by two four-center (Rh_2H_2) two-electron bonds, a_g and b_{2u} (Figure 3). The Mulliken bond order for the Rh–Rh interaction was positive but very small (0.086) largely due to Rh p-orbital bonding (0.076) whereas those for the Rh–H bonds were substantial, about 0.5 bond order (0.497), with major contributions from the rhodium s and p orbitals.

A formally related complex is the dimer of the d^9 $\{HNi[(C_6H_{11})_2PC_3H_6P(C_6H_{11})_2]\}_2$ compound, which has a short Ni–Ni bond (2.441 (1) Å) with both hydride ligands symmetrically bridging this bond.[17] The coordination geometry for each nickel atom is not planar but rather is distorted toward a dimer of tetrahedrally coordinated nickel atoms. Specifically, there is a twisting of the P_2Ni planes with respect to the Ni_2H_2 plane, the dihedral angles between the two P_2Ni planes and the Ni_2H_2 plane being ±31.7°. A molecular orbital analysis identified a small barrier for twisting motion in this 30-electron complex, suggesting that the distortion arises from ligand–ligand repulsions. The situation is different for the 28-electron, d^8 $(HRhP_2)_2$ dimer. Distorting the hydride ligands with respect to the Rh_2P_4 framework toward the tetrahedral dimer significantly destabilizes the b_{2u} bonding orbital relative to the b_{3u} HOMO in square-planar $(HRhP_2)_2$ (Figure 3). Hence, in the d^8 $(HRhP_2)_2$ dimer, there is a variation in total energy with a dihedral angle that is large; the tetrahedral dimer extreme is 100.3 kcal/mol higher in energy than the observed square-planar geometry. In contrast, the d^9 $(HNiP_2)_2$ dimer is also stabilized by the b_{1u} metal–metal bonding orbital shown in Figure 3 for the tetrahedral configuration. Thus, distortion is more facile for the d^9 complexes.

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Registry No. $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$, 65176-62-7.

Supplementary Material Available: A listing of the observed and calculated structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

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Neutral and Cationic (η^2-Dithioalkyl ester)iron(II) Complexes. Synthesis, Spectroscopic Studies, and X-ray Structure of $[Fe(\eta^2\text{-}CS_2CH_2Ph)(CO)_2(PMe_3)_2]PF_6$

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Reaction of $Fe(\eta^2\text{-}CS_2)(CO)_2L_2$ (**1**) (L = tertiary phosphine or phosphite) with MeI or $PhCH_2Br$ yields cationic complexes $[Fe(\eta^2\text{-}CS_2R)(CO)_2L_2]^+X^-$ (R = Me, $PhCH_2$; X = I, Br) via alkylation at the uncoordinated sulfur atom, of which $[Fe(\eta^2\text{-}CS_2Me)(CO)_2(PPh_3)_2]I$ (**2b**) and $[Fe(\eta^2\text{-}CS_2CH_2Ph)(CO)_2(PPh_3)_2]Br$ (**3b**) have been isolated and characterized in the solid state. The behavior of these cations depends markedly on the nature of L; good donors facilitate CO displacement giving halo complexes $Fe(\eta^2\text{-}CS_2Me)(I)(CO)(PMe_2Ph)_2$ (**6d**), $Fe(\eta^2\text{-}CS_2Me)(I)(CO)(PMe_3)_2$ (**6e**), $Fe(\eta^2\text{-}CS_2CH_2Ph)(Br)(CO)(PMe_2Ph)_2$ (**7d**), and $Fe(\eta^2\text{-}CS_2CH_2Ph)(Br)(CO)(PMe_3)_2$ (**7e**) which are fluxional in solution. Treatment of solutions of the cations $[Fe(\eta^2\text{-}CS_2R)(CO)_2L_2]^+$ with $NaPF_6$ gave excellent yields of $[Fe(\eta^2\text{-}CS_2Me)(CO)_2\{P(OMe)_3\}_2]PF_6$ (**4a**), $[Fe(\eta^2\text{-}CS_2Me)(CO)_2(PPh_3)_2]PF_6$ (**4b**), $[Fe(\eta^2\text{-}CS_2Me)(CO)_2(PMe_2Ph)_2]PF_6$ (**4d**), $[Fe(\eta^2\text{-}CS_2Me)(CO)_2(PMe_3)_2]PF_6$ (**4e**), $[Fe(\eta^2\text{-}CS_2CH_2Ph)(CO)_2(PMe_3)(PPh_3)]PF_6$ (**5c**), $[Fe(\eta^2\text{-}CS_2CH_2Ph)(CO)_2(PMe_2Ph)_2]PF_6$ (**5d**), and $[Fe(\eta^2\text{-}CS_2CH_2Ph)(CO)_2(PMe_3)_2]PF_6$ (**5e**). The complex $[Fe(\eta^2\text{-}CS_2CH_2Ph)(CO)_2(PMe_3)_2]PF_6$ crystallizes in space group $P2_1/n$ with cell dimensions $a = 14.403$ (2) Å, $b = 9.354$ (1) Å, $c = 18.648$ (2) Å, $\beta = 99.56$ (1)°, and $Z = 4$. Refinement based on 3183 observed ($I \geq 3\sigma(I)$) diffractometer data converged at $R = 0.036$ and $R_w = 0.048$. The alkylated CS_2 ligand is η^2 coordinated to iron with Fe–C(3) of 1.890 (3) Å, Fe–S(1) of 2.321 (1) Å, and C(3)–S(1) of 1.634 (3) Å. The basic stereochemistry at the iron atom is distorted trigonal bipyramidal with the CS_2CH_2Ph group occupying an equatorial site and the two phosphines in trans positions. Alkylation of the $Fe(\eta^2\text{-}CS_2)$ group leads to a shortening of the Fe–C(CS_2) and coordinated C–S bonds while the uncoordinated C–S bond is lengthened.

Introduction

There is a growing interest in the chemistry of the coordinated CS_2 ligand particularly because derivatives are frequently useful precursors for other interesting transition-metal derivatives. Thus (η^2-dithiomethyl)metal complexes can be converted to thiocarbonyls via alkylthiol elimination,[2] dithiocarbene complexes are accessible from CS_2 complexes via treatment with electrophilic alkynes[3] or excess methyl iodide,[4] metallaheterocycles can be synthesized from acetylenes,[5] and binuclear mixed-metal complexes have been prepared by utilizing the ligating properties of the sulfur atoms.[6,7] More recently, intramolecular fragmentation of CS_2 has led to the

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synthesis of novel triosmium clusters containing μ_3-SCH_2 groups[8] and mononuclear iron complexes with η^2-alkoxythiocarbonyl and chelating 1-phosphino-2-sulfidoalkene ligands.[9]

In reactions of $Fe(\eta^2\text{-}CS_2)(CO)_2L_2$ (L = tertiary phosphine or phosphite) with activated alkynes, we discovered that the electronic properties of the phosphorus ligands L played a key role in determining the behavior of the initially formed carbene–iron(0) complexes, which were stable in the presence of weak donors but readily converted to metallacyclic derivatives when strongly basic phosphines were present.[5] In an attempt to more fully understand the influence of the coligands on the chemical behavior of η^2-coordinated CS_2, we have studied the addition reactions of the alkyl halides MeI and $PhCH_2Br$ with $Fe(\eta^2\text{-}CS_2)(CO)_2L_2$.[10] In this paper we describe these results and show how the chemistry of the resulting η^2-dithioalkyl ester cations $[Fe(\eta^2\text{-}CS_2R)(CO)_2L_2]^+$ varies with the donor properties of the phosphorus ligands. A series of complexes $[Fe(\eta^2\text{-}CS_2R)(CO)_2L_2]X$ (X = Br, I) have also been synthesized and factors influencing their conversion to the halogenocarbonyls $[Fe(\eta^2\text{-}CS_2R)(X)(CO)L_2]$ explored. An X-ray structural analysis of $[Fe(\eta^2\text{-}CS_2CH_2Ph)(CO)_2(PMe_3)_2]^+PF_6^-$ was carried out not only to provide detailed stereochemical information on a reactive dithioalkyl ester cation containing ligands (PMe_3) which conferred enhanced reactivity but also to allow a comparison with the η^2-bound CS_2 molecule in $Fe(\eta^2\text{-}CS_2)(CO)_2(PMe_3)(PPh_3)$,[10] the η^2-bound CS_2Me group in $[Ru(CS_2Me)(CO)_2L_2]ClO_4$[11] or in $[V(CS_2Me)(C_5H_5)_2]I_3$,[12] and also the η^1-coordinated CS_2Me moiety in $Os(CS_2Me)(H)(CO)_2(PPh_3)_2$.[13]

Experimental Section

Preparation of Compounds. The complexes **1** were prepared according to methods already described.[10] All reactions and workup were conducted under an atmosphere of nitrogen. Starting materials were commercially available.

General Procedure for the Synthesis of $[Fe(\eta^2\text{-}CS_2R)(CO)_2L_2]X$. The complex **1** ($10^{-3}$ mol) in dichloromethane (30 mL) was stirred with alkyl halide (MeI or $PhCH_2Br$, 1 mL) at room temperature for 2 h. Compounds **2b** and **3b** were obtained as microcrystalline orange precipitates on addition of hexane.

2b (L = PPh_3, R = CH_3, X = I): 810 mg (95%); mp 130–132 °C dec. IR (Nujol): ν(CO) 2055, 1987; ν(C–S) 1150–1130 cm^{-1}. Anal. Calcd: C, 56.22; H, 3.89; P, 7.24. Found: C, 56.85; H, 4.34; P. 7.31.

3b (L = PPh_3, R = $PhCH_2$, X = Br): 680 mg (77%); mp 138–143 °C dec. IR (Nujol): ν(CO) 2050, 1970; ν(C–S) 1145, 1130 cm^{-1}. Anal. Calcd: C, 62.52; H, 4.22; P, 7.01; Fe, 6.32. Found: C, 61.81; H, 4.40; P, 7.02; Fe, 5.97.

Synthesis of Compounds 4 and 5. A saturated solution of $NaPF_6$ in water (1 mL) was added immediately to a mixture of complex **1** (10^{-3} mol) and alkyl halide (1 mL) in dichloromethane (30 mL). The mixture was stirred at room temperature for 2–3 h, and then the organic layer was washed thoroughly with water to remove unwanted sodium salts and finally dried over anhydrous sodium sulfate. The yellow or orange products crystallized from dichloromethane/hexane mixtures.

4a (L = $P(OMe)_3$, R = Me, X = PF_6): 517 mg (86%); yellow crystals, mp 114 °C. IR (Nujol): ν(CO) 2075, 2020; ν(C–S) 1160 cm^{-1}. ^1H NMR (acetone-d_6): δ 3.27 (CH_3S), 3.87 (t, J_{P-H} = 10 Hz, MeO–P). Anal. Calcd: C, 20.15; H, 3.55; P, 15.58; S, 10.75. Found: C, 20.17; H, 3.57; P, 15.45; S, 11.19.

4b (L = PPh_3, R = Me, X = PF_6): 857 mg (98%); orange crystals, mp 115 °C. IR (Nujol): ν(CO) 2050, 1978; ν(C–S) 1150 cm^{-1}. Anal. Calcd: C, 54.82; H, 3.79; P, 10.95. Found: C, 54.62; H, 3.57; P, 11.21.

4d (L = PMe_2Ph, R = Me, X = PF_6): 612 mg (98%); yellow crystals, mp 156 °C. IR (Nujol): ν(CO) 2050, 1975; ν(C–S) 1140–1122 cm^{-1}. ^1H NMR (acetone–d_6): δ 2.83 (CH_3S), 1.81 (t, J_{P-H} = 9 Hz) and 1.91 (t, J_{P-H} = 9 Hz, CH_3–P), 7.70 (m, C_6H_5–P). Anal. Calcd: C, 38.47; H, 4.03. Found: C, 38.75; H, 4.15.

4e (L = PMe_3, R = Me, X = PF_6): 457 mg (91%); orange crystals, mp 95–97 °C. IR (Nujol): ν(CO) 2060, 1985; ν(C–S) 1135 cm^{-1}. ^1H NMR (acetone-d_6): δ 3.23 (CH_3–S), 1.50 (t, J_{P-H} = 9 Hz, CH_3–P). Anal. Calcd: C 24.01; H, 4.23; P, 18.57. Found: C, 24.06; H, 4.23; P, 18.67.

5c (L = PPh_3 and PMe_3, R = $PhCH_2$, X = PF_6): 330 mg (88%) from 262 mg of **1c**; yellow crystals, mp 185–190 °C dec. IR (Nujol): ν(CO) 2068, 1990; ν(C–S) 1138 cm^{-1}. ^1H NMR (acetone-d_6): δ 4.76 (CH_2S), 1.58 (d, $^2J_{P-H}$ = 12 Hz, CH_3–P), 7.73 (C_6H_5). Anal. Calcd: C, 48.83; H, 4.09. Found: C, 48.69; H, 3.83.

5d (L = PMe_2Ph, R = $PhCH_2$, X = PF_6): 607 mg (86%); yellow crystals, mp 180–184 °C dec. IR (Nujol): ν(CO) 2050, 1990; ν(C–S) 1138 cm^{-1}. ^1H NMR (acetone-d_6): δ 4.46 (CH_2S), 7.50 (C_6H_5), 1.75 (t, J_{P-H} = 9 Hz, CH_3–P). Anal. Calcd: C, 44.58; H, 4.17; P, 13.26. Found: C, 44.52; H, 4.13; P, 13.16.

5e (L = PMe_3, R = $PhCH_2$, X = PF_6): 220 mg (80%) from 160 mg of **1e**; orange crystals, mp 127–128 °C. IR (Nujol): ν(CO) 2055, 1963; ν(C–S) 1142 cm^{-1}. ^1H NMR (acetone-d_6): δ 4.93 (CH_2S), 7.43 (C_6H_5), 1.40 (t, J_{P-H} = 8.8 Hz, CH_3–P). Anal. Calcd: C, 33.34; H, 4.37. Found: C, 33.47; H, 4.38.

General Procedures for Synthesis of $Fe(\eta^2\text{-}CS_2R)(X)(CO)L_2$. A solution of complex **1** (10^{-3} mol) and 1 mL (an excess) of alkyl halide in dichloromethane (30 mL) was stirred at room temperature for at least 24 h or at reflux for a shorter period of time. Completion of the reaction was indicated by thin-layer chromatography. The products were isolated by chromatography on silica gel with diethyl ether as eluant and crystallized from diethyl ether or ether/pentane mixtures.

6d (L = PMe_2Ph, R = Me, X = I): 480 mg (83%): dark red crystals, mp 145 °C. IR (Nujol): ν(CO) 1943; ν(C–S) 1060 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.27 (CH_3S), 1.87 (t, J_{P-H} = 9 Hz) and 2.10 (t, J_{P-H} = 7.5 Hz, CH_3–P), 7.60 (m, C_6H_5P). Anal. Calcd: C, 39.49; H, 4.40; P, 10.76. Found: C, 39.47; H, 4.36; P, 10.71.

6e (L = PMe_3, R = Me, X = I): 350 mg (80%); purple crystals, mp 159–161 °C. IR (Nujol): ν(CO) 1918–1908; ν(C–S) 1060 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.10 (CH_3–S), 1.53 (t, J_{P-H} = 9 Hz, Me–P). Anal. Calcd: C, 23.80; H, 4.66; P, 13.64; I, 27.94. Found: C, 23.49; H, 4.53; P, 13.57; I, 28.86.

7d (L = PMe_2Ph, R = $PhCH_2$, X = Br): 590 mg (97%); dark red crystals, mp 160–165 °C dec. IR (Nujol): ν(CO) 1922–1910; ν(C–S) 1055 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.03 (CH_2–S), 7.60 (C_6H_5), 1.77 (t) and 1.99 (t, J_{P-H} = 9 Hz, CH_3–P). Anal. Calcd: C, 49.44; H, 4.81; P, 10.20. Found: C, 49.65; H, 4.86; P, 11.00.

7e (L = PMe_3, R = $PhCH_2$, X = Br): 109 mg (75%) from 100 mg of **1e**; orange crystals, mp 88–90 °C. IR (Nujol): ν(CO) 1902; ν(C–S) 1085–1072 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.40 (C_6H_5), 4.67 (CH_2S), 1.33 (t, J_{P-H} = 8 Hz, CH_3P). Anal. Calcd: C, 37.28; H, 5.21. Found: C, 37.66; H, 5.63.

Transformation 4d → 6d. A two-phase reaction was carried out with 155 mg of **4d** in dichloromethane and 0.4 g of KI in 2 mL of water. The mixture was stirred for 48 h at room temperature. The product was identified by comparison with an authentic sample of **6d**.

Transformation 6d → 4d. To a solution of 500 mg (~10^{-3} mol) of compound **6d** in dichloromethane (40 mL) was added an excess of iodine (0.5 g). After 3 h at room temperature, derivative **6d** had disappeared (TLC), and an aqueous solution of $NaPF_6$ was added. By addition of ether to the dried solution in dichloromethane, 94 mg (15%) of **4d** was isolated. Anal. Calcd: C, 38.47; H, 4.03; P, 14.88. Found: C, 38,80; H, 4.41; P, 14.77. A similar reaction carried out under 1 atm of carbon monoxide afforded **4d** (310 mg, 49%).

Physical Measurements. Infrared spectra were measured on a Unicam SP 1100 spectrophotometer. Proton NMR spectra were recorded on Varian A-60 or EM-360 instruments using $CDCl_3$ or acetone-d_6 solutions with Me_4Si as an internal standard. Carbon-13 spectra of $CDCl_3$ solutions were obtained on a Bruker WP-80 system with Me_4Si as an internal standard at the Centre de Mesures Phy-

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Collection and Reduction of X-ray Data. Preliminary Weissenberg and precession photographs indicated the systematic absences $0k0$ for $k = 2n + 1$ and $h0l$ for $h + l = 2n + 1$ consistent with the space group $P2_1/n$. A crystal of overall dimensions 0.32 × 0.27 × 0.25 mm was mounted on a glass fiber and attached via a pin to a eucentric goniometer head. After the crystal was centered in the X-ray beam of a Syntex P2$_1$ diffractometer controlled by a Data General Nova 1200 computer, the unit cell dimensions were determined from the setting angles of 15 general reflections for which $22° < 2\theta < 28°$. Crystal data: $FeS_2P_3F_6O_2C_{16}H_7$, $M_r = 558.12$; monoclinic; $a = 14.403$ (2), $b = 9.354$ (1), $c = 18.648$ (2) Å; $\beta = 99.56$ (1)°; $V = 2477.4$ (6) Å^3; $Z = 4$; $\rho_m = 1.50$, $\rho_c = 1.496$ g cm^{-3}; μ(Mo Kα) = 10.36 cm^{-1}; $F(000) = 1104$; space group $P2_1/n$ (C^5_{2h}-No. 14).

Intensity data were recorded on a Syntex P2$_1$ diffractometer equipped with a Mo X-ray tube (λ(Mo Kα) = 0.71069 Å) and graphite monochromator. Intensities were gathered in a θ–2θ scan mode with a variable scan rate set to measure weak reflections more slowly to minimize counting errors. Stationary background counts with a time equal to half the scan time for each reflection were made at the beginning and end of each scan. Two standard reflections were measured after every 100 reflections to monitor crystal and system stability. No significant variation in intensity was noted. All unique data in the range $3.2° < 2\theta < 50°$ were measured, yielding a total of 4382 reflections of which 3183 had intensities $I \geq 3\sigma(I)$. These latter reflections were used in solution and refinement of the structure.

Solution and Refinement of the Structure. All calculations were carried out on an IBM 360-75 system located in the University of Waterloo Computing Centre. Computer programs used included the following: SYNDPREP (data processing), LSTSQR (full-matrix, least-squares refinement and structure factor calculations; a modification of ORFLS by Busing, Martin, and Levy), FOURIER (Fourier and Patterson synthesis; from FORDAP by Zalkin), RANGER (weighting; by Corfield), INTERVOL (distances and angles with esd's; by Chieh), and ORTEP II (plotting; by Johnson).

Scattering factors were taken from the compilation in ref 14 except for hydrogen values where the values of Stewart et al.[15] were used. Both real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion were included for the iron atom.

In least-squares refinements the function minimized was $\sum w(|F_o| - |F_c|)^2$, where w is the weight for each reflection. The discrepancy index R was defined as

$$R = \sum||F_o| - |F_c||/\sum|F_o|$$

and R_w, the weighted residual, as

$$R_w = \sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2$$

The structure was solved by a combination of Patterson, Fourier, and least-squares refinement techniques. In a Patterson map the coordinates of the iron atom were readily recognized, and a Fourier synthesis phased with the iron coordinates gave an R value of 0.55. Locations of the coordinated sulfur and phosphorus atoms were found from the initial Fourier map. Inclusion of these atoms ($R = 0.38$) and a recalculation allowed the unambiguous location of all other nonhydrogen atoms. Isotropic refinement yielded an R value of 0.11. Conversions of isotropic coefficients to anisotropic and refinement to convergence gave a relatively high residual of 0.057, anomalously high thermal parameters for F(2), F(3), F(5), and F(6) of the PF_6^- group. Examination of a difference Fourier synthesis indicated an apparent disorder of the PF_6^- anion which corresponded to a twofold rotation about F(1)–P(3)–F(4). The twofold disorder was subsequently approximated by allotting an occupancy of 0.5 to each disordered fluorine site. Hydrogen atoms were located in a new difference Fourier which included the disordered PF_6^- group. Refinement to convergence using anisotropic temperature factors for all atoms except hydrogen gave a final R value of 0.036. The weighted residual R_w was 0.048 with $w^{-1} = 3.0 - 0.17|F_o| + 0.0057|F_o|^2$. In a final difference map the maximum residual electron density was 0.35 e/Å^3 in the vicinity of the PF_6^- ion.

Table I. Final Positional Parameters for $[Fe(\eta^2\text{-}CS_2CH_2Ph)(CO)_2(PMe_3)_2]PF_6$ (Fractional, ×10^4)

atom	x	y	z
Fe	34.0 (3)	1663.5 (5)	1683.2 (2)
S(1)	−813.2 (6)	2753 (1)	2488.1 (4)
S(2)	872.5 (7)	1394 (1)	3471.1 (5)
P(1)	−896.7 (7)	−305 (1)	1646.7 (5)
P(2)	1001.4 (7)	3587 (1)	1665.8 (5)
P(3)	7298.1 (7)	4947 (1)	883.2 (6)
F(1)	6197 (2)	4790 (3)	837 (2)
F(2A)[a]	7183 (5)	6490 (8)	1154 (7)
F(2B)[a]	7243 (5)	6547 (7)	635 (6)
F(3A)[a]	7117 (7)	5472 (13)	97 (5)
F(3B)[a]	7215 (6)	4470 (13)	72 (4)
F(4)	8410 (2)	5059 (3)	920 (2)
F(5A)[a]	7372 (4)	3377 (7)	621 (6)
F(5B)[a]	7356 (4)	3414 (7)	1150 (6)
F(6A)[a]	7455 (6)	4420 (15)	1675 (4)
F(6B)[a]	7451 (7)	5455 (14)	1679 (5)
O(1)	1530 (2)	−230 (4)	1415 (2)
O(2)	−910 (2)	2246 (4)	184 (1)
C(1)	947 (3)	529 (4)	1518 (2)
C(2)	−546 (2)	2048 (4)	762 (2)
C(3)	156 (2)	1831 (3)	2704 (2)
C(4)	−641 (3)	−1487 (4)	2434 (2)
C(5)	−804 (4)	−1473 (5)	872 (3)
C(6)	−2154 (3)	47 (5)	1563 (3)
C(7)	1061 (5)	4283 (7)	772 (3)
C(8)	2229 (3)	3234 (6)	2034 (4)
C(9)	718 (4)	5159 (5)	2158 (3)
C(10)	388 (3)	2306 (4)	4198 (2)
C(11)	542 (2)	3884 (4)	4201 (2)
C(12)	1439 (3)	4459 (5)	4395 (2)
C(13)	1552 (4)	5934 (6)	4417 (3)
C(14)	786 (4)	6817 (5)	4240 (2)
C(15)	−83 (4)	6264 (5)	4044 (2)
C(16)	−216 (3)	4797 (4)	4029 (2)

[a] An occupancy of 0.5 was refined for the disordered fluorine atoms F(2), F(3), F(5), and F(6).

Table II. Methylene and Phenyl Hydrogen Atom Atomic Coordinates (Fractional, ×10^3) and Isotropic Temperature Factors for $[Fe(\eta^2\text{-}CS_2CH_2Ph)(CO)_2(PMe_3)_2]PF_6$

atom	x	y	z	β_{iso}, Å^2
H(10A)	−30 (4)	208 (5)	411 (3)	5.5 (12)
H(10B)	70 (3)	187 (4)	466 (2)	5.7 (9)
H(12)	193 (3)	384 (4)	452 (2)	5.3 (9)
H(13)	223 (4)	629 (6)	462 (3)	8.4 (13)
H(14)	93 (4)	764 (6)	426 (3)	7.7 (15)
H(15)	−58 (3)	688 (5)	390 (2)	6.3 (11)
H(16)	−89 (3)	432 (4)	389 (2)	5.2 (8)

Atomic positions are listed in Tables I and II with thermal parameters in Table III. Bond lengths and angles are tabulated in Table IV. Observed and calculated structure factor amplitudes are available.[16]

Results and Discussion

Synthetic Aspects. In the η^2-CS_2 complexes **1** the chemical behavior of the equatorially coordinated CS_2 moiety can be considerably modified by varying the nature of the trans phosphorus ligands. Such changes in patterns of reactivity are presumed to occur via a transmission of electronic effects through the metal atom to the coordinated CS_2 moiety. In order to gain further insight into these processes, we have studied the behavior of several derivatives of type **1** toward two alkyl halides, methyl iodide and benzyl bromide (Scheme I). In dichloromethane, complexes **1** were smoothly converted into the salts **2** (MeI) and **3** ($PhCH_2Br$) via nucleophilic displacement of halogen and alkylation of the uncoordinated sulfur atom. Only **2b** and **3b** could be isolated, but the remainder of the cations $[Fe(CS_2R)(CO)_2L_2]^+$ were charac-

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(14) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99–150.

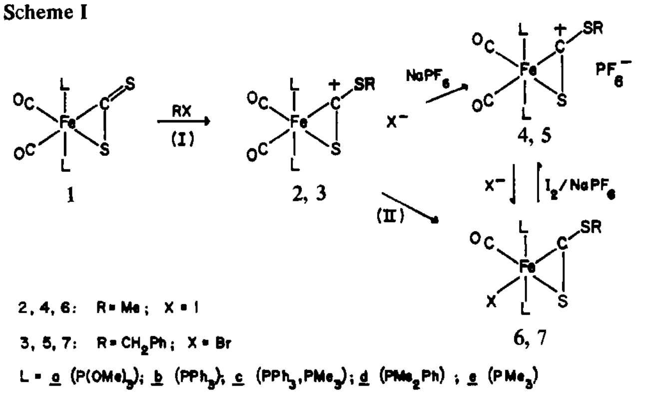
(15) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(16) See paragraph at the end of this paper regarding supplementary data.

Table III. Anisotropic Thermal Parameters (Å^2) for $[Fe(\eta^2\text{-}CS_2CH_2Ph)(CO)_2(PMe_3)_2]PF_6$

atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	46.8 (2)	104.5 (6)	23.0 (1)	2.1 (3)	6.1 (1)	−3.9 (2)
S(1)	51.7 (4)	144 (1)	25.9 (2)	14.6 (6)	6.7 (3)	−8.9 (4)
S(2)	66.3 (5)	129 (1)	25.7 (3)	19.5 (6)	1.0 (3)	−1.1 (4)
P(1)	56.3 (5)	111 (1)	30.8 (3)	−9.0 (6)	11.1 (3)	−8.4 (4)
P(2)	59.9 (5)	120 (1)	28.9 (3)	−13.6 (6)	10.1 (3)	−3.8 (4)
P(3)	57.0 (5)	126 (1)	39.7 (3)	2.5 (6)	9.6 (3)	3.9 (5)
F(1)	64 (1)	199 (4)	96 (2)	11 (2)	22 (1)	6 (2)
F(2A)	98 (5)	164 (10)	156 (7)	−4 (6)	28 (5)	−92 (6)
F(2B)	96 (4)	142 (9)	149 (7)	−17 (5)	−25 (4)	87 (6)
F(3A)	160 (8)	487 (23)	64 (4)	96 (12)	28 (4)	97 (7)
F(3B)	112 (6)	555 (26)	47 (3)	−109 (10)	15 (3)	−60 (6)
F(4)	61 (1)	212 (4)	80 (1)	−13 (2)	11 (1)	−2 (2)
F(5A)	86 (4)	153 (9)	145 (6)	2 (5)	41 (4)	−74 (5)
F(5B)	94 (4)	128 (8)	151 (6)	1 (5)	39 (4)	77 (5)
F(6A)	132 (7)	599 (33)	45 (3)	123 (12)	23 (3)	64 (7)
F(6B)	171 (9)	534 (31)	54 (3)	33 (12)	23 (4)	−74 (8)
O(1)	72 (2)	213 (5)	72 (2)	39 (3)	21 (1)	−22 (2)
O(2)	91 (2)	246 (5)	24 (1)	24 (3)	1 (1)	−2 (2)
C(1)	58 (2)	127 (5)	37 (1)	3 (3)	12 (1)	−11 (2)
C(2)	56 (2)	146 (5)	27 (1)	7 (2)	10 (1)	−9 (2)
C(3)	54 (2)	104 (4)	24 (1)	−3 (2)	7 (1)	−3 (1)
C(4)	97 (3)	130 (5)	49 (2)	−3 (3)	13 (2)	18 (2)
C(5)	114 (4)	187 (7)	52 (2)	−49 (4)	29 (2)	−51 (3)
C(6)	53 (2)	193 (7)	59 (2)	−16 (3)	10 (2)	−4 (3)
C(7)	185 (6)	332 (12)	38 (2)	−132 (7)	20 (2)	19 (3)
C(8)	60 (2)	250 (9)	92 (3)	−33 (4)	−3 (2)	2 (4)
C(9)	129 (4)	126 (6)	82 (3)	−31 (4)	40 (3)	−37 (3)
C(10)	68 (2)	146 (5)	24 (1)	−2 (3)	6 (1)	4 (2)
C(11)	56 (2)	134 (4)	19 (1)	−5 (2)	6 (1)	−3 (1)
C(12)	58 (2)	174 (6)	36 (1)	−4 (3)	7 (1)	−5 (2)
C(13)	85 (3)	210 (8)	44 (2)	−55 (4)	12 (2)	−15 (3)
C(14)	128 (5)	134 (6)	41 (1)	−19 (4)	23 (2)	−8 (2)
C(15)	98 (3)	156 (6)	32 (1)	28 (4)	14 (2)	−1 (2)
C(16)	59 (2)	168 (5)	25 (1)	11 (3)	6 (1)	−7 (2)

Scheme I



terized as their PF_6^- salts **4** and **5** by metathesis with $NaPF_6$ added immediately to the mixture of **1** and alkyl halide. In this way excellent yields of salts having a variety of different phosphorus ligands L were obtained: **2b** (95%), **3b** (77%), **4a** (86%), **4b** (98%), **4e** (91%), **5d** (86%), and **5e** (80%). Reaction I was complete in every case after ~2 h but was much more rapid for the better phosphorus donors (L = PMe_3 or PMe_2Ph) than for the weaker donors even when the latter were less sterically demanding (e.g., $P(OMe)_3$). These observations are consistent with a transfer of electron density via the metal atom to the uncoordinated sulfur of the η^2-CS_2 moiety according to the sequence $P(OMe)_3 < PPh_3 < PMe_2Ph < PMe_3$.[10] The sulfur atom is however insufficiently nucleophilic to displace bromide ion from bromobenzene, there being no observable reaction with **1** for any phosphine L. Alkylation of the coordinated CS_2 ligand, analogous to reaction I has previously been observed for other metals.[4,11,17]

In the absence of PF_6^- counterion, complexes of types **2** and **3** may undergo further reaction. Coordination of halogen with elimination of carbon monoxide was observed for those complexes with better donor ligands L. There was no evidence for reaction II (Scheme I) at ambient temperature starting with **1a** or **1b** whereas in contrast **2d**, **2e**, **3d**, and **3e** were transformed into **6d** (83%), **6e** (80%), **7d**, (97%), and **7e** (75%). These neutral products were isolated by thick-layer chromatography. The reaction was accelerated by refluxing in dichloromethane and complete in ~2 h under these conditions. Although addition of the noncoordinating anion PF_6^- did not entirely prevent the transformation of **2** and **3** (X = halide), the reaction was slowed sufficiently to allow isolation of complexes **4** and **5** containing the donor ligands PMe_3 and PMe_2Ph. Treatment of **4d** with an excess of iodide ion converted salt **4d** to neutral **6d** with coordination of iodide. Conversely cations **4** and **5** could be regenerated from **6** and **7** by addition of iodine, to give presumably the triiodide salt via iodide abstraction, followed by metathesis with $NaPF_6$. Under an atmosphere of carbon monoxide **6d** gave a 50% yield of **4d** with use of these conditions; in the absence of added CO with a nitrogen atmosphere **6d** gave a poor yield (15%) of **4d**. Since our preliminary work on this topic,[18] complexes of type **1** have also been reacted with alkyl halides by other workers.[19] Derivatives similar to **2** and **3** were obtained.

Spectroscopic Studies. For the trimethyl phosphite, trimethylphosphine, and dimethylphenylphosphine complexes **4a**, **4d**, **4e**, **5d**, **5e**, **6d**, **6e**, and **7d**, the methyl ^1H resonances of L appear as deceptively simple triplets due to virtual coupling. Similar coupling is present in the precursors **1**,[10] indicating that the mutual trans stereochemistry of the phosphorus lig-

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(17) Butler, I. S.; Fenster, A. E. *J. Organomet. Chem.* **1974**, *66*, 161 and references therein.

(18) Touchard, D.; Le Bozec, H.; Dixneuf, P. H. *J. Organomet. Chem.* **1979**, *170*, C34.

(19) Conway, P.; Grant, S. M.; Manning, A. R. *J. Chem. Soc., Dalton Trans.* **1979**, 1920.

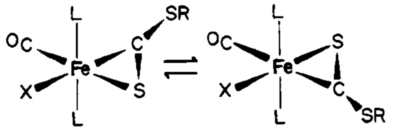
Table IV. Bond Lengths (Å) and Angles (Deg) for $[Fe(\eta^2\text{-}CS_2CH_2Ph)(CO)_2(PMe_3)_2]PF_6$

A. Metal-Ligand Distances			
Fe–S(1)	2.322 (1)	Fe–C(1)	1.756 (4)
Fe–P(1)	2.272 (1)	Fe–C(2)	1.818 (3)
Fe–P(2)	2.279 (1)	Fe–C(3)	1.890 (3)
B. Intraligand Distances			
P(1)–C(4)	1.827 (4)	C(10)–C(11)	1.493 (5)
P(1)–C(5)	1.835 (5)	C(11)–C(12)	1.391 (5)
P(1)–C(6)	1.822 (4)	C(12)–C(13)	1.390 (7)
P(2)–C(7)	1.805 (5)	C(13)–C(14)	1.374 (8)
P(2)–C(8)	1.818 (5)	C(14)–C(15)	1.347 (8)
P(2)–C(9)	1.815 (5)	C(15)–C(16)	1.385 (6)
S(1)–C(3)	1.634 (3)	C(16)–C(11)	1.381 (5)
S(2)–C(3)	1.669 (3)	C(1)–O(1)	1.141 (5)
S(2)–C(10)	1.835 (4)	C(2)–O(2)	1.132 (4)
C. Anion Distances			
P(3)–F(1)	1.581 (3)	P(3)–F(4)	1.594 (3)
P(3)–F(2A)	1.548 (8)	P(3)–F(5A)	1.557 (7)
P(3)–F(2B)	1.565 (7)	P(3)–F(5B)	1.517 (7)
P(3)–F(3A)	1.528 (9)	P(3)–F(6A)	1.537 (8)
P(3)–F(3B)	1.563 (8)	P(3)–F(6B)	1.540 (9)
D. Carbon–Hydrogen Distances			
C(10)–H(10A)	1.00 (4)	C(14)–H(14)	0.80 (6)
C(10)–H(10B)	0.99 (4)	C(15)–H(15)	0.92 (5)
C(12)–H(12)	0.91 (4)	C(16)–H(16)	1.06 (4)
C(13)–H(13)	1.03 (6)		
E. Angles around the Metal			
S(1)–Fe–P(1)	90.2 (0)	P(1)–Fe–C(3)	93.0 (0)
S(1)–Fe–P(2)	92.9 (0)	P(2)–Fe–C(1)	89.9 (1)
S(1)–Fe–C(1)	150.2 (1)	P(2)–Fe–C(2)	91.0 (1)
S(1)–Fe–C(2)	108.4 (1)	P(2)–Fe–C(3)	89.7 (0)
S(1)–Fe–C(3)	44.2 (0)	C(1)–Fe–C(2)	101.2 (1)
P(1)–Fe–P(2)	176.8 (0)	C(1)–Fe–C(3)	106.2 (1)
P(1)–Fe–C(1)	87.7 (1)	C(2)–Fe–C(3)	152.6 (1)
P(1)–Fe–C(2)	87.4 (1)		
F. Angles around Phosphorus			
Fe–P(1)–C(4)	115.3 (1)	Fe–P(2)–C(8)	114.2 (1)
Fe–P(1)–C(5)	112.7 (1)	Fe–P(2)–C(9)	116.3 (1)
Fe–P(1)–C(6)	115.4 (1)	C(7)–P(2)–C(8)	102.8 (2)
C(4)–P(1)–C(5)	104.0 (2)	C(7)–P(2)–C(5)	102.9 (2)
C(4)–P(1)–C(6)	104.1 (2)	C(8)–P(2)–C(9)	104.0 (2)
C(5)–P(1)–C(6)	104.0 (2)		
Fe–P(2)–C(7)	114.9 (2)		
G. Angles within the CS_2CH_2Ph and CO Ligands			
Fe–S(1)–C(3)	53.7 (1)	C(10)–C(11)–C(12)	120.9 (2)
Fe–C(1)–O(1)	178.7 (1)	C(10)–C(11)–C(16)	120.0 (2)
Fe–C(2)–O(2)	178.0 (1)	C(16)–C(11)–C(12)	119.0 (2)
Fe–C(3)–S(1)	81.1 (0)	C(11)–C(12)–C(13)	119.4 (2)
Fe–C(3)–S(2)	141.6 (0)	C(12)–C(13)–C(14)	120.3 (2)
S(1)–C(3)–S(2)	136.2 (0)	C(13)–C(14)–C(15)	120.5 (2)
C(3)–S(2)–C(10)	105.2 (1)	C(14)–C(15)–C(16)	120.4 (2)
S(2)–C(10)–C(11)	112.8 (1)	C(15)–C(16)–C(11)	120.4 (2)
H. Angles within the PF_6^- Group			
F(1)–P(3)–F(2A)	86.8 (3)	F(4)–P(3)–F(6A)	89.7 (4)
F(1)–P(3)–F(2B)	94.1 (3)	F(4)–P(3)–F(6B)	87.5 (4)
F(1)–P(3)–F(3A)	88.1 (4)	F(2A)–P(3)–F(3A)	90.1 (5)
F(1)–P(3)–F(3B)	90.3 (3)	F(2A)–P(3)–F(5A)	177.5 (4)
F(1)–P(3)–F(4)	178.3 (1)	F(2A)–P(3)–F(6A)	89.6 (5)
F(1)–P(3)–F(5A)	90.9 (3)	F(3A)–P(3)–F(5A)	90.7 (5)
F(1)–P(3)–F(5B)	88.2 (3)	F(3A)–P(3)–F(6A)	178.6 (5)
F(1)–P(3)–F(6A)	90.5 (4)	F(5A)–P(3)–F(6A)	89.1 (5)
F(1)–P(3)–F(6B)	93.6 (4)	F(2B)–P(3)–F(3B)	89.7 (4)
F(4)–P(3)–F(2A)	94.9 (3)	F(2B)–P(3)–F(5B)	177.2 (4)
F(4)–P(3)–F(2B)	87.2 (3)	F(2B)–P(3)–F(6B)	89.0 (5)
F(4)–P(3)–F(3A)	91.7 (4)	F(3B)–P(3)–F(5B)	92.1 (4)
F(4)–P(3)–F(3B)	88.6 (3)	F(3B)–P(3)–F(6B)	175.9 (5)
F(4)–P(3)–F(5A)	87.4 (3)	F(5B)–P(3)–F(6B)	89.6 (4)
F(4)–P(3)–F(5B)	90.6 (3)		

ands is retained in reaction I and II. Furthermore, for derivatives **4d** and **6d** containing PMe_2Ph ligands, the methyl groups on phosphorus are nonequivalent and appear as chemically shifted apparent triplets. This diastereotopy results from the lack of a plane of symmetry along the P–Fe–P axis and presumably indicates that the η^2-bound CS_2R group is not undergoing rapid rotation on the NMR time scale.

^{13}C NMR spectra show that compound **5e** is rigid at ambient temperature, as observed for the precursors **1a** and **1e**, while derivative **6e** is fluxional at 310 K.

In contrast, at 215 K the ^{13}C spectrum of **6d** showed the existence of two isomers of probable structures A and B.



A B

Although a single-crystal X-ray analysis[20] of **6e** established a configuration A with the CO group "trans" to the coordinated sulfur atom of the η^2-CS_2Me group, the spectroscopic data do not allow an unequivocal distinction between the major and minor isomers in this mixture (Table V). For each isomer the ^{13}C NMR resonances corresponding to the η^2-CS_2R and CO groups occur as regular triplets indicating coupling to two equivalent trans phosphines. It is worth noting that alkylation of the uncoordinated sulfur atom gives rise to a deshielding of the $^{13}CS_2$ nuclei. Thus $\delta = 293.4$ for the cationic complex **5e** and $\delta = 312.9$ and 311.9 for the neutral isomers **6d** compared to $\delta = 288.0$ for **1e**. This is consistent with the increase of carbene character of the carbon atom in the CS_2R ligand.[3]

Since the relative trans stereochemistry of the phosphorus ligands is retained in all derivatives of types **2**–**7** (Scheme I) a valid comparison of ν(CO) and ν(C–S) frequencies in these derivatives is possible (Table VI). For compounds **4** and **5** the two ν(CO) bands appear at considerably higher frequencies than in the precursors **1**. This frequency increase is undoubtedly due to the effects of the positive charge in **4** and **5**. Expressed differently, the ligand $[\eta^2\text{-}CS_2R]^+$ is more electron withdrawing than neutral η^2-CS_2, resulting in a greater transfer of electron density from the iron atom to the $[\eta^2\text{-}CS_2R]^+$ fragment and hence less π back-bonding to CO. In agreement with this argument, a medium-intensity band in the 1130–1150-cm^{-1} region, readily assignable to ν(C–S) of the uncoordinated C–S moiety, has a lower frequency than the corresponding band in the η^2-CS_2 derivatives **1**.[10] These two effects, consistent with a lowering of the uncoordinated C–S bond order on alkylation of sulfur, are accentuated by the presence of strong donor phosphines (Table VI).

For the neutral species **6** and **7** a single broad ν(CO) band appears in chloroform solution at frequencies much lower than for complexes of types **1**, **4**, and **5** (Table VII). Replacement of a strong π acceptor (CO) by a much poorer acceptor (X^-) presumably accounts in large part for these changes although

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(20) Crystals of **6e** ($Fe(\eta^2\text{-}CS_2Me)(CO)(I)(PMe_3)_2$, $M_r = 454.09$) are tetragonal, of space group $P4_2/n$ with $a = 19.908$ (2) Å, $c = 9.116$ (1) Å, $V = 3613$ Å^3, $Z = 8$, $\rho_c = 1.670$ g cm^{-3}, $\rho_m = 1.66$ g cm^{-3}, $F(000) = 1792$, and μ(Mo Kα) = 29.61 cm^{-1}. A total of 3187 reflections were measured on a Syntex P2_1 diffractometer ($2\theta \leq 50°$) of which 2119 had intensities $I \geq 3\sigma(I)$ and were considered as observed. Although the structure was solved and refined to an R value of 0.040, using the observed data the molecule is severely disordered with the disorder corresponding approximately to a mirror plane passing through the iron, iodine, and two phosphorus atoms. While the basic stereochemistry (configuration A in the text) was well established, with CO approximately trans to the coordinated sulfur atom, and the Fe–I (2.672 (1) Å), Fe–P(1) (2.272 (4) Å), and Fe–P(2) (2.270 (4) Å) distances were reasonable, overlap of peaks due to the CO and CS_2Me ligands of different molecules did not allow precise definition of bond lengths and angles within the η^2-CS_2Me group. The Fe–C(CS_2Me) distance of 1.85 (1) Å is however of reasonable precision since C(1)(CS_2Me) was accurately located and refined. Data sets collected from two other crystals of **6e** suffered from the same disorder problem. We are currently attempting to obtain single crystals of other derivatives of types **6** and **7** for a more detailed comparison of bonding with **5e**.

Table V. Carbon-13 NMR Data[a]

complex	T, K	$\delta(CS_2)/^2J_{P-C}$	$\delta(CO)/^2J_{P-C}$	$\delta(SCH_3)$	$\delta(PCH_3)/^2J_{P-C}$
1e (6)	310	288.0 (t)/15.6	215.4 (t)/28.6, 213.8 (t)/21.3		
5e	310	293.4 (t)/16.5	212.7 (t)/26.4, 212.1 (t)/23.1	29.3	14.8 (t)/33.0
6e	310				15.6 (t)/29.7
6d					
major	215	312.9 (t)/17.7	219.4 (t)/30.5	27.1	15.3 (t)/34.8
minor	215	311.9 (t)/18.4	220.7 (t)/32.1	20.8	12.9 (t)/30.5

[a] Chemical shifts in ppm downfield from Me_4Si; solvent $CDCl_3$; coupling constants in Hz.

Table VI. Infrared Data for $[Fe(\eta^2\text{-}CS_2R)(CO)_2L_2]X$ Compounds[a]

complex	$\nu(C{\equiv}O)$, cm^{-1}	$\nu(C{=}S)$, cm^{-1}
2b	2055, 1987	1150–1130[b]
3b	2050, 1970	1145–1130[b]
4a	2075, 2020	1160
4b	2050, 1978	1150
4d	2050, 1975	1140–1122[b]
4e	2060, 1985	1135
5c	2068, 1990	1138
5d	2050, 1990	1138
5e	2055, 1963	1142

[a] Nujol mull. [b] Weak band.

Table VII. Infrared Data for $[Fe(\eta^2\text{-}CS_2R)(X)(CO)L_2]$ Compounds

	$\nu(C{\equiv}O)$, cm^{-1}		$\nu(C{=}S)$, cm^{-1}	
complex	Nujol	$CHCl_3$	Nujol	$CHCl_3$
6d	1913	1925	1060	1062
6e	1918–1908	1925	1060	1075–1060
7d	1922–1910	1922	1055	1085
7e	1902	1928	1085–1072	1075

there is some evidence from X-ray analysis (Fe–C(CS_2Me) is 1.85 (1) Å in **6e**) for carbenoid character in the Fe–C(CS_2R) bond.[20]

Description and Discussion of the Molecular Structure of $[Fe(\eta^2\text{-}CS_2CH_2Ph)(CO)_2(PMe_3)_2]PF_6$ (5e). The molecule crystallizes in the monoclinic space group $P2_1/n$ with the four cations and PF_6 anions in the unit cell separated by normal van der Waals distances. An ORTEP II plot of the molecular structure of the cation is illustrated in Figure 1. The PF_6^- anions are disordered, and in a best-fit model a twofold disorder of the fluorine atoms with 50% occupancy was refined. In the $[Fe(CS_2CH_2Ph)(CO)_2(PMe_3)_2]^+$ cation the basic stereochemistry is that of a trigonal bipyramid with axial phosphines and equatorial CO groups and the remaining equatorial site occupied by a $\eta^2\text{-}CS_2CH_2Ph$ ligand. Thus the configuration is similar to that found for $Fe(CS_2)(CO)_2(PMe_3)(PPh_3)$ (**1c**) and predicted for **1e** the precursor of **5e**. The average Fe–P bond length (2.276 Å) is somewhat longer than the Fe–P(Me_3P) (2.252 (2) Å) distance in **1c**, and the C(1)–Fe–C(2) angle (101.2 (1)°) is more acute than the corresponding angle in **1c** (109.7 (3)°).[10]

The major structural parameters of interest in the present context are associated with the $\eta^2\text{-}CS_2CH_2Ph$ group. In particular the present study allows an analysis of the structural changes accompanying alkylation of a $\eta^2\text{-}CS_2$ group (as in $Fe(CS_2)(CO)_2(PMe_3)(PPh_3)$) and facilitates a comparison of $\eta^2\text{-}CS_2R$ groups in **5e** and $[Ru(\eta^2\text{-}CS_2Me)(CO)_2(PPh_3)_2]ClO_4$.[11b] Comparable data are also available for the $\eta^2\text{-}CS_2R$ group in $[V(CS_2Me)(C_5H_5)_2]I_3$[12] and for the $\eta^1\text{-}CS_2Me$ group in $Os(H)(\eta^1\text{-}CS_2Me)(CO)_2(PPh_3)_2$.[13]

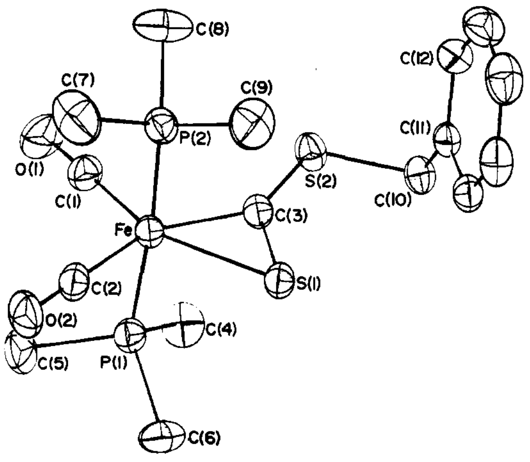

Figure 1.

The uncoordinated C–S bond length in **5e** (C(3)–S(2) of 1.669 (3) Å) is significantly longer than the comparable distance (1.615 (8) Å) in **1c** but is still significantly shorter than the C–S single bond length of 1.81 Å in Me_2S[21] or the C–S(Me) bond length in $Os(H)(\eta^1\text{-}CS_2Me)(CO)_2(PPh_3)_2$ (1.724 Å) where the sulfur ligand is present as a dithiomethyl ester.[13] Not unexpectedly the C–S (Me) bond lengths in $[Ru(\eta^2\text{-}CS_2Me)(CO)_2(PPh_3)_2]ClO_4$ (1.67 (1) Å)[11b] and $[V(CS_2Me)(C_5H_5)_2]I_3$ (1.66 (1) Å)[12] are comparable to that in **5e**. Paralleling the lengthening of the uncoordinated C–S linkage on alkylation is a shortening of the Fe–C(3) bond (1.890 (3) Å in **5e** vs. 1.983 (8) Å in **1c**[10]) consistent with greater π-acid character for the moiety $[\eta^2\text{-}CS_2CH_2Ph]^+$ than for $[\eta^2\text{-}CS_2]$ as predicted from the IR frequencies. For comparison, the iron–carbon distance Fe–C(2) (1.818 (5) Å) involving the multiply bonded carbonyl group is less than 0.1 Å shorter than the Fe–C(3) bond length. While the Fe–S(1) distances [2.321 (1) Å in **5e** vs. 2.334 (2) Å in **1c**] barely differ significantly, there is a noticeably shorter coordinated C–S bond in **5e** (C(3)–S(1) of 1.634 (3) Å; cf. 1.676 (8) Å in **1c**) which approaches the normal C=S bond length in thioketones.[22] A very similar C–S bond length of 1.648 Å has been reported for the monodentate dithiomethyl ester in $OsH(\eta^1\text{-}CS_2Me)(CO)_2(PPh_3)_2$.[13] In contrast the C(10)–S(2) distance (1.835 (4) Å) is typical of a single bond between these atoms.[23] Thus it is apparent that alkylation of the uncoordinated sulfur atom in the Fe–$\eta^2\text{-}CS_2$ moiety by a benzyl group results in a decrease in bond order of the uncoordinated C–S (C(3)–S(2) in **5e**) bond, a strengthening of the metal–carbon interaction, and a shortening of the coordinated C–S (C(3)–S(1) in **5e**) bond. While the alkylation of $[V(CS_2)(C_5H_5)_2]$ did not significantly affect the V–C(CS_2Me) bond [2.075 (4) Å in $[V(CS_2)(C_5H_5)_2]$ and 2.08 (1) Å in $[V(CS_2Me)(C_5H_5)_2]I_3]$,[12] analogous changes in the C–S bond distances [C–S(1) and C–S(2): 1.667 (4) and 1.618 (4) Å in $V(CS_2)(C_5H_5)_2$; 1.63 (1) and 1.66 (1) Å in $[V(CS_2Me)(C_5H_5)_2]I_3$] were observed.[12] It is also worth pointing

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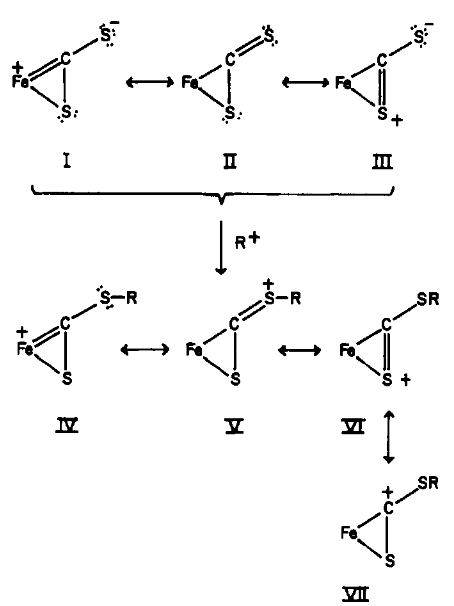
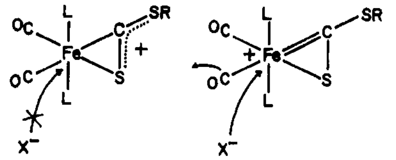
Scheme II



Scheme III



out that the $Fe(\eta^2-CS_2)$ group in a derivative of type **1** is modified in a similar though less pronounced fashion by attachment of a manganese atom to the uncoordinated sulfur site. Thus in $(PhMe_2P)_2(CO)_2FeCS_2Mn(CO)_2(C_5H_5)$[7] the Fe–C distance is 1.939 (6) Å, with C–S(1) of 1.658 (6) Å and C–S(2) of 1.642 (6) Å.

In order to adequately account for the structural features, electronic charge distribution, and reactivity of the precursor **1c**, we earlier suggested contributions from canonical forms I–III to the ground state description of this molecule. Pictorially, alkylation of these forms by R^+ would lead to the valence-bond representations IV–VI (Scheme II). Additionally the reasonable carbonium ion structure VII might be expected to contribute to the electronic structure of **5e**. The detailed comparison of structural parameters for **5e** and **1c** outlined above suggests that form IV makes a substantially greater contribution to **5e** than the corresponding form I to **1c** and that the weight given to structures with double-bond character in the uncoordinated C–S bond is reduced from **1c** to **5e**. These conclusions regarding the electronic structure of **5e** have significance for the chemistry of compounds **4** and **5**. Thus for molecules of this type with strong donor ligands (**4d,e** and **5d,e**) displacement of CO and coordination of halide ion are facilitated by stabilization of the positive charge on iron (form IV) while for the weak donor ligands $P(OMe)_3$ and PPh_3 (**4a,b** and **5a,b**) those forms with the positive charge localized on the ligand predominate (Scheme III).

Registry No. **1a**, 64424-66-4; **1b**, 64424-68-6; **1c**, 64424-59-5; **1d**, 64424-57-3; **1e**, 64424-58-4; **2b**, 72598-18-6; **3b**, 76648-71-0; **4a**, 71004-17-6; **4b**, 71004-19-8; **4d**, 71004-23-4; **4e**, 71004-25-6; **5c**, 76648-73-2; **5d**, 76648-75-4; **5e**, 76648-77-6; **6d**, 76704-54-6; **6e**, 71004-27-8; **7d**, 76648-78-7; **7e**, 76648-79-8; MeI, 74-88-4; $PhCH_2Bu$, 100-39-0.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structures of *cis*- and *trans*-Dichlorobis(cyclobutylamine-*N*)platinum(II), $PtCl_2(C_4H_7NH_2)_2$, and Some Comments on the Conversion of Cis to Trans

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The X-ray crystal structures of the cis and trans forms of dichlorobis(cyclobutylamine-*N*)platinum(II) have been determined. The cis form, monoclinic $P2_1/c$, has cell dimensions $a = 5.975$ (2) Å, $b = 20.459$ (8) Å, $c = 11.512$ (2) Å, and $\beta = 116.18$ (2)° and has 4 formula units in the cell. The crystal structure was determined by standard methods and refined to $R_1 = 0.0515$ and $R_2 = 0.0635$ on the basis of 1852 independent reflections. The trans form is also monoclinic $P2_1/c$ with $a = 7.760$ (2) Å, $b = 9.319$ (3) Å, $c = 8.621$ (2) Å, and $\beta = 97.61$ (2)° and has 2 formula units in the cell. The crystal structure, which was determined similarly, refined to $R_1 = 0.0281$ and $R_2 = 0.0333$ on the basis of 1383 independent reflections. The crystal structure, which was determined similarly, refined to $R_1 = 0.0281$ and $R_2 = 0.0333$ on the basis of 1383 independent reflections. Both data sets were collected by using Mo Kα radiation and a Syntex $P2_1$ diffractometer. Bond lengths (Pt–N range 2.047 (8)–2.06 (3) Å, Pt–Cl range 2.298 (3)–2.326 (9) Å) are similar in the two compounds and agree with values for other amine complexes. Both compounds were prepared by the same preparative method but with different crystallization procedures. It is shown that recrystallization from acetone causes facile cis to trans isomerization.

Introduction

Platinum amine complexes of the type *cis*-$PtCl_2(RNH_2)_2$, where R is a cyclic alkyl group, have been shown[1,2] to have a much better therapeutic index against certain cancers in animals than the first platinum anticancer drug, *cis*-dichlorodiammineplatinum(II).[3] This is caused primarily by a decrease in toxicity of the drug as ring size increases. The corresponding trans analogues are inactive. Attempts to

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