Inorg. Chem. **1982**, *21*, 4161–4165

Contribution from the Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione del CNR, Florence, Italy

Reactivity of the Triethylphosphine–Carbon Disulfide Adduct ($Et_3P{\cdot}CS_2$) toward Cobalt(II) Cations in the Presence of the Tris(tertiary phosphines) triphos and etriphos. X-ray Crystal Structure of the Complex $[(etriphos)Co(S_2C(H)PEt_3)](BPh_4)_2$

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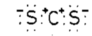
Received April 16, 1982

Depending on the reaction conditions, three different products, $[(triphos)Co(S_2CPEt_3)](BPh_4)_2$ (**1**), $[(triphos)Co(S_2C(H)PEt_3)](BPh_4)_2$ (**2**), and $[(triphos)Co(\mu\text{-}CS_2)Co(triphos)](BF_4)_2$ (**6**), are obtained from the reaction of the triethylphosphine–carbon disulfide adduct $Et_3P{\cdot}CS_2$ with cobalt(II) aquo cations in the presence of the tris(tertiary phosphine) 1,1,1-tris((diphenylphosphino)methyl)ethane, triphos. The substitution of the triphos with the etriphos ligand (etriphos = 1,1,1-tris((diethylphosphino)methyl)ethane) has helped us to clarify many aspects concerning both the structure and the formation mechanism of **2**. The further reactivity of the complexes obtained toward reducing and oxidizing agents has been also probed. The X-ray structure determination of the cobalt(III) complex $[(etriphos)Co(S_2C(H)PEt_3)](BPh_4)_2$ (**4**), has been carried out from counter diffraction data. Crystal data for **4**: a = 18.774 (8) Å, b = 25.094 (10) Å, c = 15.842 (7) Å, β = 114.2 (1)°, monoclinic, space group $P2_1/n$, Z = 4. The structure was refined by full-matrix least-squares techniques to R and R_w factors of 0.078 and 0.080, respectively. The metal atom is surrounded by the three phosphorus atoms of the etriphos ligand and by the two sulfur atoms of the $S_2C(H)PEt_3$ group in a distorted-square-pyramidal geometry.

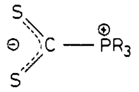
Introduction

It is well-known that carbon disulfide has a great tendency to assume the dithiolate dianion structure



having a highly electrophilic carbon, and in fact, a major class of sulfur-containing ligands is obtained by reaction of carbon disulfide with various nucleophiles. These ligands are classified into two categories: the uninegative 1,1-dithio acids and the dinegative 1,1-dithiolates.

We have recently found that the condensation products of carbon disulfide with tertiary phosphines form a new class of neutral disulfido ligands. These adducts can be regarded as zwitterions and have the general formula I. In particular,



I

the triethylphosphine–carbon disulfide adduct has been found to display three different binding modes to metals: η^1- or η^2-σ donor by means of the sulfur atoms or η^3-π donor through the conjugated CS_2 pseudoallylic system (Figure 1).[1-4]

For the obtainment of further information about the coordinative behavior and the reactivity of the $Et_3P{\cdot}CS_2$ ligand, this zwitterion was reacted with cobalt(II) aquo cations in the presence of the tripodlike tris(tertiary phosphines) 1,1,1-tris((diphenylphosphino)methyl)ethane, triphos, or 1,1,1-tris((diethylphosphino)methyl)ethane, etriphos; as a result the mononuclear complexes $[(triphos)Co(S_2CPEt_3)](BPh_4)_2$ (**1**), $[(triphos)Co(S_2C(H)PEt_3)](BPh_4)_2$ (**2**), and $[(etriphos)Co(S_2C(H)PEt_3)](BPh_4)_2$ (**4**) and the dinulcear complex $[(triphos)Co(\mu\text{-}CS_2)Co(triphos)](BF_4)_2$ (**6**) have been isolated. The further reactivity of these products toward reducing or oxidizing agents had also been probed.

In this paper we report in detail all the reactions performed, the chemical and physical properties of the products, and the complete X-ray structural determination of **4**. This is of particular interest since five-coordinate cobalt(III) complexes are quite rare and crystal structure determinations are indeed limited to very few examples.[5]

A preliminary account of part of this work has already been published.[6]

Experimental Section

$Et_3P{\cdot}CS_2$,[7] triphos,[8] and etriphos[8] were prepared according to published procedures. Tetrahydrofuran was dried by refluxing over $LiAlH_4$, before distillation. All other chemicals and solvents employed were reagent grade and were used without further purification.

Preparation of the Complexes. All reactions were routinely performed in an atmosphere of dry nitrogen. The solid complexes were collected on a sintered-glass frit and washed successively with ethanol and petroleum ether (bp 40–70 °C) before being dried in a stream of dry nitrogen.

$[(triphos)Co(S_2CPEt_3)](BPh_4)_2$ (1). A solution of $Et_3P{\cdot}CS_2$ (1 mmol) in CH_2Cl_2 (20 mL) was added to a mixture of $[Co(H_2O)_6](BF_4)_2$ (1 mmol) in ethanol (10 mL) and triphos (1 mmol) in CH_2Cl_2 (20 mL). $NaBPh_4$ (2 mmol) dissolved in ethanol (10 mL) was immediately added to the resultant red-brown solution. Brown crystals precipitated in a short time.

$[(triphos)Co(S_2C(H)PEt_3)](BPh_4)_2$ (2). A. $Et_3P{\cdot}CS_2$ (1 mmol) in CH_2Cl_2 (20 mL) was added to a mixture of $[Co(H_2O)_6](BF_4)_2$ (1 mmol) in ethanol (10 mL) and triphos (1 mmol) in CH_2Cl_2 (20 mL). The resultant solution was stirred for 2 h at room temperature. Addition of $NaBPh_4$ (2 mmol) in ethanol (10 mL) led to the precipitation within few minutes of red-brown crystals. **2** can also be obtained by heating the reaction mixture under reflux for 25 min before adding $NaBPh_4$.

B. A suspension of **1** (0.3 mmol) in THF (20 mL) was allowed to react with a solution of I_2 (0.6 mmol) in THF (10 mL). Within few minutes the suspended solid dissolved to give a red-brown solution. On addition of butanol (30 mL) and slow evaporation of the solvent, red-brown crystals were formed.

$[(triphos)Co(S_2C(H)PEt_3)]BPh_4$ (3). A solution of $NaBH_4$ (0.7 mmol) in ethanol (20 mL) was added to a suspension of **2** (0.5 mmol) in CH_2Cl_2 (30 mL). The suspended solid slowly dissolved to give a brown solution. Orange-brown crystals were obtained on addition of ethanol (20 mL) and slow evaporation of the solvent. They were recrystallized from acetone and butanol.

$[(etriphos)Co(S_2C(H)PEt_3)](BPh_4)_2$ (4). A mixture of $[Co(H_2O)_6](BF_4)_2$ (1 mmol) in ethanol (10 mL) and etriphos (1 mmol) in acetone (20 mL) was added to an acetone solution (10 mL) of $Et_3P{\cdot}CS_2$ (1 mmol). On addition of $NaBPh_4$ (2 mmol) in butanol (20 mL), dark green crystals were formed within a few minutes, which were recrystallized from acetone and butanol.

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Table I. Analytical and Some Physical Data for the Complexes

compd	% calcd			% found			μ_{eff}(293 K), μ_B	Λ_M,[e] Ω^{-1} mol^{-1} cm^2
	C	H	Co	C	H	Co		
[(triphos)Co(S_2CPEt_3)]$(BPh_4)_2$[a]	76.03	6.24	3.88	75.86	6.30	3.75	1.95	
[(triphos)Co($S_2C(H)PEt_3$)]$(BPh_4)_2$[b]	75.98	6.31	3.88	75.83	6.37	3.81	diamag	
[(triphos)Co($S_2C(H)PEt_3$)]BPh_4[c]	72.17	6.31	4.91	71.98	6.29	4.88	2.02	45
[(etriphos)Co($S_2C(H)PEt_3$)]$(BPh_4)_2$	70.35	7.79	4.79	69.88	7.84	4.75	diamag	97
[(etriphos)Co($S_2C(H)PEt_3$)]BPh_4[d]	63.36	8.30	6.47	63.11	8.29	6.45	2.15	48

[a] P: 8.17% calcd; 8.23% found. S: 4.22% calcd; 4.21% found. [b] P: 8.16% calcd; 8.18% found. [c] P: 10.34% calcd; 10.29% found. [d] S: 7.04% calcd; 7.00% found. [e] Molar conductance values for ca. 10^{-3} M nitroethane solutions.

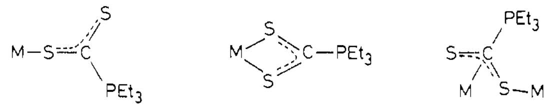

Figure 1. Binding modes of the $Et_3P{\cdot}CS_2$ adduct to metals.

[(etriphos)Co($S_2C(H)PEt_3$)]BPh_4 (5). A solution of 4 (0.5 mmol) in acetone (20 mL) was treated with $NaBH_4$ (0.7 mmol) in ethanol (10 mL). There was an immediate color change from dark green to light red. Within 1 h the solution turned to yellow-green. On addition of butanol (15 mL), yellow green crystals precipitated.

[(triphos)Co(μ-CS_2)Co(triphos)]$(BF_4)_2$ (6). A solution of $Et_3P{\cdot}CS_2$ (1 mmol) in CH_2Cl_2 (20 mL) was added to a mixture of [$Co(H_2O)_6$]$(BF_4)_2$ (1 mmol) in ethanol (10 mL) and triphos (1 mmol) in CH_2Cl_2 (20 mL). The resultant solution was heated under reflux for 90 min. On addition of butanol (30 mL) and slow concentration, dark brown crystals separated, which were recrystallized from CH_2Cl_2 and butanol.

Physical Measurements. Infrared spectra were obtained as Nujol mulls with a Perkin-Elmer 283 spectrophotometer. ^1H and ^{31}P NMR spectra were taken at 295 K on a Varian CFT 20 spectrometer. Phosphorus shifts are downfield (+) from external H_3PO_4. The methods used for the magnetic and molar conductance measurements and the recording of the UV-visible spectra have been described previously.[9] The analytical, magnetic, and conductivity data for the complexes are given in Table I. The electronic spectral data are listed in Table II.

Collection and Reduction of X-ray Intensity Data. A dark green sample, very irregularly shaped, of approximate dimensions 0.15 × 0.5 × 0.5 mm, was used for data collection. The compound crystallizes in the monoclinic system, space group $P2_1/n$, as resulted from the systematic absences $0k0$ for $k = 2n + 1$ and $h0l$ for $h + l = 2n + 1$. Cell constants, which were determined from a least-squares refinement of the setting angles of 20 carefully centered reflections, are $a = 18.774$ (8) Å, $b = 25.094$ (10) Å, $c = 15.842$ (7) Å, $\beta = 114.2$ (1)°, and $V = 6807.5$ Å^3. The calculated density is 1.199 g cm^{-3} for four molecules in the unit cell. The data were collected on a Philips PW 1100 automatic computer-controlled diffractometer using Mo Kα radiation ($\lambda = 0.7107$ Å) monochromated with a flat graphite crystal. The diffraction peaks were collected by using ω–2θ scan technique with a constant scan width of 0.7° and a scan speed of 0.09°/s. Background times were taken equal to half the scan time on each side of the peak. Three standard reflections were monitored every 120 min of exposure, and no significant variation was observed. After correction for background the intensities were assigned standard deviations $\sigma(I)$, calculated as described elsewhere, with the value of 0.03 for the instability factor k.[10] The intensities were corrected for Lorentz and polarization effects. No absorption correction was applied, owing to the difficulty in indexing the faces of the crystal, very irregular in shape. On the other hand the small value of the linear absorption coefficient (μ(Mo Kα) = 4.40 cm^{-1}) renders the correction unnescessary. From the 6805 collected reflections (5° ≤ 2θ ≤ 40°), 4233 were considered observed with $I \geq 3\sigma(I)$. Atomic scattering factors for non-hydrogen atoms from ref 11 and those for hydrogen atoms from ref 12. The effects of anomalous dispersion were included in the calculation of F_c, for both real and imaginary components.[13]

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

compd	abs max,[a] cm^{-1} (ϵ_M for soln)
[(triphos)Co(S_2CPEt_3)]$(BPh_4)_2$	a: 9200, 11 300, 12 750, 21 050
[(triphos)Co($S_2C(H)PEt_3$)]$(BPh_4)_2$	a: 14 600
[(triphos)Co($S_2C(H)PEt_3$)]BPh_4	a: 10 550, 16 000, 20 850 b: 10 650 (418), 15 650 (279), 20 618 (1256)
[(etriphos)Co($S_2C(H)PEt_3$)]$(BPh_4)_2$	a: 15 400 b: 15 900 (1100)
[(etriphos)Co($S_2C(H)PEt_3$)]BPh_4	a: 11 250, 17 400, 22 750 b: 11 450 (320), 16 300 (413), 21 750 (1357)

[a] Key: a, solid; b, 1,2-dichloroethane solution.

Solution and Refinement of the Structure. All the calculations were performed by using the SHELX-76 crystallographic system on a SEL 32/70 computer, installed in our institute.[14] The least-squares procedure used minimized the function $\sum w(|F_o| - F_c|)^2$, where the weights are given as $w = 1/\sigma(F_o)^2$. The structure was solved by conventional Patterson, Fourier, and least-squares refinement techniques. The phenyl rings were treated as rigid bodies of D_{6h} symmetry. Cobalt, phosphorus, and sulfur atoms were assigned anisotropic thermal parameters. Hydrogen atoms, except those belonging to methyl carbon atoms and that linked to the $S_2C<$ carbon atom, were introduced in their geometrical positions but not refined. A final difference map shows no particular feature except some electronic density near the terminal carbon atoms o the ethylenic chains. Therefore, whenever possible, two distinct positions were attributed to the disordered carbon atoms. The refinement converged to R and R_w of 0.078 and 0.080, respectively. The final positional and thermal parameters with their estimated standard deviations for non-hydrogen atoms are listed in Tables III–V. A listing of F_o and F_c amplitude factors is given as supplementary material.

Results and Discussion

In the reactions of the triethylphosphine–carbon disulfide adduct, $Et_3P{\cdot}CS_2$, with cobalt(II) aquo cations in the presence of triphos, factors such as temperature or presence of determinate counterions are extremely important in determining the course of the reaction. In fact, three different products are obtained according to whether BPh_4^- anions are immediately added to the reaction mixture, [(triphos)Co(S_2CPEt_3)]$(BPh_4)_2$ (**1**), whether the BPh_4^- anions are added after 2 h at room temperature or after 25 min at reflux temperature, [(triphos)Co($S_2C(H)PEt_3$)]$(BPh_4)_2$ (**2**), or whether the reaction mixture is maintained at reflux temperature for 90 min, [(triphos)Co(μ-CS_2)Co(triphos)]$(BF_4)_2$ (**6**).

Compound **1** is fairly air stable and virtually insoluble in all common organic solvents. It is paramagnetic with a

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Table III. Positional and Thermal Parameters for $[(\text{etriphos})\text{Co}(S_2C(H)PEt_3)](BPh_4)_2$[a]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	2633 (1)	1339 (1)	6934 (1)	38 (1)	53 (1)	34 (1)	−3 (1)	17 (1)	−2 (1)
P1	2602 (2)	2096 (1)	6180 (2)	42 (2)	56 (2)	50 (2)	−1 (2)	18 (2)	4 (2)
P2	3894 (2)	1246 (1)	7303 (2)	39 (2)	64 (2)	35 (2)	−4 (2)	15 (2)	0 (2)
P3	2397 (2)	870 (1)	5702 (2)	38 (2)	59 (2)	33 (2)	−4 (2)	13 (2)	−2 (2)
P4	1730 (2)	1231 (2)	8980 (2)	56 (2)	99 (3)	47 (2)	−4 (2)	27 (2)	1 (2)
S1	2581 (2)	728 (1)	7906 (2)	73 (2)	62 (2)	67 (2)	5 (2)	45 (2)	12 (2)
S2	1592 (2)	1586 (1)	7108 (2)	49 (2)	81 (2)	51 (2)	11 (2)	28 (2)	8 (2)

[a] The form of the thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. Coordinates are multiplied by 10^4; temperature factors, by 10^3.

Table IV. Positional and Thermal Parameters for $[(\text{etriphos})\text{Co}(S_2C(H)PEt_3)](BPh_4)_2$[a]

atom	x	y	z	U, Å^2
C1	3925 (7)	1613 (5)	4707 (8)	65 (4)
C2	3521 (6)	1544 (4)	5422 (7)	53 (3)
C3	3258 (6)	2091 (4)	5595 (8)	64 (4)
C4	4152 (6)	1290 (4)	6311 (7)	60 (3)
C5	2835 (6)	1150 (4)	4962 (7)	53 (3)
C6	1635 (7)	2242 (5)	5265 (8)	73 (4)
C7	1577 (8)	2797 (6)	4760 (10)	103 (5)
C8	2900 (6)	2710 (4)	6860 (8)	63 (4)
C9	2345 (8)	2902 (5)	7320 (10)	94 (5)
C10	4465 (7)	1777 (4)	8073 (8)	64 (4)
C11	4364 (7)	1823 (5)	9007 (9)	76 (4)
C12	4394 (6)	641 (4)	7911 (8)	61 (3)
C13	5289 (7)	643 (5)	8243 (8)	69 (4)
C14	2738 (6)	179 (4)	5889 (7)	54 (3)
C15	2496 (7)	−175 (5)	5017 (8)	66 (4)
C16	1358 (6)	827 (4)	4966 (7)	54 (3)
C17	863 (7)	497 (4)	5375 (8)	63 (4)
C18	1677 (6)	1012 (4)	7835 (7)	52 (3)
C19	860 (8)	1620 (5)	8748 (9)	86 (4)
C20	800 (14)	1960 (11)	9625 (17)	56 (8)
C201	727 (17)	1669 (13)	9662 (22)	84 (11)
C21	2603 (9)	1633 (6)	9545 (11)	111 (5)
C22	2829 (11)	1760 (7)	10567 (14)	147 (7)
C23	1684 (11)	585 (7)	9549 (14)	142 (7)
C24	2428 (20)	321 (13)	9989 (23)	123 (11)
C241	1562 (24)	526 (17)	10302 (32)	185 (16)
B1	5257 (7)	1256 (5)	2996 (9)	49 (4)
B2	4720 (7)	3940 (5)	7038 (9)	51 (4)

[a] Coordinates are multiplied by 10^4; temperature factors, by 10^3. Atoms C20, C201, C24, and C241 are assigned a population parameter of 0.5.

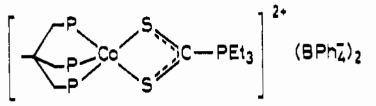

Figure 2. Schematic drawing of the complex cation $[(\text{triphos})\text{Co}(S_2CPEt_3)]^{2+}$.

Table V. Positional and Thermal Parameters for $[(\text{etriphos})\text{Co}(S_2C(H)PEt_3)](BPh_4)_2$[a]

atom	x	y	z	U, Å^2
C1-1	4860 (4)	1846 (3)	2536 (4)	46 (3)
C2-1	4389 (4)	2112 (3)	2890 (4)	66 (4)
C3-1	4088 (4)	2614 (3)	2551 (4)	73 (4)
C4-1	4259 (4)	2850 (3)	1858 (4)	73 (4)
C5-1	4729 (4)	2585 (3)	1504 (4)	70 (4)
C6-1	5030 (4)	2083 (3)	1843 (4)	60 (3)
C1-2	5955 (4)	1408 (3)	4041 (5)	46 (3)
C2-2	5897 (4)	1267 (3)	4863 (5)	57 (3)
C3-2	6489 (4)	1410 (3)	5712 (5)	72 (4)
C4-2	7137 (4)	1693 (3)	5741 (5)	80 (4)
C5-2	7194 (4)	1835 (3)	4919 (5)	72 (4)
C6-2	6603 (4)	1692 (3)	4069 (5)	64 (4)
C1-3	4607 (3)	815 (3)	3103 (5)	50 (3)
C2-3	4901 (3)	354 (3)	3620 (5)	58 (3)
C3-3	4390 (3)	−29 (3)	3692 (5)	78 (4)
C4-3	3585 (3)	50 (3)	3247 (5)	80 (4)
C5-3	3291 (3)	511 (3)	2729 (5)	80 (4)
C6-3	3802 (3)	894 (3)	2657 (5)	70 (4)
C1-4	5585 (4)	956 (3)	2280 (4)	47 (3)
C2-4	6372 (4)	857 (3)	2500 (4)	52 (3)
C3-4	6596 (4)	630 (3)	1843 (4)	67 (4)
C4-4	6033 (4)	502 (3)	965 (4)	69 (4)
C5-4	5246 (4)	602 (3)	745 (4)	71 (4)
C6-4	5022 (4)	828 (3)	1403 (4)	67 (4)
C1-5	5453 (5)	3526 (2)	7128 (5)	55 (3)
C2-5	6223 (5)	3702 (2)	7434 (5)	65 (4)
C3-5	6816 (5)	3341 (2)	7527 (5)	79 (4)
C4-5	6638 (5)	2804 (2)	7315 (5)	93 (5)
C5-5	5868 (5)	2628 (2)	7009 (5)	110 (5)
C6-5	5275 (5)	2989 (2)	6915 (5)	87 (4)
C1-6	4429 (4)	3820 (2)	7891 (5)	50 (3)
C2-6	3886 (4)	4154 (2)	8016 (5)	65 (4)
C3-6	3656 (4)	4058 (2)	8735 (5)	72 (4)
C4-6	3969 (4)	3627 (2)	9329 (5)	77 (4)
C5-6	4512 (4)	3293 (2)	9205 (5)	71 (4)
C6-6	4742 (4)	3390 (2)	8485 (5)	58 (3)
C1-7	3972 (4)	3862 (3)	5978 (7)	68 (4)
C2-7	4121 (4)	3646 (3)	5255 (7)	108 (5)
C3-7	3520 (4)	3606 (3)	4372 (7)	117 (6)
C4-7	2770 (4)	3781 (3)	4212 (7)	116 (6)
C5-7	2621 (4)	3996 (3)	4935 (7)	122 (6)
C6-7	3222 (4)	4036 (3)	5819 (7)	94 (5)
C1-8	5035 (4)	4581 (3)	7083 (5)	58 (3)
C2-8	5251 (4)	4754 (3)	6385 (5)	83 (4)
C3-8	5588 (4)	5256 (3)	6444 (5)	97 (5)
C4-8	5707 (4)	5585 (3)	7201 (5)	96 (5)
C5-8	5490 (4)	5411 (3)	7899 (5)	86 (4)
C6-8	5154 (4)	4909 (3)	7839 (5)	65 (4)

[a] Coordinates are multiplied by 10^4; temperature factors, by 10^3.

room-temperature magnetic moment corresponding to a doublet ground state. The electronic spectrum exhibits bands at 9200, 11 300, 12 750, and 21 050 cm^{-1} and is similar to those of distorted five-coordinate cobalt(II) complexes with a P_3S_2 donor set.[15] The IR spectrum shows a band in the $-CS_2$ stretching region at 975 cm^{-1}, which may be assigned to the $\nu(CS_2)_{\text{asym}}$ stretching vibrational mode of the $Et_3P{\cdot}CS_2$ ligand.[4] On the basis of analytical, spectroscopic, and magnetic measurements a structure can be assigned to 1 where the cobalt atom is five-coordinated by the three phosphorus atoms of the triphos ligand and by the two sulfur atoms of the $Et_3P{\cdot}CS_2$ ligand (Figure 2).

Metal complexes containing zwitterions of the present type as monometallic chelating ligands are quite rare, and only the crystal structure determinations for the two complexes $[\text{Ir}(S_2CPPh_3)(CO)(PPh_3)_2]BF_4$[16] and $[(\text{depe})_2\text{Fe}(S_2CPEt_3)](BPh_4)_2$[3] (depe = 1,2-bis(diethylphosphino)ethane) have been so far reported. The iridium compound has been obtained by insertion of carbon disulfide into a Ir–P bond, while the iron derivative has been obtained by reaction of the $Et_3P{\cdot}CS_2$ ligand with iron(II) aquo cations in the presence of the bis(tertiary

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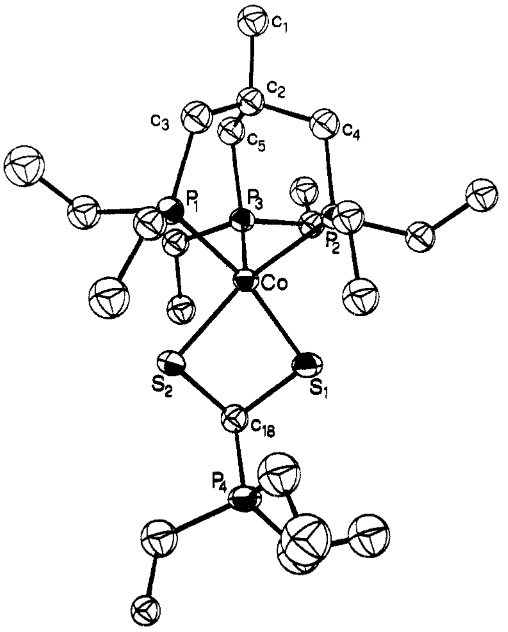

Figure 3. Perspective view of the complex cation [(etriphos)Co($S_2C(H)PEt_3$)]$^{2+}$ (ORTEP drawing with 30% probability ellipsoids).

phosphine) depe. In both complexes the zwitterionic ligand has been found to chelate the metal, forming a four-membered ring.

Compound **2** is diamagnetic and fairly air stable. It is practically insoluble in common organic solvents. For this reason it has not been studied in solution. This obstacle has been overcome by the synthesis of the complex [(etriphos)Co($S_2C(H)PEt_3$)](BPh_4)$_2$ (**4**) obtained from the reaction of $Et_3P{\cdot}CS_2$ with cobalt(II) aquo cations and BPh_4^- anions in the presence of the tris(tertiary phosphine) 1,1,1-tris((diethylphosphino)methyl)ethane, etriphos, which differs from triphos in having ethyl substituents in place of phenyl on the phosphorus atoms. Compound **4** is diamagnetic, air stable in the solid state, and very soluble in common organic solvents, in which it behaves as a 1:2 electrolyte. The reflectance spectra of **2** and **4** are similar to each other, the substitution of the triphos by the etriphos ligand causing only a hypsochromic shift of the bands. The crystal and molecular structure of **4** consists of monomeric complex cations of [(etriphos)Co(S_2C(H)PEt_3)]$^{2+}$ and BPh_4^- anions. Figure 3 shows a perspective view of the complex cation; selected bond distances and angles are given in Table VI. The cobalt atom is surrounded by the three phosphorus atoms of the etriphos ligand and by the two sulfur atoms of the $S_2C(H)PEt_3^-$ ligand in a distorted-square-pyramidal environment. The distortion from the idealized geometry evidenced by the values of the P1–Co–S1 and P2–Co–S2 bond angles, 165.4 (1) and 156.9 (1)°, respectively, can be mainly attributed to the short bite of the S_2C fragment, the S1–Co–S2 angle being 79.0 (1)°. The bond distances and angles involving the $S_2C<$ fragment clearly imply the presence of a hydrogen atom linked to the carbon atom; indeed S–C, 1.805 (10) Å (average), and C–P, 1.86 (1) Å, approaching the values expected for single bonds, indicate that this carbon atom is sp^3 hybridzed. The values of the S–C–S and S–C–P angles ranging from 100.8 (5) to 112.6 (6)° are very consistent with this inference. A look at the zwitterionic ligand $Et_3P{\cdot}CS_2$, either free or coordinated, where the carbon atom is sp^2 hybridized with pertinent bond distances and angles, is a further support.[3,4,16,17] An ulterior comparison can be made with the complex [Ru($S_2C(H)PMe_2Ph$)(PMe_2Ph)$_3$]PF_6, which contains the $S_2C(H)PMe_2Ph$ group, in excellent agreement with the present compound.[18] All the other bond distances and angles present normal values.

Table VI. Selected Bond Distances (Å) and Angles (Deg) for [(etriphos)Co($S_2C(H)PEt_3$)](BPh_4)$_2$

Co–P1	2.231 (3)	P3–C5	1.83 (1)
Co–P2	2.206 (3)	P3–C14	1.83 (1)
Co–P3	2.164 (3)	P3–C16	1.82 (1)
Co–S1	2.203 (3)	P4–C18	1.86 (1)
Co–S2	2.172 (3)	P4–C19	1.81 (1)
P1–C3	1.82 (1)	P4–C21	1.82 (2)
P1–C6	1.84 (1)	P4–C23	1.87 (2)
P1–C8	1.83 (1)	S1–C18	1.80 (1)
P2–C4	1.83 (1)	S2–C18	1.81 (1)
P2–C10	1.83 (1)	Co···C18	2.84 (1)
P2–C12	1.84 (1)		

P1–Co–P2	91.2 (2)	C4–P2–C12	104.0 (5)
P1–Co–P3	91.6 (1)	C10–P2–C12	102.7 (5)
P1–Co–S1	165.4 (1)	Co–P3–C5	113.0 (3)
P1–Co–S2	89.9 (1)	Co–P3–C14	116.1 (4)
P2–Co–P3	88.9 (1)	Co–P3–C16	112.3 (4)
P2–Co–S1	95.2 (1)	C5–P3–C14	104.5 (5)
P2–Co–S2	156.9 (1)	C5–P3–C16	105.0 (5)
P3–Co–S1	101.6 (1)	C14–P3–C16	105.0 (5)
P3–Co–S2	114.1 (1)	C18–P4–C19	106.2 (6)
S1–Co–S2	79.0 (1)	C18–P4–C21	108.7 (6)
Co–P1–C3	113.2 (4)	C18–P4–C23	102.7 (7)
Co–P1–C6	113.2 (4)	C19–P4–C21	111.0 (7)
Co–P1–C8	117.8 (4)	C19–P4–C23	110.4 (7)
C3–P1–C6	104.8 (5)	C21–P4–C23	117.0 (8)
C3–P1–C8	101.4 (5)	Co–S1–C18	89.5 (4)
C6–P1–C8	105.1 (5)	Co–S2–C18	90.3 (4)
Co–P2–C4	113.6 (4)	S1–C18–P4	112.6 (6)
Co–P2–C10	111.8 (4)	S2–C18–P4	110.0 (5)
Co–P2–C12	119.3 (4)	S1–C18–S2	100.8 (5)
C4–P2–C10	103.9 (5)	Co–C18–P4	127.9 (5)

The IR spectra of **2** and **4** with no bands attributable to C=S stretching modes as well as the ^{31}P and ^{1}H NMR spectra of **4** are fully consistent with the assigned structure. The ^{31}P NMR spectrum in CD_3COCD_3 at 295 K shows two multiplets centered at 44.72 and 37.58 ppm, which are assigned to the three phosphorus atoms of the etriphos ligand and to the phosphorus atom of the $S_2C(H)PEt_3^-$ ligand, respectively. Assignment of the peaks was made on the basis of their intensities and by reference to existing data.[19] The ^{1}H NMR spectrum in $CDCl_3$ shows a multiplet centered at δ 5.72, attributable to the hydrogen atom of the $S_2C(H)PEt_3$ group.[19]

1,1-Dithio ligands of the type $S_2C(H)PR_3^-$ have been so far reported to exist in the three complexes [Mn(CO)$_3$(DPM)(HCS_2)],[20] [Ru($S_2C(H)PMe_2Ph$)(PMe_2Ph)$_3$]PF_6,[18] and [(PR_3)$_2$Pd($S_2C(H)PR_3$)]BPh_4.[19] In the first two complexes the formation of this ligand has been suggested to involve a nucleophilic attack by a phosphine at the carbon atom of hydrometalated carbon disulfide, while in the third complex the author suggests the initial insertion of CS_2 into a P–R bond, followed by migration of a hydridic hydrogen atom from the metal to the carbon atom. Concerning the formation of **2** and **4**, on the basis of the reactivity pattern summarized in Scheme I, and of these reports, it is possible to propose a mechanism involving the initial formation of the cations [LCo(S_2CPEt_3)]$^{2+}$ (L = triphos, **2**; L = etriphos, **4**), followed by nucleophilic attack by hydride ion at the $-CS_2$ carbon atom. Support for this mechanism is provided by some considerations. In metal complexes with the $Et_3P{\cdot}CS_2$ ligand or with 1,1-dithio ligands such as xanthates or dithiocarbamates, the carbon atom of the $-CS_2$ group is undoubtedly electrophilic, undergoing attack by a great variety of nucleophiles.[6,21] Thus, if no other nu-

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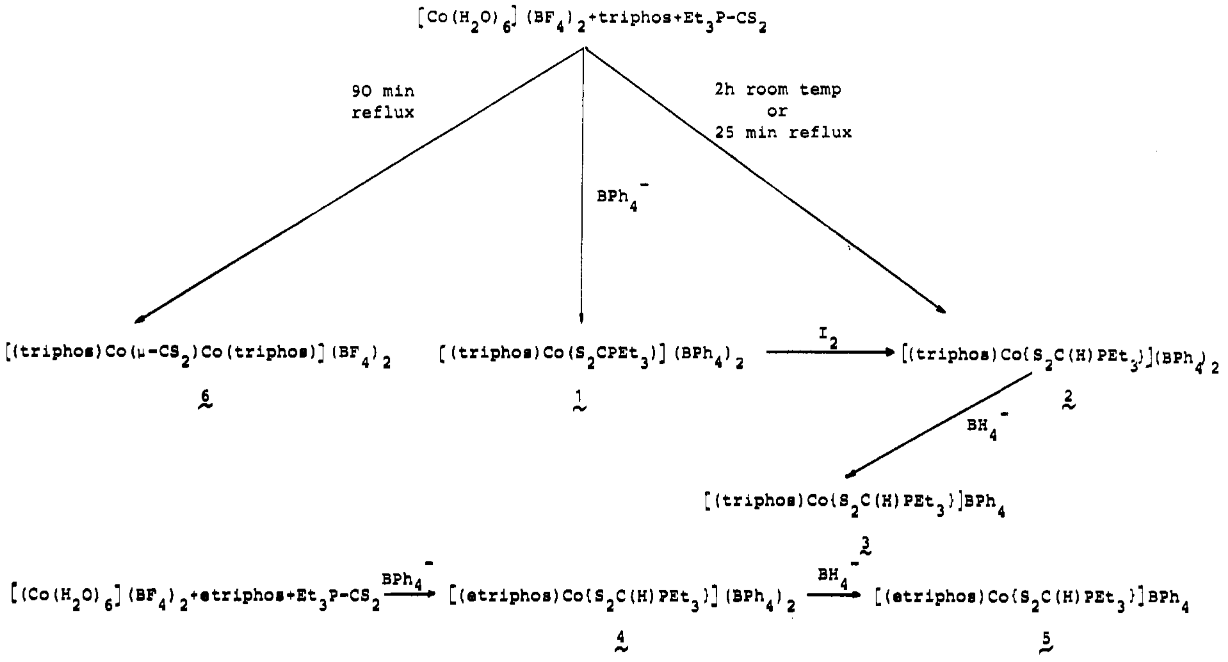
Scheme I. Flow Diagram Illustrating Preparations and Reactions of the Complexes Described



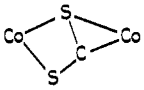


Figure 4. Bonding mode of CS_2 in the $[(triphos)Co(\mu\text{-}CS_2)Co(triphos)](BF_4)_2$ complex.

cleophiles are present, the electrophilic nature of this carbon may be sufficient to enable it to abstract a hydride ion from the solvent. On the other hand, the formation of **2** and **4** occurs only when the $[LCo(S_2CPEt_3)]^{2+}$ cations are allowed to remain in solution for a reasonable period of time. This is obtained with the initial absence of BPh_4^- anions in the reaction mixture for **2** or by using the etriphos ligand for **4**.

As regards the increase in the oxidation number of cobalt from +2 in **1** to +3 in **2** and **4**, no definitive conclusions are reached, but it is useful to report that 1,1-dithio acid complexes of divalent cobalt are often unstable and are quickly oxidized to the corresponding cobalt(III) derivatives.[22] Compounds **2** and **4** are of further particular interest since five-coordinate cobalt(III) complexes are very rare, being limited to few examples, most of them with nitrogen-donor quadridentate ligands.

In confirmation of the oxidation number of cobalt in **2** and **4**, these can be reduced by $NaBH_4$ to the corresponding cobalt(II) derivatives. The complexes obtained have the empirical formula $[LCo(S_2C(H)PEt_3)]BPh_4$ (L = triphos, **3**; L = etriphos, **5**). Compounds **3** and **5** are air unstable and soluble in common organic solvents, in which they behave as 1:1 electrolytes. They are paramagnetic with μ_{eff} close to that expected for one unpaired spin. The solution and reflectance spectra of both compounds are similar to each other and fully comparable with those of distorted-square-pyramidal cobalt(II) complexes with triphos and bidentate ligands.[23]

On the basis of these results a structure can be assigned to both compounds **3** and **5**, where the cobalt atom is five-coordinated by the three phosphorus atoms of the triphos or etriphos ligands and by the two sulfur atoms of the $S_2C(H)PEt_3^-$ ligand.

Finally, **1** is oxidized by iodine to the cobalt(III) derivative **2**.

When the reaction mixture formed by cobalt tetrafluoroborate, triphos, and $Et_3P{\cdot}CS_2$ is maintained at reflux temperature for at least 90 min, dark brown crystals are obtained. A complete characterization of this product allowed its identification as the dinuclear $\mu\text{-}CS_2$ complex $[(triphos)Co(\mu\text{-}CS_2)Co(triphos)](BF_4)_2$ (**6**) recently prepared in this laboratory.[24] In Figure 4 the bonding mode at CS_2 is given. The cleavage of the $P\text{–}CS_2$ bond in a $Et_3P{\cdot}CS_2$ molecule is essential for the formation of **6**. Such a cleavage is not completely unexpected since we have recently observed that this zwitterion can react with metal species behaving as a source of PEt_3 groups.[1,2]

This series of reactions highlights a new aspect of the chemistry of the adduct $Et_3P{\cdot}CS_2$. On account of the high electrophilicity of the $-CS_2$ carbon atom, this zwitterion may be usefully employed as a route to metal complexes containing various disulfido ligands.[6] Furthermore the lability of the $P\text{–}CS_2$ bond makes it a potential source of activated CS_2.

Acknowledgment. We thank G. Scapacci, D. Masi, and F. Cecconi for technical assistance and F. Nuzzi and G. Vignozzi for microanalyses.

Registry No. **1**, 83024-97-9; **2**, 83024-99-1; **3**, 82585-02-2; **4**, 83025-01-8; **5**, 83025-03-0; **6**, 83025-05-2; $[Co(H_2O)_6](BF_4)_2$, 37041-75-1.

Supplementary Material Available: A listing of structure factor amplitudes (23 pages). Ordering information is given an any current masthead page.

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