexes **1** and **2**. This distortion within the Co–CS_2–Co fragment with respect to complexes **1** and **2** is evident also in the decrease in the Co′–C distance (1.72 (5) Å vs. 1.88 (1) and 1.87 (2) Å (average)) and in the increase in the Co′–S(1) distance (2.29 (1) vs. 2.206 (4) and 2.200 (8) (average) Å). It is interesting to notice that the two Co–S(1) and Co–S(2) bond distances are close to each other (2.27 (1) and 2.31 (1) Å) suggesting that the involvement of the CS_2 molecule in π bonding with the cobalt atom does not greatly affect the σ donor capabilities of the two sulfur atoms. These geometrical details suggest a partial loss of double bond character of the C═S linkages and a consequent delocalization of the electron density toward the cobalt atoms. The absence of IR bands attributable to C═S stretching modes seems to support this view.

The diamagnetism of this complex is consistent with the configuration of 34 valence electrons attained for the dinuclear complex cation, i.e., 16 electrons supplied by the two cobalt(I) ions, 12 supplied by the two triphos ligands, and 6 supplied by the CS_2 molecule.

Acknowledgment. Thanks are expressed to Mr. F. Nuzzi and Mr. G. Vignozzi for microanalyses.

Registry No. **1**, 74244-56-7; **2**, 74244-57-8; **3**, 74244-58-9; **4**, 74244-60-3; $Co_2(CO)_8$, 10210-68-1; $Cr(CO)_5(THF)$, 15038-41-2; $(\eta^5\text{-}C_5H_5)Mn(CO)_2(THF)$, 12093-26-4.

Supplementary Material Available: Listings of structure factor amplitudes for $[(triphos)Co(\pi\text{-}CS_2)]$, $[(triphos)Co(\mu\text{-}CS_2)Cr(CO)_5]\cdot 0.25CH_2Cl_2$ and $[(triphos)Co(\mu\text{-}CS_2)Co(triphos)]$ (57 pages). Ordering information is given on any current masthead page.