and partially decoupled modes with a Varian FT-80 spectrometer.

Tetrakis(triphenylphosphine)palladium(0) was prepared following the procedure of Coulson,[9] and bis(dibenzylideneacetone)palladium(0)[10] and the Pd(diphos)$_2$ catalyst[11] were synthesized by using literature procedures. The organic reactants were commercial reagents. Solvents were dried and purified by standard methods.

General Procedure for the Palladium(0) and Phase Transfer Catalyzed Carbonylation of Halides. A mixture of tetrahexylammonium hydrogensulfate (0.11 mmol) in 5 N NaOH (15 mL) and the palladium catalyst [0.05 mmol, except Pd(dba)$_2$ where 0.20 mmol is used] in 15 mL of methylene chloride (or benzene) was stirred under a carbon monoxide atmosphere at room temperature. Then the halide (4.5–5.0 mmol) in methylene chloride (3–5 mL) was added, drop-by-drop, and after addition was complete, the reaction mixture was stirred for 6–10 h (followed by thin-layer chromatography). The layers were separated, and the acid **7** was obtained from the aqueous layer by acidification (pH 3) of the latter (followed by extraction if necessary). The organic layer was washed with water, dried (MgSO$_4$), and concentrated. Pure **8–10** were obtained by chromatography of the crude product(s) on silica gel.

Reactions effected in the absence of the phase-transfer agent or the palladium catalyst were run following the general procedure, except without the noted species. **23** is a new compound: ^{1}H NMR (CDCl$_3$) δ 1.50 (m, 6 H, methyls), 3.71 (q, 1 H, J = 7 Hz, PhCHCO), 5.83 (q, 1 H, J = 7 Hz, OCHPh), 7.10 (m, 10 H, aromatic protons); MS m/e 254 [M]$^+$. Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 79.69; H, 7.46.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council for support of this work.

Registry No. 6 (Ar = 2-naphthyl, X = Br), 939-26-4; **6** (Ar = Ph, X = Br), 100-39-0; **6** (Ar = p-$CH_3C_6H_4$, X = Br), 104-81-4; **6** (Ar = o-$CH_3C_6H_4$, X = Br), 89-92-9; **6** (Ar = o-$CH_3C_6H_4$, X = Cl), 552-45-4; **6** (Ar = p-FC_6H_4, X = Br), 459-46-1; **7** (Ar = 2-naphthyl), 581-96-4; **7** (Ar = Ph), 103-82-2; **7** (Ar = p-$CH_3C_6H_4$), 622-47-9; **7** (Ar = o-$CH_3C_6H_4$), 644-36-0; **7** (Ar = p-FC_6H_4), 405-50-5; **10** (Ar = 2-naphthyl), 53342-33-9; **10** (Ar = p-$CH_3C_6H_4$), 36707-18-3; **10** (Ar = o-$CH_3C_6H_4$), 80720-85-0; **21**, 585-71-7; **22**, 492-37-5; **23**, 80720-86-1; Pd(PPh$_3$)$_4$, 14221-01-3; Pd(dba)$_2$, 32005-36-0; Pd(diphos)$_2$, 31277-98-2.

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Reactivity of the Triethylphosphine–Carbon Disulfide Adduct toward Metal Carbonyls. X-ray Structures of the Complexes [Cr(CO)$_5$(S$_2$CPEt$_3$)] and [Mo(CO)$_2$(PEt$_3$)(μ-S$_2$CPEt$_3$)]$_2$

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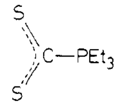
Received December 17, 1981

By reaction of the triethylphosphine–carbon disulfide adduct Et$_3$P·CS$_2$, Z, with group 6B metal carbonyls or isoelectronic iron and manganese carbonyl derivatives, the monomeric [M(CO)$_5$Z] (M = Cr, Mo, W), [Mn(η^5-C$_5$H$_5$)(CO)$_2$Z], and [Fe(η^5-C$_5$H$_5$)(CO)$_2$Z]BPh$_4$ and the dimeric [Mo(CO)$_2$(PEt$_3$)Z]$_2$ complexes have been prepared. The X-ray structure determinations of [Cr(CO)$_5$(S$_2$CPEt$_3$)] (**1**) and [Mo(CO)(PEt$_3$)(μ-S$_2$CPEt$_3$)]$_2$ (**6**) have been carried out from counter diffraction data. Crystal data for **1** are as follows: space group $P2_1/a$, a = 13.631 (7) Å, b = 12.311 (6) Å, c = 11.037 (6) Å, β = 100.76 (4) °, and Z = 4. Crystal data for **6** are as follows: space group $Pbca$, a = 14.132 (5) Å, b = 23.693 (9) Å, c = 12.667 (4) Å, and Z = 4. Both structures were solved by the heavy-atom method and refined by full-matrix least-squares techniques to R values of 0.057 and 0.056, respectively. The mononuclear complex **1** exhibits slightly distorted octahedral geometry with the Z molecule linked to the chromium atom by one sulfur atom as a two-electron σ donor. In the dimeric complex **6** each zwitterion coordinates to one metal through a η^3-S$_2$C-delocalized linkage as a four-electron pseudoallylic ligand and to the other metal through one sulfur atom as a two-electron σ donor. The coordination around each metal atom completed by two carbonyl groups and one phosphine may be considered pseudooctahedral. The mechanism for the formation of the dinuclear compound is proposed and discussed.

Introduction

The reactivity of the triethylphosphine–carbon disulfide adduct Et$_3$P·CS$_2$, Z, toward metal–ligand moieties formed by transition-metal cations and poly (tertiary phosphines) has been recently investigated in this laboratory. In particular, several mononuclear complexes have been described.[1,2] These complexes contain as ligands either Z coordinated to the metal via both sulfur atoms or different groups deriving from Z. The carbon atom of the CS$_2$ group, in fact, can be attacked by a variety of nucleophiles to give different disulfido ligands such as S$_2$CO^{2-}, S$_2$CS^{2-}, S$_2$CH$^-$, and S$_2$C(H)PEt$_3^-$. Furthermore, the P–CS$_2$ bond can be



Z

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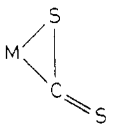
cleaved by simple heating to give CS_2 and PEt_3.

The zwitterion $Et_3P{\cdot}CS_2$ has indeed nucleophilic character, undergoing reaction with a variety of electrophiles such as alkyl halides[3] or M(phosphines) moieties.

In this finding Z could be usefully employed to mimic the chemical properties of metal-activated carbon disulfide. CS_2–metal complexes of type I and II are, in fact, highly activated toward electrophilic reagents displacing the halide ion from alkyl halides or weakly bound ligands from other organometallic derivatives.[4,5]



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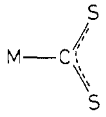

II

With the aim to get more information about the reactivity of Z toward electrophilic groups a systematic work of synthesis and characterization has been carried out. This involves reactions with a variety of carbonyls derivatives and in particular with those containing weakly bound ligands.

We have succeeded in preparing the mononuclear compounds $[M(CO)_5(S_2CPEt_3)]$(M = Cr, **1**; Mo, **2**; W, **3**), $[Mn(\eta^5\text{-}C_5H_5)(CO)_2(S_2CPEt_3)]$, **4**, and $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(S_2CPEt_3)]BPh_4$, **5**, and the dinuclear compound $[Mo(CO)_2(PEt_3)(\mu\text{-}S_2CPEt_3)]_2$, **6**.

All the compounds have been characterized and their physical properties studied by the usual methods.

Complete X-ray structure determinations have been performed for compounds **1** and **6**.

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

Experimental Section

$[Fe(\eta^5\text{-}C_5H_5)(CO)_2(THF)]BF_4$[7] and $Et_3P{\cdot}CS_2$[8] were synthetized according to literature procedures. $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, $[Mn(\eta^5\text{-}C_5H_5)(CO)_3]$, and $[Mo(C_7H_8)(CO)_3]$ were purchased from Strem Chemicals Inc., Dauvers, Mass., and were used without further purification. All other chemicals employed were of reagent grade quality. Ethanol was dried over molecular sieves. All other solvents were dried and distilled under a nitrogen atmosphere from an appropriate drying agent. All operations were performed under a nitrogen atmosphere and with oxygen-free solvents. The solid complexes were collected on a sintered-glass frit and dried in a stream of nitrogen.

Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer while the ^{31}P NMR spectra were obtained on a Varian CFT 20 spectrometer. Chemical shifts are downfield (+) from external H_3PO_4. Conductivity measurements were recorded by using a previously described method.[9]

Syntheses. $[M(CO)_5(S_2CPEt_3)]$ (M = Cr (1), Mo (2), W (3)). A solution of $[M(CO)_5(THF)]$ formed by UV irradiation[10] of the corresponding hexacarbonyl complex (0.22, 0.26, and 0.35 g, 1 mmol) in THF (40 mL) was added to a stirred suspension of $Et_3P{\cdot}CS_2$ (0.20 g, 1 mmol) in THF (10 mL) cooled to −10 °C. The reaction mixture was allowed to warm to room temperature and the THF removed under reduced pressure. The red residue was dissolved in CH_2Cl_2 (10 mL), and red crystals were separated by addition of heptane (30 mL) and slow evaporation of the solvent. They were collected by filtration and washed with cold heptane; yield 60%, 30%, and 40%, respectively. Alternatively, compounds 1 and 3 were prepared by UV irradiation for 30 min at reflux temperature of a mixture of $M(CO)_6$ (1 mmol) and $Et_3P{\cdot}CS_2$ (2 mmol) in THF (50 mL). Comparable yields of products were obtained.

Anal. Calcd for $C_{12}H_{15}CrO_5PS_2$: C, 37.30; H, 3.91; Cr, 13.46; S, 16.59. Found: C, 37.50; H, 4.15; Cr, 13.20; S, 16.32. Anal. Calcd for $C_{12}H_{15}MoO_5PS_2$: C, 33.49; H, 3.51; Mo, 22.29; P, 7.19. Found: C, 33.25; H, 3.50; Mo, 21.90; P, 7.30. Anal. Calcd for $C_{12}H_{15}O_5PS_2W$; C, 27.81; H, 2.91; W, 35.47. Found: C, 28.00; H, 3.05; W, 35.40.

$[Mn(\eta^5\text{-}C_5H_5)(CO)_2(S_2CPEt_3)]$ (4). This dark blue complex was prepared by the same procedure as the above derivatives except for substitution of $[Mn(\eta^5\text{-}C_5H_5)(CO)_3]$ (0.20 g, 1 mmol) for $M(CO)_6$; yield 70%.

Anal. Calcd for $C_{14}H_{20}MnO_2PS_2$: C, 45.40; H, 5.44; Mn, 14.83; P, 8.36. Found: C, 45.76; H, 5.88; Mn, 15.10; P, 8.45.

$[Fe(\eta^5\text{-}C_5H_5)(CO)_2(S_2CPEt_3)]BPh_4$ (5). A mixture of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(THF)]BF_4$ (0.33 g, 1 mmol) and $Et_3P{\cdot}CS_2$ (0.20 g, 1 mmol) was stirred in CH_2Cl_2 (30 mL) for 20 min at room temperature. On addition of $NaBPh_4$ (0.35 g, 1 mmol) in ethanol (30 mL) and slow evaporation of the solvent, yellow crystals were obtained, which were collected by filtration and washed with ethanol and petroleum ether. They were recrystallized from CH_2Cl_2/ethanol; yield 70%.

Anal. Calcd for $C_{38}H_{40}BFeO_2PS_2$: C, 66.09; H, 5.83; Fe, 8.08; S, 9.28. Found: C, 66.10; H, 5.93; Fe, 7.80; S, 9.15.

$[Mo(CO)_2(PEt_3)(\mu\text{-}S_2CPEt_3)]_2$ (6). A. A mixture of $Mo(CO)_6$ (0.26 g, 1 mmol) and $Et_3P{\cdot}CS_2$ (0.40 g, 2 mmol) in THF (40 mL) was irradiated at reflux temperature for 30 min. After filtration, the solvent volume was reduced to about 15 mL and butanol (20 mL) added to precipitate red crystals which were filtered off and washed with butanol and petroleum ether; yield 20%.

B. $[Mo(C_7H_8)(CO)_3]$ (0.27 g, 1 mmol) in THF (15 mL) was added at room temperature to a stirred suspension of $Et_3P{\cdot}CS_2$ (0.40 g, 2 mmol) in THF (10 mL). There was an immediate color change to dark red. Butanol (30 mL) was added. Slow evaporation of the solvent produced red crystals which were removed by filtration and washed as above; yield 60%.

C. A mixture of **2** (0.43 g, 1 mmol) and PEt_3 (0.18 g, 1.5 mmol) in THF (20 mL) was irradiated for about 30 min at 0 °C. On addition of butanol and slow evaporation of the solvent red crystals were formed which were separated and washed as above; yield 40%.

Anal. Calcd for $C_{30}H_{60}Mo_2O_4P_4S_4$: C, 38.79; H, 6.51; Mo, 20.65; P, 13.33; S, 13.80. Found: C, 38.85; H, 6.66; Mo, 20.82; P, 13.50; S, 13.63.

Collection and Reduction of X-ray Intensity Data. Unit cell parameters for both the complexes were determined at room temperature from a least-squares refinement of the angular setting of 20 and 22 reflections, carefully centered on a Philips PW 1100 automatic diffractometer for compounds 1 and 6 respectively. Systematic absences for 1 ($h0l$ for $h = 2n + 1$ and $0k0$ for $k = 2n + 1$) and 6 ($h0l$ for $l = 2n + 1$, $0kl$ for $k = 2n + 1$ and $hk0$ for $h = 2n + 1$) indicated the space groups $P2_1/a$ and $Pbca$, respectively. Details of crystal data and data collection for the two compounds are given in Table I. All data processing was carried out as previously described.[11] After correction for background the intensities were assigned standard deviations calculated as described elsewhere,[12] by using for the instability factor k the value of 0.03 for both the complexes. Intensity data were corrected for Lorentz and polarization effects and merged to a unique set of reflections. No absorption correction was applied, the linear absorption coefficients being 9.33 and 9.45 cm^{-1} for complexes 1 and 6, respectively.

Atomic scattering factors of the appropriate neutral atoms were taken from ref 13 for nonhydrogen atoms and from ref 14 for

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Table I. Crystal Data and Data Collection Details

	$[Cr(CO)_5(S_2CPEt_3)]$	$[Mo(CO)_2(PEt_3)(\mu\text{-}S_2CPEt_3)]_2$
mol formula	$C_{12}H_{15}CrO_5PS_2$	$C_{30}H_{60}Mo_2O_4P_4S_4$
mol wt	386.35	928.84
a, Å	13.631 (7)	14.132 (5)
b, Å	12.311 (6)	23.693 (9)
c, Å	11.037 (6)	12.667 (4)
β, deg	100.76 (4)	
d_{calcd}, g cm^{-3}	1.410	1.454
U, $Å^3$	1819.6	4241.3
Z	4	4
space group	$P2_1/a$	*Pbca*
abs coeff, μ(Mo Kα), cm^{-1}	9.33	9.45
color	red	red
habit	irregular prism	truncated octahedron
dimensions, mm	0.05 × 0.1 × 0.1	0.2 × 0.3 × 0.3
diffractometer	Philips PW 1100	Philips PW 1100
λ(Mo Kα), Å	0.7107	0.7107
monochromator	flat graphite crystal	flat graphite crystal
method	$\omega-2\theta$ scan technique	$\omega-2\theta$ scan technique
scan speed, deg/s	0.07	0.08
scan width, deg	$(0.70 + 0.69 \tan\theta)$	$(0.74 + 0.69 \tan\theta)$
bkgd time	half the scan time	half the scan time
stds	3 every 120 min	3 every 120 min
max dev std, %	4	5
2θ limits, deg	$5 \leqslant 2\theta \leqslant 40$	$5 \leqslant 2\theta \leqslant 50$
no. of total data	1910	3107
no. of data used $(I \geqslant 3\sigma(I))$	829	1286
final no. of variables	115	123

hydrogen atoms. Both the $\Delta f'$ and $\Delta f''$ components of anomalous dispersion were included for all nonhydrogen atoms.[15] The function $\Sigma w(|F_o| - |F_c|)^2$ was minimized during the least-squares refinement process; the assigned weights are given as $w = 1/\sigma^2(F_o)$. The calculations were carried out by using the SHELX 76 crystallographic system[16] on a SEL 32/70 computer, installed in our institute.

Solution and Refinement of the Structures. $[Cr(CO)_5(S_2CPEt_3)]$ (1). A three-dimensional Patterson synthesis revealed the positions of the chromium atom and of one sulfur atom. Successive Fourier maps led to the location of the atomic positions of all nonhydrogen atoms. Hydrogen atoms were introduced in their calculated positions but not refined. Full-matrix least-squares cycles, with anisotropic temperature factors associated to chromium, sulfur, and phosphorus atoms and isotropic thermal factors for oxygen and carbon atoms, were carried out. The final discrepancy factors R and R_w are 0.057 and 0.053, respectively. The final positional and thermal parameters with their estimated standard deviations are given in Table II.

$[Mo(CO)_2(PEt_3)(\mu\text{-}S_2CPEt_3)]_2$ (6). A three-dimensional Patterson map revealed the position of the molybdenum atom. All the nonhydrogen atoms were located from successive Fourier syntheses. The electron density map showed well-defined regions for all atoms except for the terminal carbons of the ethylenic chains, which were displayed as diffuse density regions, characteristic of disorder. Therefore, whenever possible, two distinct positions were located for the disordered carbon atoms. The hydrogen atoms belonging to the disordered methyl groups were not introduced. The other hydrogen atoms were introduced in their calculated positions, but not refined. Full-matrix least-squares refinement of all positional parameters, anisotropic thermal parameters for molybdenum, phosphorus, and sulfur, and isotropic thermal parameters for the other atoms, resulted in final convergence with R and R_w values of 0.056 and 0.056, respectively. The final positional and thermal parameters with their estimated standard deviations are reported in Table III.

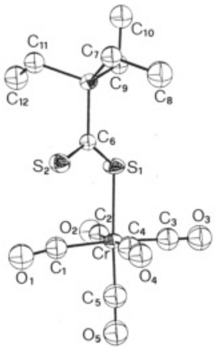

Figure 1. Perspective view of the complex molecule $[Cr(CO)_5(S_2CPEt_3)]$, ORTEP drawing with 30% probability ellipsoids.

Results and Discussion

By reaction of the zwitterion $Et_3P{\cdot}CS_2$ with $[M(CO)_5THF]$ (M = Cr, **1**; Mo, **2**; W, **3**) red crystals of empirical formula $[M(CO)_5(S_2CPEt_3)]$ are obtained. These compounds are air-stable and very soluble in common organic solvents. Their IR spectra, taken as Nujol mulls, are similar to each other with bands in the CO region at 2058, 1996, 1960, 1930, and 1900 cm^{-1}, for **1**, 2060, 1995, 1955, 1925, and 1890 cm^{-1} for **2**, and 2060, 1992, 1950, 1920, and 1890 cm^{-1} for **3**. The IR spectrum of $[Cr(CO)_5(S_2CPEt_3)]$ in CH_2Cl_2 solution shows bands in the CO region at 2060 (w), 1993 (vw), 1948 (s), and 1915 (m) cm^{-1}. The first, third, and fourth bands are assigned to the three infrared active CO stretching fundamental of a $[LM(CO)_5]$ derivative: $A_1{}^1$, E, and $A_1{}^2$, respectively.[17] The splitting of the band at 1948 cm^{-1} observed in the solid-state spectrum is in agreement with this assignment. The very weak band at 1993 cm^{-1} may be attributed to the formally infrared inactive B_1 mode, which becomes IR active due to the ligand-induced molecular distortion.[17]

The diamagnetic complexes $[Mn(\eta^5\text{-}C_5H_5)(CO)_2(S_2CPEt_3)]$, **4**, and $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(S_2CPEt_3)]\ BPh_4$, **5**, dark blue and yellow in color, respectively, are similarly prepared by the reaction of Z with $[Mn(\eta^5\text{-}C_5H_5)(CO)_2THF]$ and $[Fe(\eta^5\text{-}C_5H_5)(CO)_2THF]BF_4$. They are air-stable in the solid state and soluble in common organic solvents where compoud 5 behaves as a 1:1 electrolyte (molar conductance in 10^{-3} M nitroethane solution: 42 $cm^2\ \Omega^{-1}\ mol^{-1}$). Their IR spectra in CH_2Cl_2 solution show bands in the CO region at 1920, 1860 cm^{-1}, and 2060, 2020 cm^{-1}, which well compare with those found for other $[Mn(\eta^5\text{-}C_5H_5)(CO)_2L]$[18] and $[Fe(\eta^5\text{-}C_5H_5)(CO)_2L]Y$[7] derivatives, respectively. The IR spectra of all these five derivatives further contain a strong band at 1068 cm^{-1} which can be attributed to the asymmetric –CSS stretching vibration.[3,19]

The crystal and molecular structure of the complex **1** consists of monomeric complex molecule $[Cr(CO)_5(S_2CPEt_3)]$. A perspective view of the molecule is given in Figure 1. Selected bond distances and angles are reported in Table IV. The coordination geometry about the chromium atom, which is surrounded by five carbonyl groups and one sulfur atom of the zwitterionic ligand, can

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Table II. Atomic Parameters for $[Cr(CO)_5(S_2CPEt_3)]$[a]

atom	x	y	z	U(11)	U(22)	U(33)	U(12)	U(13)	U(23)
Cr1	1868 (2)	1414 (2)	1312 (2)	72 (2)	65 (2)	36 (1)	-2 (1)	1 (1)	-3 (2)
P1	3301 (3)	1919 (3)	5943 (3)	43 (3)	52 (3)	42 (2)	-2 (2)	3 (2)	-4 (2)
S1	2885 (3)	1276 (3)	3318 (3)	77 (3)	81 (3)	37 (2)	21 (2)	5 (2)	-11 (3)
S2	1544 (3)	2851 (3)	4356 (3)	59 (3)	64 (3)	57 (3)	15 (2)	6 (2)	-2 (2)

atom	x	y	z	U, Å^2	atom	x	y	z	U, Å^2
O1	1527 (8)	3845 (10)	1211 (11)	108 (4)	C5	1173 (13)	1429 (14)	-225 (17)	100 (6)
O2	3767 (9)	1701 (10)	311 (11)	112 (4)	C6	2515 (9)	2033 (10)	4418 (11)	44 (4)
O3	2118 (9)	-989 (10)	1018 (11)	115 (4)	C7	2561 (10)	1503 (11)	7028 (12)	65 (4)
O4	-62 (9)	1097 (9)	2225 (11)	106 (4)	C8	2064 (12)	416 (12)	6673 (16)	96 (6)
O5	680 (8)	1470 (9)	-1233 (11)	109 (4)	C9	4310 (9)	993 (10)	5961 (12)	57 (4)
C1	1690 (11)	2923 (14)	1324 (14)	81 (5)	C10	5002 (11)	853 (13)	7209 (14)	90 (6)
C2	3034 (12)	1593 (13)	721 (15)	79 (5)	C11	3763 (10)	3236 (11)	6401 (13)	67 (5)
C3	2009 (12)	-85 (15)	1138 (15)	91 (5)	C12	4474 (11)	3649 (13)	5602 (14)	95 (6)
C4	694 (13)	1214 (13)	1918 (15)	86 (5)					

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

Table III. Atomic Parameters for $[Mo(CO)_2(PEt_3)(\mu\text{-}S_2CPEt_3)]_2$[a]

atom	x	y	z	U(11)	U(22)	U(33)	U(12)	U(13)	U(23)
Mo	-345 (1)	760 (1)	-397 (1)	38 (1)	35 (1)	44 (1)	1 (1)	3 (1)	4 (1)
S1	404 (2)	858 (1)	1426 (3)	44 (2)	58 (2)	54 (2)	1 (2)	-5 (2)	-6 (2)
S2	-1043 (2)	-35 (1)	669 (2)	39 (2)	39 (2)	55 (2)	1 (2)	4 (2)	3 (1)
P1	-1706 (2)	948 (1)	1921 (3)	52 (2)	48 (2)	54 (2)	6 (2)	10 (2)	2 (2)
P2	795 (2)	1427 (1)	-1230 (3)	57 (2)	50 (2)	62 (2)	-8 (2)	4 (2)	11 (2)

atom	x	y	z	U, Å^2	atom	x	y	z	U, Å^2
O1	-1757 (6)	1748 (4)	-681 (6)	67 (2)	C9	-3429 (17)	1340 (10)	1101 (19)	56 (7)
O2	-1579 (7)	497 (4)	-2362 (8)	85 (3)	C91	-3156 (28)	550 (18)	823 (32)	146 (15)
C1	-1203 (8)	1367 (5)	-534 (10)	53 (3)	C10	2005 (8)	1377 (6)	-752 (11)	76 (4)
C2	-1102 (9)	570 (5)	-1629 (10)	60 (4)	C11	2745 (10)	1799 (6)	-1192 (11)	80 (5)
C3	-761 (7)	624 (4)	1205 (9)	41 (3)	C12	500 (11)	2196 (6)	-1087 (13)	105 (6)
C4	-1846 (10)	591 (6)	3164 (11)	77 (4)	C13	551 (12)	2383 (8)	40 (16)	131 (7)
C5	-978 (11)	608 (6)	3899 (12)	92 (5)	C14	1002 (15)	1345 (8)	-2653 (17)	138 (7)
C6	-1477 (9)	1687 (5)	2138 (10)	70 (4)	C15	258 (24)	1357 (14)	-3317 (27)	107 (11)
C7	-2081 (10)	1976 (6)	3026 (12)	81 (4)	C151	957 (22)	924 (13)	-3179 (25)	87 (9)
C8	-2853 (11)	877 (7)	1258 (14)	90 (5)					

[a] Coordinates multiplied by 10^4, temperature factors by 10^3. Atoms C9, C91, C15, and C151 are assigned a population parameter of 0.5. The form of the thermal ellipsoid is $\exp[-2\pi^2(U(11)h^2a^{*2} + U(22)k^2b^{*2} + U(33)l^2c^{*2} + 2U(12)hka^*b^* + 2U(13)hla^*c^* + 2U(23)klb^*c^*)]$.

be described as distorted octahedral. No bonding interaction between the chromium and the second sulfur atom of the $Et_3P{\cdot}CS_2$ group is envisaged, the Cr···S distance being 3.895 Å. The Cr-S bond distance, 2.389 (4) Å, somewhat longer than the sum of covalent radii (2.22 Å)[20] is only slightly shorter than the average value of 2.444 (7) Å reported for the $[(triphos)Co(\mu\text{-}CS_2)Cr(CO)_5]$ compound.[4a] Also the Cr–CO bond distances, both cis and trans, fall in the range of values previously found for other Cr–CO linkages.[21] In particular the Cr–C bond distance for CO trans to the sulfur atom (1.78 (2) Å) is somewhat shorter than the average value of the Cr–C cis bond lengths (1.86 (1) Å). The significantly large difference of 0.08 Å is indicative of a large trans effect. A comparison with the differences found between the equatorial and the axial distances in $[Cr(CO)_5(PPh_3)]$ and $[Cr(CO)_5P(OC_6H_5)_3]$, 0.036 and 0.035 Å, respectively,[21] indicates that in the present complex the sulfur atom of the zwitterion acts essentially as a σ donor.

In regard to $Et_3P{\cdot}CS_2$, acting as monodentate ligand, small differences are to be pointed out with respect to the uncoordinated zwitterion. Indeed both the S–C bond distances and the S–C–S bond angle are close to the values of the free ligand (1.65 (1), 1.68 (1) Å, 130.8 (7) ° vs. 1.69 (2) Å (av), 127 (1)°, respectively).[22]

Table IV. Selected Bond Distances (Å) and Angles (Deg) for $[Cr(CO)_5(S_2CPEt_3)]$

Bond Distances

Cr-S1	2.389 (4)	P1-C6	1.82 (1)
Cr-C1	1.87 (2)	P1-C7	1.78 (1)
Cr-C2	1.84 (2)	P1-C9	1.78 (1)
Cr-C3	1.87 (2)	P1-C11	1.78 (1)
Cr-C4	1.86 (2)	O1-C1	1.16 (2)
Cr-C5	1.78 (2)	O2-C2	1.18 (2)
S1-C6	1.68 (1)	O3-C3	1.13 (2)
S2-C6	1.65 (1)	O4-C4	1.15 (2)
		O5-C5	1.19 (2)

Bond Angles

S1-Cr-C1	96.7 (5)	Cr1-S1-C6	115.4 (4)
S1-Cr-C2	86.9 (5)	C6-P1-C7	109.5 (6)
S1-Cr-C3	88.4 (5)	C6-P1-C9	112.3 (6)
S1-Cr-C4	92.7 (5)	C6-P1-C11	108.0 (6)
S1-Cr-C5	175.1 (6)	C7-P1-C9	109.9 (6)
C1-Cr-C2	90.3 (7)	C7-P1-C11	106.6 (7)
C1-Cr-C3	174.6 (7)	C9-P1-C11	110.4 (6)
C1-Cr-C4	90.4 (7)	S2-C6-P1	114.4 (7)
C1-Cr-C5	87.2 (7)	S1-C6-P1	114.8 (7)
C2-Cr-C3	88.2 (7)	S1-C6-S2	130.8 (7)
C2-Cr-C4	179.2 (7)	Cr1-C1-O1	173.0 (15)
C2-Cr-C5	90.1 (7)	Cr1-C2-O3	178.1 (14)
C3-Cr-C4	91.0 (7)	Cr1-C3-O3	178.1 (16)
C3-Cr-C5	87.7 (7)	Cr1-C4-O4	176.1 (15)
C4-Cr-C5	90.2 (7)	Cr1-C5-O5	177.0 (16)

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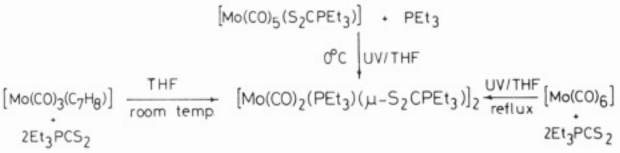
Scheme I



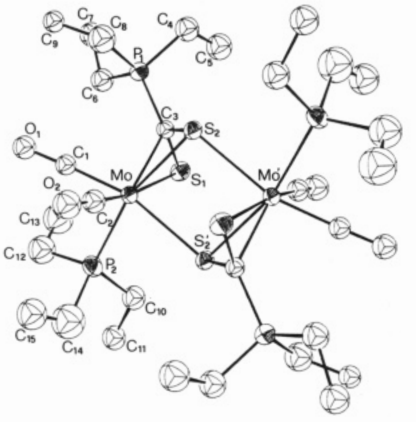


Figure 2. Perspective view of the complex molecule [Mo$(CO)_2(PEt_3)(\mu\text{-}S_2CPEt_3)]_2$, ORTEP drawing with 30% probability ellipsoids.

On the basis of this structural determination and of the information gathered from the spectroscopic measurements, the above anchoring mode of the Z ligand can be extended to compounds **2**–**5**.

When Z is reacted with $[M(CO)_6]$ (M = Cr, W) in THF under UV irradiation, at reflux temperature, the above reported chromium and tungsten derivatives **1** and **3** are obtained, but if the same reaction is carried out by using $[Mo(CO)_6]$, the red dinuclear compound $[Mo(CO)_2(PEt_3)(\mu\text{-}S_2CPEt_3)]_2$, **6**, is isolated. Alternatively compound **6** can be obtained by two other different routes: the reaction of $[Mo(CO)_5(S_2CPEt_3)]$ with PEt_3 under UV irradiation at 0 °C or the reaction of $[Mo(CO)_3(C_7H_8)]$ with Z at room temperature (Scheme I).

Compound **6** slowly decomposes in air both in the solid state and in solution. It is moderately soluble in most organic solvents in which it behaves as nonelectrolyte. The IR spectrum shows two bands in the CO stretching region at 1890 and 1760 cm^{-1}, which well compare with those found for *cis*-$L_4M(CO)_2$ derivatives.[17] No absorption in the –CSS stretching region is observed. The ^{31}P NMR spectrum in CH_2Cl_2 at 295 K consists of two triplets at 44.45 ppm ($^3J(PP)$ = 1.4 Hz) and 28.93 ppm ($^3J(PP)$ = 1.4 Hz), which are assigned to the triethylphosphine ligand and to the phosphorus atom of Z, respectively. Indeed the mononuclear compounds **1**–**3**, which contain only the triethylphosphine group belonging to Z, have ^{31}P NMR spectra showing a unique singlet at 30.65, 31.04, and 32.17 ppm, respectively.

The crystal and molecular structure of compound **6** consists of dimeric centrosymmetric complex molecules $[Mo(CO)_2(PEt_3)(\mu\text{-}S_2CPEt_3)]_2$. Figure 2 shows a perspective view of the complex molecule. Table V reports selected bond distances and angles.

The two molybdenum atoms are held together by two zwitterion ligands, which exhibit in this complex a new bonding mode. Indeed each $Et_3P{\cdot}CS_2$ zwitterion coordinates to one metal through an η^3-S_2C delocalized linkage as a 4π-electron ligand and to the other metal through one sulfur atom as a two-electron σ donor. The coordination around each metal atom can be described as pseudooctahedral, two carbonyl groups and one phosphine being also linked to each molybdenum atom. The most interesting feature of this structure is given by the bonding mode of the zwitterion: indeed the chelate ring MoS_2C is clearly nonplanar, with the molybdenum atom significantly displaced from the S_2C plane (the dihedral angle between the MoS1S2 and the C3S1S2 planes reaching a value of 87.5°), and the central carbon atom clearly within the bonding distance of the metal (2.14 (1) Å).

Table V. Selected Bond Distances (Å) and Angles (Deg) for $[Mo(CO)_2(PEt_3)(\mu\text{-}S_2CPEt_3)]_2$

Bond Distances

Mo-S1	2.551 (3)	P1-C4	1.80 (1)
Mo-S2	2.520 (3)	P1-C6	1.80 (1)
Mo-S2'	2.631 (3)	P1-C8	1.83 (2)
Mo-P2	2.489 (3)	P2-C10	1.82 (1)
Mo-C1	1.89 (1)	P2-C12	1.88 (2)
Mo-C2	1.94 (1)	P2-C14	1.84 (2)
Mo-C3	2.14 (1)	O1-C1	1.21 (1)
S1-C3	1.76 (1)	O2-C2	1.16 (1)
S2-C3	1.75 (1)	Mo···Mo'	3.866 (2)
P1-C3	1.79 (1)	Mo···S1'	4.051 (3)

Bond Angles

S1-Mo-S2	75.2 (1)	Mo-S2-Mo'	97.2 (1)
S1-Mo-S2'	82.4 (1)	Mo-S2-C3	56.7 (4)
S1-Mo-P2	93.3 (1)	C3-P1-C4	109.0 (6)
S1-Mo-C1	106.3 (4)	C3-P1-C6	111.1 (5)
S1-Mo-C2	167.3 (4)	C3-P1-C8	112.9 (7)
S1-Mo-C3	43.0 (3)	C4-P1-C6	110.0 (6)
S2-Mo-S2'	82.7 (1)	C4-P1-C8	105.1 (7)
S2-Mo-P2	162.7 (1)	C6-P1-C8	108.5 (7)
S2-Mo-C1	111.5 (4)	Mo-P2-C10	115.2 (5)
S2-Mo-C2	92.3 (4)	Mo-P2-C12	115.5 (5)
S2-Mo-C3	43.2 (3)	Mo-P2-C14	116.9 (7)
P2-Mo-S2'	82.9 (1)	C10-P2-C12	103.8 (7)
P2-Mo-C1	83.9 (3)	C10-P2-C14	99.8 (8)
P2-Mo-C2	99.4 (4)	C12-P2-C14	103.4 (8)
P2-Mo-C3	132.5 (3)	Mo-C1-O1	176.3 (11)
S2'-Mo-C1	164.6 (4)	Mo-C2-O2	175.0 (11)
S2'-Mo-C2	98.8 (4)	S1-C3-S2	123.8 (6)
S2'-Mo-C3	103.3 (3)	S1-C3-P1	118.9 (6)
C1-Mo-C2	75.5 (5)	S2-C3-P1	114.2 (6)
C1-Mo-C3	91.5 (5)	Mo-C3-P1	128.5 (6)
C2-Mo-C3	125.1 (5)	Mo-C3-S1	81.1 (4)
Mo-S1-C3	55.9 (4)	Mo-C3-S2	80.1 (4)

This geometry suggests the existence of a π interaction between the metal and the zwitterion, which can be so regarded as an η^3-coordinated pseudoallylic ligand. In agreement with this bonding picture is the planarity of the S_2CP group and the equivalence of the two S–C bond distances, indicating that the central carbon atom remains sp^2 hybridized.

There are two different types of molybdenum–sulfur bonds: those involving the π system averaging 2.535 (15) Å and the molybdenum–sulfur σ bond of 2.631 (3) Å. All these distances, somewhat longer than the sum of covalent radii (2.37 Å)[20] are indicative of appreciable trans influence by the carbonyl and phosphine groups. These values however are comparable with those reported for other molybdenum compounds where a similar trans effect has been noticed.[23,24] These distances are much longer than the corresponding values reported for the monomeric $MoO(S_2CS\text{-}i\text{-}C_3H_7)_2$ complex, which contains a η^3-CS_2 thioxanthate group.[25] This difference can be justified on

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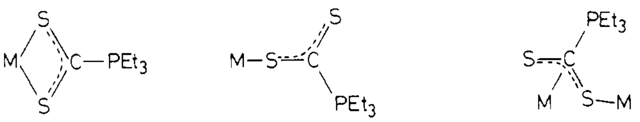
Chart I



the basis of steric requirements due to the larger coordination number and of the different oxidation number of the metal.

Conclusions

The triethylphosphine–carbon disulfide adduct $Et_3P{\cdot}CS_2$ is a very versatile ligand. Indeed this zwitterion can act as a monodentate or bidentate σ donor by means of its electron-rich sulfur atoms, but it can be also π bonded to a metal through the conjugated CS_2 pseudoallylic system, as a four-electron donor (Chart I).

The formation of the complexes **1**–**5**, in which the zwitterion acts as a monodentate ligand, by displacement of the weakly coordinated THF ligand from carbonyl derivatives, is not unexpected. In fact Z has undoubtely nucleophilic character, undergoing alkylation with a variety of electrophiles such as CH_3I to give the phosphonium salt $[Et_3PCSSCH_3]I$.

Concerning the formation of the unexpected complex **6**, on the basis of the reactivity pattern summarized in Scheme I, it is possible to propose a reaction mechanism involving the initial formation of the mononuclear compound **2**. The CS_2 group of the coordinated zwitterion in **2** can, in fact, displace two CO groups from another $[Mo(CO)_5(S_2CPEt_3)]$ molecule by the four-electron donor pseudoallylic CS_2 group. The successive displacement of another CO molecule by triethylphosphine suggests a remarkable back-donation in the metal–pseudoallylic group linkage.

As it is shown in the Experimental Section, at least in two cases the triethylphosphine ligand in compound **6** comes from the cleavage of the P–CS_2 bond in a zwitterion molecule. Such a cleavage is not completely unexpected in reactions carried out at high temperature: it has been previously observed in the reaction of Z with Co(II) aquocations and the triphospine 1,1,1-tris((diphenylphosphino)methyl)ethane,[26] but it is rather surprising in the reaction of Z with $[Mo(CO)_3(C_7H_8)]$ which is carried out under mild conditions. On the other hand the reaction of tertiary phosphines and carbon disulfide is somewhat reversible, expecially when higher trialkylphosphines are employed.[27]

Acknowledgment. Thanks are expressed to Mr. F. Cecconi and Mr. G. Scapacci for technical assistance and to Mr. F. Nuzzi and Mr. G. Vignozzi for microanalyses.

Registry No. **1**, 80975-88-8; **2**, 80975-89-9; **3**, 80975-90-2; **4**, 80975-91-3; **5**, 80975-93-5; **6**, 80137-00-4; $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(THF)]BF_4$, 63313-71-3; $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0; $[Mn(\eta^5\text{-}C_5H_5)(CO)_3]$, 12079-65-1; $[Mo(C_7H_8)(CO)_3]$, 12125-77-8; $Et_3P{\cdot}CS_2$, 997-47-7.

Supplementary Material Available: Listings of structure factor amplitudes for compounds 1 and 6 (16 pages). Ordering information is given on any current masthead page.

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Synthesis and Reactions of Dicarbonyl(η-cyclopentadienyl)dihydridorhenium(III)

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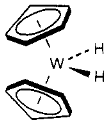
Received December 10, 1981

The title compound $(\eta\text{-}C_5H_5)Re(CO)_2H_2$ (**2**), a thermally stable colorless crystalline solid melting at 36–37 °C, was prepared in 49% yield by UV irradiation of $(\eta\text{-}C_5H_5)Re(CO)_3$ with Et_2SiH_2 and treatment of the intermediate hydridosilylrhenium compound with silica gel in $CHCl_3$. Ethanolic KOH deprotonates **2** forming $[(\eta\text{-}C_5H_5)Re(CO)_2]^{2-}$ which was isolated as its tetraethylammonium salt. Derivatives prepared from **2** or its dianion are $(\eta\text{-}C_5H_5)Re(CO)_2(SnCl_3)H$ (**4**), $(\eta\text{-}C_5H_5)Re(CO)_2(SnMe_3)_2$ (**5**), $(\eta\text{-}C_5H_5)Re(CO)_2Me_2$ (**7**), and $(\eta\text{-}C_5H_5)Re(CO)_2(1\text{-}2\text{-}\eta^2\text{-}C_7H_8)$ (**6**). IR intensities of carbonyl stretching bands indicate trans stereochemistry for **2**, **4**, **5**, and **7**. An unusual reaction of the dianion with acetyl chloride forms $(\eta\text{-}C_5H_5)Re(CO)_2(\eta^2\text{-vinyl acetate})$ (**8**).

Introduction

The interest and importance of molecular hydrides of transition metals is attested by several major reviews of the subject over the past 25 years.[1] Much current work involves hydrido cluster complexes,[1e] but numerous gaps remain in our knowledge of mononuclear hydrides, especially mononuclear polyhydrides. Thus, a number of organometallic hydrides which could reasonably be expected to exist on the basis of 18-electron formalism have not been prepared.

The dihydrides **1** and **3** are well-known, and many aspects of their chemistry have been explored.[1] We now report the synthesis and some reactions of the novel dihydride **2**, which constitutes the middle member of an isoelectronic series formed by successive replacement η-



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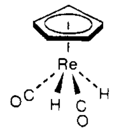

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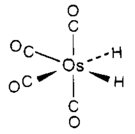

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