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Chemistry of η^2-CS_2 Metal Complexes: Synthesis of Dithiolene Complexes of Iron via Acetylene Additions to $Fe(\eta^2\text{-}CS_2)(CO)_2(PR_3)_2$. X-ray Structure of $Fe[S_2C(COMe)C(C_6H_4NO_2)](CO)[P(OMe)_3]_2$

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The synthesis of a series of (dithiolato)iron carbonyl complexes $Fe[S_2C(Z^1)C(Z^2)](CO)L^1L^2$ ($L^1L^2 = PMe_3$, $P(OMe)_3$) via the reaction of unsymmetrical, activated acetylenes $Z^1—C≡C—Z^2$ with the η^2-CS_2 complexes $Fe(\eta^2\text{-}CS_2)(CO)_2L^1L^2$ is described. These compounds have been characterized by microanalysis, infrared spectroscopy, and ^1H, ^{31}P, and ^{13}C NMR as well as mass spectroscopy. Crystals of a typical derivative $Fe[S_2C(COMe)C(C_6H_4NO_2)](CO)[P(OMe)_3]_2$ are monoclinic, space group $P2_1/n$ with $a = 8.176$ (1) Å, $b = 29.308$ (3) Å, $c = 11.021$ (1) Å, $\beta = 99.06$ (1)°, $Z = 4$, $\rho_m = 1.50$ g cm^{-3}, and $\rho_c = 1.494$ g cm^{-3}. The structure was solved by Patterson and Fourier methods using 2591 observed ($I \geq 3\sigma(I)$) intensities measured on a Syntex $P2_1$ diffractometer. Refinement by full-matrix least-squares methods gave R and R_w values of 0.031 and 0.042. The iron atom stereochemistry is best described as distorted trigonal bipyramidal with apical positions occupied by one sulfur atom of a dithiolate ligand and a trans carbonyl group. The remaining dithiolate sulfur atom occupies an equatorial site; two phosphite phosphorus atoms are also equatorial. The structure thus differs substantially from those of square-pyramidal α- and β-$Ru[S_2C_2(CF_3)_2](CO)(PPh_3)_2$. The method of synthesis that involves 1,3-dithiocarbene complexes as intermediates is a useful route to unsymmetrical carbonyl dithiolates.

Introduction

Although a substantial number of CS_2–transition-metal complexes are now known, the chemistry of the η^2-CS_2 moiety has only recently become the focus of increased attention. Reactions of the η^2-CS_2 group include alkylation at the nucleophilic sulfur atom,[2] abstraction of sulfur to generate thiocarbonyl–metal complexes,[3] fragmentation of the ligand in mononuclear[4] or polynuclear derivatives,[5] and formation of dinuclear or polynuclear complexes via utilization of one[6] and both[7] sulfur atoms in coordination to other metals. We recently showed that alkynes with electron-withdrawing substituents add readily to the η^2-CS_2 complexes **1** leading to 1,3-dithiocarbene complexes **2**.[8] We now show that the air-sensitive derivatives of type **2** decompose to dithiolene species **3**. The reactions indicated in Scheme I represent a novel and potentially useful route to dithiolene complexes, since the usual methods of synthesis, employing for example sodium salts of maleonitrile dithiol,[9] *cis*-dimercaptoethylene,[10] and arene-1,2-dithiols[11] with inorganic metal salts or bis(trifluoromethyl)dithiete with metal carbonyls,[12] lead only to symmetrical dithiolates. We have now synthesized a number of unsymmetrical dithiolate complexes of iron containing functional groups Z via the reaction of unsymmetrical acetylenes $Z^1—C≡C—Z^2$ with $Fe(\eta^2\text{-}CS_2)(CO)_2L^1L^2$ (**1**). In this paper we report the characterization of $Fe[S_2C(Z^1)C(Z^2)](CO)(L^1)(L^2)$ **3a–g** (Scheme I) and the X-ray structural analysis of one such compound carbonylbis(trimethyl phosphite)[(*cis*-1-acetyl-2-(*p*-nitrophenyl)ethylene)dithiolato]iron, $Fe[S_2C(COMe)C(C_6H_4NO_2)](CO)[P(OMe)_3]_2$. The structure of this molecule is of particular interest in view of the trigonal-bipyramidal stereochemistry of the coordinated iron atom, which contrasts sharply with the square-pyramidal configuration at the ruthenium atoms in both isomers of $Ru[S_2C_2(CF_3)_2](CO)(PPh_3)_2$.[13]

Experimental Section

Physical Measurements. Infrared spectral determinations were made with use of Beckman IR 33 and Perkin-Elmer 157 G spectrometers. NMR spectra were recorded on Varian EM-360 (^1H) and on Bruker WP-80 (^{13}C) instruments. Mass spectra were obtained at 70 eV with use of a Varian MAT-311 mass spectrometer (Centre de Mêsures Physiques, Rennes). Microanalyses were determined by CNRS-Villeurbanne.

Alkynes were commercial grade (Aldrich) or were synthesized according to the literature.[14]

Synthesis. Derivatives $Fe[S_2C(Z^1)C(Z^2)](CO)[P(OMe)_3]_2$ (3a–c) by Oxidation of Carbene–Iron Complexes. Benzene solutions of compounds **2a**, **2b**, or **2c**[8] were passed through a silica gel column in air. Oxidation to the desired compounds gradually occurred on the column. Slow elution with hexane, progressively enriched with ether finally eluted a violet band containing the products.

3a ($Z^1 = Z^2 = CO_2Me$). A 260-mg quantity of **3a** (35%) was obtained from 800 mg of **2a**, after crystallization in a mixture of

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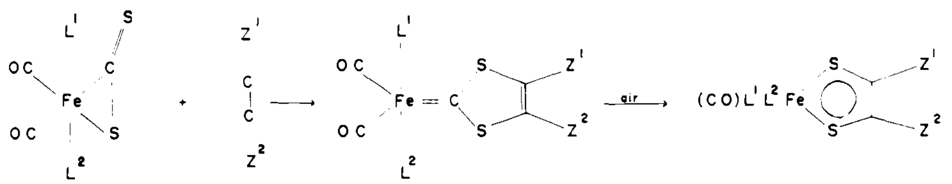
Scheme I



1 $L^1, L^2 = P(OMe)_3$ a-g 2a-g 3a-g

4 $L^1 = PMe_3$, $L^2 = P(OMe)_3$ g 5g 6g

Z^1, Z^2: a (CO_2Me, CO_2Me); b (H, CO_2Et); c (C_6H_5, $COCH_3$); d (p-$NO_2C_6H_4$, CO_2Me), e (C_6H_5, CHO), f (p-ClC_6H_4, CHO); g (p-$NO_2C_6H_4$, $COCH_3$).

hexane–dichloromethane: mp 90–91 °C; mass spectrum, *m/e* 537.998 (calcd 537.998) $[M]^+$, 510 $[M - CO]^+$, 386 $[M - (CO + P(OMe)_3)]^+$; IR (Nujol) 1967, 1730–1715 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.00 (s, CO_2Me), 3.53 (t, $P(OMe)_3$, J_{P-H} = 12.0 Hz). Anal. Calcd for $C_{13}H_{24}FeO_{11}S_2P_2$: C, 28.29; H, 4.44; S, 11.99; P, 11.52. Found: C, 28.81; H, 4.43; S, 11.83; P, 11.29.

3b (Z^1 = H; Z^2 = CO_2Et). A 250-mg quantity of **3b** (23%, oil) was obtained from 1.17 g of **2b**: mass spectrum, *m/e* $[M]^+$ 493.968 (calcd 493.969) $[M]^+$, 466 $[M - CO]^+$, 342 $[M - (CO + P(OMe)_3)]^+$; IR (Nujol) 1965, 1700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.33 (t, HC=, $^4J_{P-H}$ = 2 Hz), 4.27 (q, OCH_2), 3.42 (t, $P(OMe)_3$, J_{P-H} = 11.5 Hz), 1.40 (t, CH_3).

3c (Z^1 = C_6H_5; Z^2 = $COCH_3$). A 170-mg quantity of **3c** (30%, oil) was obtained from 0.6 g of **2c**: mass spectrum, *m/e* 539.991 (calcd 539.989) $[M]^+$, 512 $[M - CO]^+$, 388 $[M - (CO + P(OMe)_3)]^+$; IR (Nujol) 1960, 1655 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.43 (C_6H_5), 3.46 (t, $P(OMe)_3$, J_{P-H} = 12.0 Hz), 2.40 (s, CH_3).

Tetrathiafulvalenes 9a and 9b. From the reaction mixture of **2a** and **2b** the orange compounds **9a** [17%; IR (Nujol) 1743, 1715, 1575 cm^{-1}] and **9b** [(20%; IR (Nujol) 1720, 1560 cm^{-1}; mass spectrum, *m/e* 347.961 (calcd 347.962) $[M]^+$; ^{1}H NMR ($CDCl_3$) δ 7.83 (H—C=, 4.40 (q, OCH_2), 1.40 (t, CH_3); (geometry *E* or *Z* undetermined)] were isolated, by column chromatography (hexane–ether) prior to elution of **3a** and **3b**.

Derivative 10b. Chromatography of the reaction mixture from **2b** afforded besides **9b** and **3b** 5% of **10b** (pink): IR (Nujol) 2030, 1985, 1720 cm^{-1}; mass spectrum, *m/e* 397.935 (calcd 397.934) $[M]^+$, 370 $[M - CO]^+$, 342 $[M - 2CO]^+$.

Derivative 3a from Compound 7. An excess (1.5 mL) of dimethyl acetylenedicarboxylate **a** was added with a syringe to a stirred solution of 7.2 g of 7[15-17] (10 mmol) in 50 mL of dry benzene at 25 °C under N_2. After 1 h, 3 mL of trimethyl phosphite (24 mmol) was added and the mixture was refluxed for 2 h and then exposed to air. After silica gel chromatography 1.5 g of **3a** was obtained (28% overall yield).

Derivatives 3d–g from Compound 1. Compound 1[16] was stirred at 25 °C under N_2 with an excess of the alkyne **d**, **e**, **f**, or **g** in 10–20 mL of dichloromethane for a period of time that depended on the alkyne. The solutions of the resulting intermediates **3d–g** were chromatographed on thick-layer silica gel plates with use of hexane–ether mixtures.

3d (Z^1 = p-$O_2NC_6H_4$, Z^2 = CO_2Me). A 0.5-g quantity of **3d** (37%, oil) was obtained from 0.97 g of **1** and 0.56 g of alkyne **d** (stirring for 4 h): mass spectrum, *m/e* 600.970 (calcd 600.970) $[M]^+$, 573 $[M - CO]^+$; 449 $[M - (CO + P(OMe)_3)]^+$; IR (Nujol) 1970, 1705 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.86 (d), 8.54 (d) ($^3J_{H-H}$ = 9 Hz, C_6H_4), 3.90 (s, CO_2Me), 3.52 (t, $P(OMe)_3$, J_{P-H} = 11.5 Hz); ^{31}P NMR (CD_2Cl_2) δ 174.6 (s) (309 K), 175.6 (s) (213 K).

3e (Z^1 = C_6H_5, Z^2 = CHO). A 0.25-g quantity of **3e** (46%, oil) was obtained from 0.44 g of **1** and 0.15 mL of alkyne **e** (stirring for 15 h): mass spectrum, *m/e* 525.975 (calcd 525.974) $[M]^+$, 497.978 (calcd 497.979) $[M - CO]^+$, 373.950 (calcd 373.950) $[M - (CO + P(OMe)_3)]^+$; IR (Nujol) 1962, 1655 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.83 (s, CHO), 7.53 (m, C_6H_5), 3.53 (t, $P(OMe)_3$, J_{P-H} = 11.5 Hz).

3f (Z^1 = p-ClC_6H_4, Z^2 = CHO). A 0.19-g quantity of **3f** (22%, oil) was obtained from 0.70 g of **1** and 0.32 g of alkyne **f** (stirring for 15 h): mass spectrum, *m/e* 559.933 (calcd 559.935) $[M]^+$, 532 $[M - CO]^+$, 408 $[M - (CO + P(OMe)_3]^+$; IR (Nujol) 1970, 1660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.83 (s, CHO), 7.74 (m, C_6H_4), 3.50 (t, $P(OMe)_3$, J_{P-H} = 12.0 Hz).

3g (Z^1 = p-$O_2NC_6H_4$, Z^2 = $COCH_3$). A 0.3-g quantity of **3g** (26%, mp 104–105 °C (hexane–CH_2Cl_2)) was obtained from 0.87 g of **1** and 0.38 g of alkyne **g** (stirring for 15 h): mass spectrum, *m/e* 584.975 (calcd 584.974) $[M]^+$, IR (Nujol) 1980, 1670 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.19 (d), 7.51 (d, $^3J_{HH}$ = 9 Hz, –C_6H_4–), 3.52 (t, $P(OMe)_3$, J_{P-H} = 11.5 Hz), 2.70 (s, CH_3). Anal. Calcd for $C_{17}H_{25}FeNO_{10}P_2S_2$: C, 34.20; H, 4.04; N, 2.50; S, 10.62. Found: C, 34.88; H, 4.61; N, 2.39; S, 10.94.

Derivative 6g (Z^1 = p-$O_2NC_6H_4$, Z^2 = $COCH_3$). A solution of 1.2 g of **4** (3 mmol) and of 0.6 g (a slight excess) of alkyne **g** in 40 mL of dichloromethane was stirred for 4 h at 20 °C under N_2. The brown solution of **5g** (not isolated) was chromatographed in air on a silica gel thick-layer plate (eluant: hexane–ether). A 0.4-g quantity of **6g** (24%, oil) was then obtained from the violet, eluted solution: mass spectrum, *m/e* 536.988 (calcd 536.990) $[M]^+$, 508.994 (calcd 508.995) $[M - CO]$, 385 $[M - (CO + P(OMe)_3)]^+$; IR (Nujol) 1960, 1665 cm^{-1}; ^{1}H NMR, ($CDCl_3$) δ 7.90 (d), 8.63 (d, $^3J_{HH}$ = 9 Hz, –C_6H_4–), 3.55 (d, $P(OMe)_3$, $^3J_{P-H}$ = 12.0 Hz), 2.77 (s, $COCH_3$), 1.55 (d, PMe_3, $^2J_{PH}$ = 11.0 Hz).

Synthesis of Derivative 12 (Z^1 = Z^2 = CF_3) from 2a. A 0.9-g quantity (4 mmol) of bis(trifluoromethyl)dithiete was added to a solution of 1.16 g (2 mmol) of **2a** in 20 mL of dry benzene. The solution was stirred for 2 h under N_2 and then chromatographed on a silica gel column (eluant: hexane–ether). A 0.75-g quantity (67%) of a violet compound was isolated: mass spectrum, *m/e* 557.922 (calcd 557.922) $[M]^+$, 530 $[M - CO]^+$, 406 $[M - (CO + P(OMe)_3)]^+$; IR (C_6H_6) 1970 cm^{-1}; ^{1}H NMR, (C_6D_6) δ 3.07 (t, $P(OMe)_3$, J_{P-H} = 12.0 Hz).

X-ray Structure Determination. Collection and Reduction of X-ray Data. Violet-red crystals of the title compound were obtained via recrystallization from dichloromethane–hexane. Preliminary precession and Weissenberg photographs indicated systematic absences *h0l*, *h* + *l* = 2*n* + 1, and 0*k*0, *k* = 2*n* + 1, consistent with the monoclinic space group $P2_1/n$ (nonstandard setting of $P2_1/c$, C_{2h}^5, No. 14). Unit cell parameters were refined by least-squares analysis of 2θ values for 15 reflections well dispersed in reciprocal space using a Syntex $P2_1$ diffractometer with Mo Kα radiation. Crystal data: $FeS_2P_2O_{10}NC_{17}H_{25}$; M_r = 585.07; V = 2607.9 Å^3; a = 8.176 (1), b = 29.308 (3), c = 11.021 (1) Å; β = 99.06 (1)°; Z = 4; ρ_c = 1.494, ρ_m(flotation in CCl_4–C_6H_{14}) = 1.50 g cm^{-3}; $F(000)$ = 1208; μ(Mo Kα) = 9.22 cm^{-1}.

A suitable crystal chosen for intensity measurements had dimensions of 0.30 × 0.28 × 0.23 mm. This crystal was mounted on a glass fiber with epoxy glue, transferred to a eucentric goniometer head, and secured on the diffractometer. Intensity data were collected at 24 ± 1° with 2θ = 3.2–45° with use of monochromated Mo Kα (λ = 0.710 69 Å) radiation and the θ–2θ scan method with a variable scan

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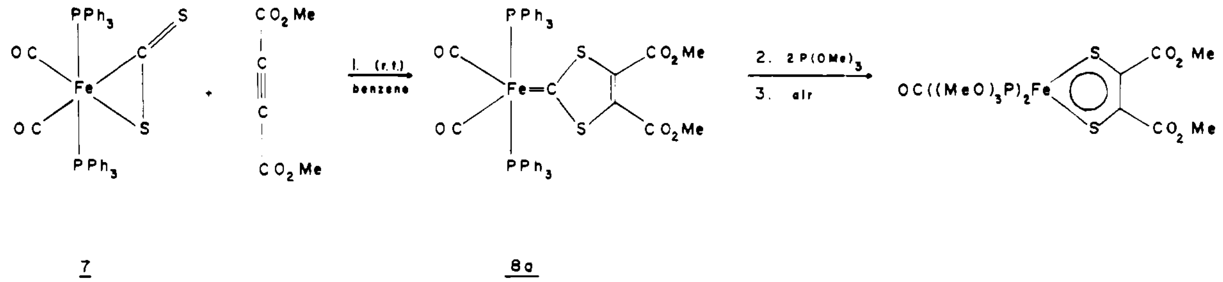
Scheme II



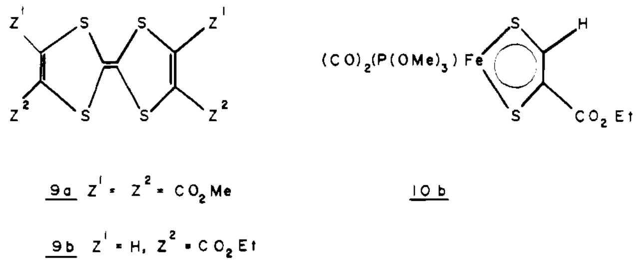
rate (2–29.3° min^{-1}) chosen to minimize counting errors on weak reflections. Two standard reflections [(15$\bar{5}$), (305)] monitored after every 100 measurements showed intensity fluctuations within the acceptable range of ±2%. A total of 3428 independent reflections were obtained of which 2591 with intensities $I \geq 3\sigma(I)$ were used in the subsequent structure solution and refinement. Lorentz and polarization corrections were applied in the normal way to the derivation of structure amplitudes. With μ(Mo Kα) = 9.22 cm^{-1} no absorption correction was deemed necessary.

Solution and Refinement of the Structure. The position of the iron atom was determined from a three-dimensional Patterson synthesis. A Fourier synthesis phased with the iron atom coordinates yielded an R value ($R = \sum(|F_o| - |F_c|)/\sum(|F_o|)$) of 0.56 and revealed the locations of the phosphorus and sulfur atoms. Refinement of these heavy-atom positions and a scale factor followed by a Fourier synthesis gave the positions of all other nonhydrogen atoms. Full-matrix least-squares refinement of isotropic thermal parameters for all nonhydrogen atoms converged with R = 0.12. Refinement of anisotropic thermal parameters for all 33 atoms gave R = 0.046. A difference Fourier calculated at this stage provided chemically reasonable positions for all 25 hydrogen atoms. In final cycles of full-matrix least-squares refinement hydrogen atom positions were refined with fixed isotropic thermal parameters. A weighting scheme of the type $w^{-1} = 2.0 - 0.032|F| + 0.0009|F^2|$ was then introduced with weights derived from the program RANGER.[18] Final values of R and R_w ($R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$) were 0.031 and 0.042. A final difference map revealed no peaks higher than 0.5 e Å^{-3}. The function minimized in least-squares refinements was $\sum w(|F_o| - |F_c|)^2$. Scattering factors for neutral heavy atoms were taken from the compilations in the International Tables[19] and included corrections for the real and imaginary components of anomalous dispersion for the iron atom. Hydrogen atom parameters were those of Stewart et al.[20] All calculations were performed on an IBM 360-75 system in the University of Waterloo Computing Centre. Computer programs used have been described elsewhere.[18] Table I contains a listing of atomic positions for nonhydrogen atoms. Hydrogen atom positions and isotropic temperature factors (Table S1) and structure factors are available as supplementary data. Anisotropic temperature factors are listed in Table II, bond lengths in Table III, and bond angles in Table IV.

Table I. Fractional Atomic Coordinates (× 10^4) for Fe[S$_2$C(COMe)C(C$_6$H$_4$NO$_2$)](CO)[P(OMe)$_3$]$_2$

atom	x	y	z
Fe	1465.3 (7)	1604.2 (2)	1006.8 (4)
S(1)	1584 (1)	1706.4 (3)	−913.8 (8)
S(2)	−786 (1)	1198.1 (4)	454 (8)
P(1)	2346 (1)	1148.3 (4)	2501.6 (9)
P(2)	289 (1)	2053.3 (4)	2114.5 (9)
O(1)	4453 (5)	2155 (2)	1400 (3)
O(2)	−1838 (4)	1512 (1)	−3678 (3)
O(3)	3955 (4)	1336 (1)	3327 (3)
O(4)	2808 (5)	651 (1)	2116 (3)
O(5)	1324 (4)	1016 (1)	3546 (3)
O(6)	−1027 (5)	1840 (1)	2870 (3)
O(7)	−821 (3)	2442 (1)	1385 (2)
O(8)	1569 (5)	2320 (1)	3079 (3)
O(9)	−8294 (4)	376 (2)	−3086 (4)
O(10)	−6872 (4)	−19 (1)	−4145 (3)
N	−6985 (4)	267 (1)	−3368 (3)
C(1)	3290 (6)	1933 (2)	1274 (4)
C(2)	−1179 (4)	1213 (1)	−1128 (3)
C(3)	−140 (4)	1445 (1)	−1751 (3)
C(4)	−449 (5)	1527 (1)	−3108 (3)
C(5)	993 (6)	1641 (2)	3748 (4)
C(6)	4810 (7)	1074 (2)	4368 (5)
C(7)	3500 (17)	558 (3)	1033 (8)
C(8)	26 (8)	694 (3)	3468 (6)
C(9)	−2286 (7)	2032 (5)	3383 (6)
C(10)	−161 (7)	2738 (2)	542 (5)
C(11)	1235 (7)	2726 (2)	3706 (5)
C(12)	−2679 (4)	957 (1)	−1705 (3)
C(13)	−2575 (4)	615 (1)	−2574 (3)
C(14)	−3983 (5)	384 (1)	−3112 (3)
C(15)	−5478 (4)	499 (1)	−2781 (3)
C(16)	−5628 (5)	827 (1)	−1908 (3)
C(17)	−4211 (5)	1051 (1)	−1364 (3)

Chart I



Results and Discussion

Synthesis. We have already shown[8] that the addition of a variety of electrophilic alkynes to Fe(η^2-CS$_2$)(CO)$_2$L$_2$ complexes **1** leads to thermally stable, but air-sensitive carbene–iron derivatives of type **2**. The decomposition of these (1,3-dithiol-2-ylidene)iron complexes **2** in air has now been studied in detail. Brown benzene solutions of derivatives **2a–c** prepared from the η^2-CS$_2$ complex **1** according to Scheme I[8] were exposed to air and chromatographed on short silica gel columns. The violet products were identified as (dithiolene)iron complexes **3a** (35%), **3b** (23%), and **3c** (30%). Similar (dithiolene)iron derivatives **3d–g** or **6g** were prepared in a one-pot reaction, directly from their precursors **1** or **4** by addition of alkyne and oxidation of the resulting carbene–iron intermediate. Overall yields were in the range 22–46%. The derivative **3a** was more readily prepared by three successive reactions performed in one flask: (i) addition of 1 equiv of dimethyl acetylenedicarboxylate at room temperature to compound **7**,[15] prepared in one step from Fe(CO)$_5$,[17] (ii) displacement from the intermediate **8a** of both PPh$_3$ ligands with an excess of P(OMe)$_3$, and (iii) exposure to air of the resulting solution, followed by chromatography (Scheme II).

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[18] Computer programs used in the X-ray analysis have been described in detail elsewhere. See: Carty, A. J.; Mott, G. N.; Taylor, N. J.; Yule, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 3051.

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Table II. Anisotropic Thermal Parameters (×10^4) for $Fe[S_2C(COMe)C(C_6H_4NO_2)](CO)[P(OMe)_3]_2$[a]

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	181 (1)	12.7 (1)	59.5 (7)	7.1 (3)	8.2 (6)	1.1 (2)
S(1)	148 (2)	13.1 (2)	59 (1)	−2.7 (4)	17 (1)	0.0 (3)
S(2)	217 (3)	16.6 (2)	60 (1)	−21.7 (6)	16 (1)	0.7 (4)
P(1)	201 (2)	11.7 (2)	69 (1)	−3.7 (5)	18 (1)	2.0 (3)
P(2)	221 (3)	11.8 (2)	68 (1)	−1.7 (5)	−21 (1)	0.6 (3)
O(1)	294 (9)	31 (1)	140 (5)	−51 (3)	−37 (5)	15 (2)
O(2)	207 (7)	28.3 (8)	85 (3)	−13 (2)	−15 (4)	12 (1)
O(3)	228 (7)	16.6 (6)	111 (4)	−7 (2)	−33 (4)	12 (1)
O(4)	436 (12)	15.4 (6)	98 (4)	13 (2)	46 (5)	0 (1)
O(5)	297 (8)	17.8 (6)	109 (4)	−9 (2)	61 (5)	6 (1)
O(6)	507 (13)	17.4 (6)	139 (5)	28 (1)	165 (7)	14 (1)
O(7)	192 (6)	15.5 (5)	106 (4)	2 (1)	8 (4)	9 (1)
O(8)	339 (9)	18.6 (7)	137 (4)	21 (2)	−88 (5)	−21 (1)
O(9)	182 (8)	31 (1)	275 (8)	−22 (2)	57 (6)	−40 (2)
O(10)	249 (9)	25.2 (8)	183 (6)	−22 (2)	28 (6)	−32 (2)
N	186 (8)	16.3 (7)	130 (5)	−10 (2)	24 (5)	−8 (2)
C(1)	237 (11)	18.9 (9)	75 (5)	−17 (3)	−17 (6)	8 (2)
C(2)	160 (8)	10.3 (6)	66 (4)	0 (2)	14 (4)	−1 (1)
C(3)	145 (8)	11.4 (6)	61 (4)	4 (2)	15 (4)	−1 (1)
C(4)	188 (9)	15.0 (7)	67 (4)	−2 (2)	10 (5)	0 (1)
C(5)	217 (11)	29 (1)	60 (4)	−9 (3)	28 (6)	0 (2)
C(6)	319 (14)	19 (1)	149 (7)	1 (3)	−76 (8)	18 (2)
C(7)	1131 (44)	31 (2)	176 (9)	101 (7)	297 (18)	25 (3)
C(8)	319 (15)	29 (1)	164 (8)	−47 (4)	18 (9)	16 (3)
C(9)	229 (13)	35 (2)	232 (11)	15 (4)	81 (9)	28 (3)
C(10)	264 (12)	16.0 (8)	152 (7)	3 (3)	56 (7)	20 (2)
C(11)	322 (15)	16.2 (9)	162 (8)	1 (3)	3 (8)	−24 (2)
C(12)	158 (8)	11.2 (6)	61 (4)	−1 (2)	17 (4)	0 (1)
C(13)	160 (8)	12.1 (7)	85 (4)	2 (2)	18 (5)	−3 (1)
C(14)	190 (9)	11.1 (6)	84 (4)	0 (2)	10 (5)	−5 (1)
C(15)	144 (8)	11.2 (6)	88 (4)	−3 (2)	13 (5)	−1 (1)
C(16)	165 (9)	12.7 (7)	92 (5)	−2 (2)	29 (5)	−1 (1)
C(17)	177 (9)	12.4 (7)	82 (4)	−1 (2)	32 (5)	−4 (1)

[a] The form of the anisotropic thermal parameters is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

Table III. Bond Lengths (Å) for $Fe[S_2C(COMe)C(C_6H_4NO_2)(CO)[P(OMe)_3]_2$

Fe–S(1)	2.155 (1)	O(5)–C(8)	1.412 (8)
Fe–S(2)	2.196 (1)	O(6)–C(9)	1.372 (7)
Fe–P(1)	2.155 (1)	O(7)–C(10)	1.437 (6)
Fe–P(2)	2.125 (1)	O(8)–C(11)	1.423 (6)
Fe–C(1)	1.756 (5)	O(9)–N	1.204 (5)
S(1)–C(3)	1.736 (3)	O(10)–N	1.212 (5)
S(2)–C(2)	1.722 (3)	N–C(15)	1.465 (5)
P(1)–O(3)	1.575 (3)	C(2)–C(3)	1.355 (5)
P(1)–O(4)	1.581 (3)	C(3)–C(4)	1.496 (5)
P(1)–O(5)	1.573 (3)	C(4)–C(5)	1.503 (6)
P(2)–O(6)	1.588 (4)	C(2)–C(12)	1.491 (5)
P(2)–O(7)	1.592 (3)	C(12)–C(13)	1.398 (5)
P(2)–O(8)	1.576 (4)	C(13)–C(14)	1.385 (5)
O(1)–C(1)	1.142 (6)	C(14)–C(15)	1.372 (5)
O(2)–C(4)	1.210 (5)	C(15)–C(16)	1.379 (5)
O(3)–C(6)	1.464 (6)	C(16)–C(17)	1.383 (5)
O(4)–C(7)	1.429 (11)	C(17)–C(12)	1.390 (5)

Table IV. Bond Angles (Deg) for $Fe[S_2C(COMe)C(C_6H_4NO_2)](CO)[P(OMe)_3]_2$

S(1)–Fe–S(2)	88.2 (0)	P(2)–O(6)–C(9)	131.9 (2)
S(1)–Fe–P(1)	140.9 (0)	P(2)–O(7)–C(10)	121.1 (2)
S(1)–Fe–P(2)	124.9 (0)	P(2)–O(8)–C(11)	122.4 (2)
S(1)–Fe–C(1)	85.4 (1)	Fe–C(1)–O(1)	177.1 (1)
S(2)–Fe–P(1)	92.3 (0)	S(2)–C(2)–C(3)	119.6 (1)
S(2)–Fe–P(2)	93.4 (0)	S(2)–C(2)–C(12)	115.6 (1)
S(2)–Fe–C(1)	173.6 (1)	C(3)–C(2)–C(12)	125.1 (1)
P(1)–Fe–P(2)	94.1 (0)	S(1)–C(3)–C(2)	118.2 (1)
P(1)–Fe–C(1)	92.3 (1)	S(1)–C(3)–C(4)	117.1 (1)
P(2)–Fe–C(1)	90.7 (1)	C(2)–C(3)–C(4)	124.5 (2)
Fe–S(1)–C(3)	107.6 (1)	O(2)–C(4)–C(3)	120.7 (2)
Fe–S(2)–C(2)	106.3 (1)	O(2)–C(4)–C(5)	120.4 (2)
Fe–P(1)–O(3)	111.9 (1)	C(3)–C(4)–C(5)	118.9 (2)
Fe–P(1)–O(4)	115.6 (1)	C(2)–C(12)–C(13)	121.2 (2)
Fe–P(1)–O(5)	124.0 (1)	C(2)–C(12)–C(17)	120.0 (2)
O(3)–P(1)–O(4)	105.3 (1)	C(17)–C(12)–C(13)	118.8 (2)
O(3)–P(1)–O(5)	98.9 (1)	C(12)–C(13)–C(14)	120.5 (2)
O(4)–P(1)–O(5)	98.4 (1)	C(13)–C(14)–C(15)	118.8 (2)
Fe–P(2)–O(6)	117.5 (1)	C(14)–C(15)–C(16)	122.5 (2)
Fe–P(2)–O(7)	115.2 (0)	C(14)–C(15)–N	119.4 (2)
Fe–P(2)–O(8)	112.4 (1)	C(16)–C(15)–N	118.1 (2)
O(6)–P(2)–O(7)	99.7 (1)	C(15)–C(16)–C(17)	118.2 (2)
O(6)–P(2)–O(8)	105.9 (1)	C(16)–C(17)–C(12)	121.2 (2)
O(7)–P(2)–O(8)	104.6 (1)	C(15)–N–O(9)	118.8 (2)
P(1)–O(3)–C(6)	121.5 (2)	C(15)–N–O(10)	118.8 (2)
P(1)–O(4)–C(7)	123.0 (4)	O(9)–N–O(10)	122.4 (2)
P(1)–O(5)–C(8)	126.9 (2)		

The yields of (dithiolene)iron complexes **3a–g** isolated never exceeded 50%, and these compounds are clearly not the only products of oxidation of the carbenes **2a–g**. Very small quantities of other compounds were also observed. Thus, as well as **3a** and **3b**, the corresponding tetrathiafulvalenes **9a** and **9b** resulting from the dimerization of the carbene ligand were isolated by chromatography in yields of 17 and 20%, respectively. These products were shown to be identical in every respect to the compounds described by Hartzler.[22] Moreover in addition to the complex **3b**, a small amount (5%) of the (1,2-dithiolene)iron complex **10b** was obtained (Chart I). This compound was uniquely identified by infrared spectroscopy (ν(CO) (Nujol) 2030, 1985, 1720 cm^{-1}) and by mass spectrometry [M$^+$ 397.935 (calcd 397.934)]. The (1,2-dithiolene)iron complexes **3a–g** and **6g** were characterized by mass spectrometry, which showed a parent ion for each compound and subsequent loss of one carbonyl ligand, by microanalysis for the crystalline compounds **3a** and **3g**, and by infrared and NMR spectroscopy.

The unexpected formation of the (1,2-dithiolene)iron complexes **3**, by decomposition with oxygen of the (1,3-dithiol-2-ylidene)iron derivatives **2** (Scheme I), has not been fully

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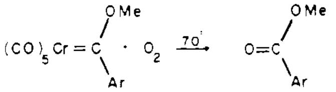
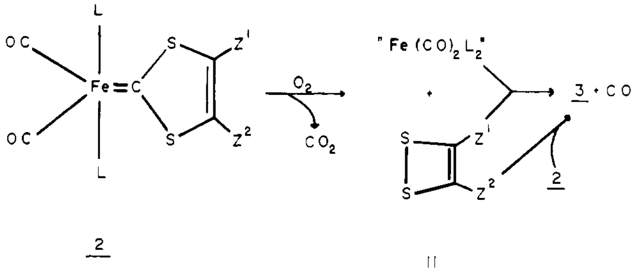
[22] Hartzler, H. D. *J. Am. Chem. Soc.* **1973**, *95*, 4379.

elucidated, but it should be pointed out that this reaction differs from that of Fischer-type carbene metal complexes, which have been shown[23] to react according to eq 1. In an attempt to



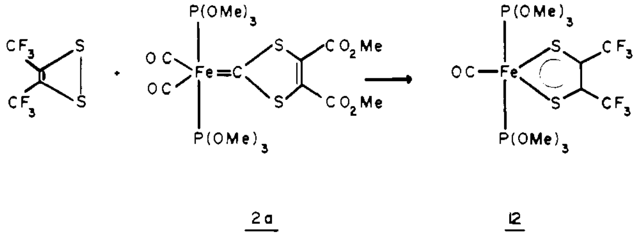
$$(CO)_5Cr{=}C(OMe)(Ar) + O_2 \xrightarrow{70^\circ} O{=}C(OMe)(Ar) \quad (1)$$

understand how the reaction proceeds, we studied the nature of the gas evolved after reaction of a benzene solution of **2a** with molecular oxygen; by mass spectrometry we observed besides the excess of oxygen the presence of carbon monoxide and carbon dioxide. Carbon dioxide can result from two reactions: *either* the oxidation of free carbon monoxide in the presence of iron residues *or* the oxidation of the 1,3-dithiol ligand affording CO_2 and the dithiete **11** (eq 2).



(2)

In the latter case the dithietene **11** could react *either* with the "$Fe(CO)_2L_2$" residue, for it is known that bis(trifluoromethyl)dithiete gives a similar (dithiolene)iron product with $Fe_2(CO)_9$,[12] *or* with the carbene complex **2** remaining in solution to afford **3**. Indeed we observed that bis(trifluoromethyl)dithiete reacted with the compound **2a** in benzene to afford 67% of the (dithiolene)iron complex **12** for which the spectroscopic properties are similar to that of $Fe[S_2C_2(CF_3)_2](CO)[P(OEt)_3]_2$[12] (eq 3). However, in this case, the



(3)

formation of the tetrathiafulvalene **9a**, which could have been expected from the displacement of the carbene ligand from **2a**, was not observed. The organic decomposition products in this reaction sequence were not identified. The intermediacy of the dithiete in eq 2 and the ability of an additional molecule of (1,3-dithiol-2-ylidene)iron complex to react with this intermediate provides a ready explanation for the relatively low yields of compounds **3** in the oxidation of the carbene compounds.

Spectroscopic Studies. Compounds **3a–g** and **6g** exhibited a very intense carbonyl band between 1960 and 1980 cm^{-1}, which corresponds well with that observed for the analogous derivative $Fe[S_2C_2(CF_3)_2](CO)[P(OEt)_3]_2$ prepared via another route.[12] Like their precursors **2a–g**, compounds **3a–g** showed a single triplet NMR resonance for the $P(OMe)_3$ protons as a result of *virtual coupling between phosphorus nuclei*. This result implies that the phosphite ligands are equivalent with a large $^2J_{P-P}$ value, which would suggest that they are mutually trans. The ^{31}P NMR spectrum of compound **3g** at ambient temperature consists of a single resonance at 175.1 ppm downfield of H_3PO_4 confirming that the phosphorus ligands are chemically equivalent. For compound **3d** at low temperature (213 K) the phosphorus nuclei are still equivalent (175.6 ppm). The symmetrically substituted complex **3a** ($Z^1 = Z^2 = CO_2Me$) gave a triplet ^{13}C resonance at both 309 K and 233 K due to the carbonyl carbon nucleus coupled with two identical phosphorus nuclei [δ ($CDCl_3$) (233 K) 211.5 (t), $^2J_{PC} = 36.6$ Hz] and gave equivalent carbon nuclei for the ester groups [δ (233 K) 166.7 (s) C=O]. More significantly the ethylenic carbon atoms of the dithiolene ligand are indistinguishable at 309 or 233 K, showing only a triplet resonance due to coupling to phosphorus [δ (233 K) 156.3 (t), $^3J_{PC} = 4.3$ Hz]. The above spectroscopic data are incompatible with a structure similar to one of the two types of square-pyramidal configurations α and β found for the ruthenium isomers of formula $Ru[S_2C_2(CF_3)_2](CO)(PPh_3)_2$.[13]

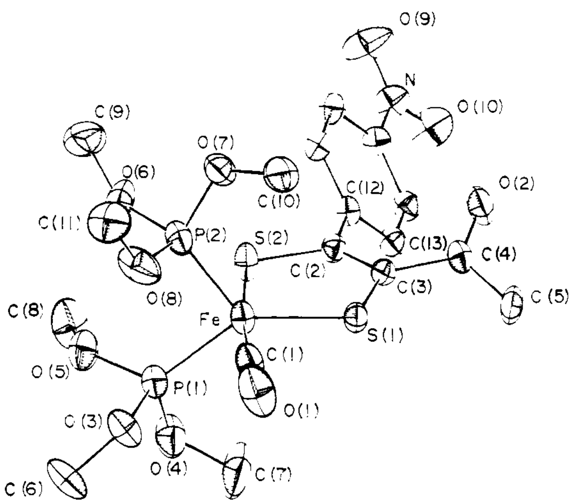


Figure 1. Perspective view of the structure of $Fe[S_2C(COMe)C(C_6H_4NO_2)](CO)[P(OMe)_3]_2$ drawn by ORTEP. Ellipsoids are drawn at the 30% level.

Description and Discussion of the Structure of $Fe[S_2C(COMe)C(C_6H_4NO_2)](CO)[P(OMe)_3]_2$. The crystal structure consists of isolated individual molecules separated by normal van der Waals distances. There are no intermolecular contacts of significance, the shortest intermolecular Fe···S distance being 7.54 Å. Thus the molecule differs significantly from $Fe[S_2C_2(CF_3)_2](CO)_3$ where relatively strong intermolecular Fe···S interactions of 2.33 Å produce a dimer in the solid state.[21] An ORTEP II plot of one molecule without hydrogen atoms is illustrated in Figure 1. The iron atom is pentacoordinated by two phosphite phosphorus atoms, a unique carbonyl, and the two sulfur atoms of a chelating dithiolate ligand. While the immediate stereochemistry of the metal atom deviates significantly from that of an idealized polyhedron, it is clear that the best description of the configuration is that of a distorted trigonal bipyramid with apical positions occupied by S(2) and C(1) and equatorial sites by S(1), P(1), and P(2). This description is supported by the values of the angles S(2)–Fe–P(1) = 92.3 (0)°, S(2)–Fe–P(2) = 93.4 (0)°, and S(2)–Fe–S(1) = 88.2 (0)° and C(1)–Fe–P(1) = 92.3 (1)°, C(1)–Fe–P(2) = 90.7 (1)°, and C(1)–Fe–S(1) = 85.4 (1)° as well as the angle subtended at the metal by the apical atoms (S(2)–Fe–C(1) = 173.6 (1)°). Within the equatorial plane consisting of Fe, P(1), P(2), and S(1) the sum of the angles subtended at the metal is 359.9° but P(1)–Fe–P(2) (94.1 (0)°) is much smaller than P(1)–Fe–S(1) (140.9 (1)°) and differs considerably from the ideal value of 120°. Despite these deviations from the idealized trigonal bipyramid the alternative description in terms of a square-based pyramid with P(2) oc-

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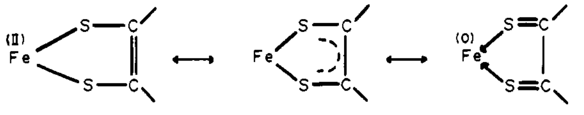
[23] Fischer, E. O.; Riedmuller, S. *Chem. Ber.* **1974**, *107*, 915.

cupying the apical position is much less satisfactory. Thus the atoms S(1) and P(1) lie well below and Fe, S(2) and C(1) well above a best plane through these five atoms (S(1) -0.426, P(1) -0.398, Fe +0.309, S(2) +0.222, C(1) + 0.294 Å) while the angles S(1)-Fe-P(2) = 124.9 (0)° and S(1)-Fe-P(1) = 140.9 (0)° differ markedly from idealized values of 90 and 180°, respectively. The structure contrasts sharply with the structures of orange and violet $Ru[S_2C_2(CF_3)_2](CO)(PPh_3)_2$ where the coordination about the central atom is demonstrably square pyramidal with the carbonyl group respectively axial and equatorial in the two isomers.[13] In the ruthenium systems no evidence was found for trigonal-bipyramidal species either in solution or in the solid state. A number of iron complexes of the type $Fe[S_2C_2(CF_3)_2](CO)L_2$ (L = tertiary phosphine or phosphite) have been prepared by Lewis base additions to $\{Fe[S_2C_2(CF_3)_2](CO)_3\}_2$,[12] but no structural data are available. While it might be tempting to deduce structures analogous to that of **3g**, it seems clear from a comparison of **3g** with the ruthenium complexes that very subtle electronic and steric differences are sufficient to modify solid-state configurations in these systems. Thus any structural generalizations are probably hazardous. In solution compounds **3** do not retain the rigid trigonal bipyramid of the solid state for, even at low temperature, the ^{31}P nuclei are equivalent and in **3a** ^{13}C NMR shows that the two backbone carbon atoms of the dithiolene ligand are indistinguishable.

The dithiolene skeleton defined by the atoms S(3), S(2), C(2), and C(3) in $Fe[S_2C(COMe)C(C_6H_4NO_2)](CO)[P(OMe)_3]_2$ is strictly planar as is invariably found for these ligands. Nevertheless there are some interesting features of the FeS_2C_2 ring that reflect the unsymmetrical nature of the substituents and the stereochemistry of the metal. Thus the Fe-S(2) (trans to CO) bond length (2.196 (1) Å) is significantly longer than the equatorial Fe-S(1) distance (2.155 (1) Å). Both of these bond lengths are however markedly shorter than the Fe-S(1) distances in $Fe(\eta^2\text{-}CS_2)(CO)_2(PPh_3)(PMe_3)$ (2.334 (2) Å)[16] or $Fe[C(S)OMe][Ph_2PCH{=}C(t\text{-}Bu)S](CO)[P(OMe)_3]$ (2.307 (2) Å)[4] where six ligand atoms are present. Comparison of the Fe-S bond lengths (average 2.175 Å) in **3g** with the sum of covalent radii for iron (~1.26 Å) and sulfur (1.04 Å) suggests that the Fe-S bonds are slightly shortened single bonds. The C(3)-S(2) and C(3)-S(1) distances (1.722 (3) and 1.736 (5) Å), which are marginally different, compare favorably with corresponding distances in other dithiolate complexes[24] and are close to the expected value of 1.75 Å for a C(sp^2)-S single bond.[25] The C(2)-C(3) bond length (1.355 (5) Å) corresponds to that expected for a double bond differing from the sp^2-sp^2 single bond length found in the related dithiolate derivative $(C_5H_5)Co[S_2C_2(CF_3)_2]$ (C-C = 1.48 Å)[26] but being rather similar to the corresponding distance (1.364 (10) Å) in $(C_5H_5)[CoS_2C_2(CN)_2]$.[27] There has been considerable discussion in the literature concerning metal-dithiolate bonding and in particular whether the ground states of these molecules are best described in terms of the dithiolate A or the dithioketone B.[24] The structural parameters for **3g** suggest that while there is some delocalization over the S_2C_2 portion of the chelate ring, the canonical from A predominates.



A B

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Registry No. **1**, 64424-66-4; **2a**, 67228-20-0; **2b**, 67228-18-6; **2c**, 77357-83-6; **3a**, 78803-84-6; **3b**, 78790-98-4; **3c**, 78790-99-5; **3d**, 78791-00-1; **3e**, 78791-01-2; **3f**, 78791-02-3; **3g**, 78791-03-4; **4**, 78853-55-1; **5g**, 78791-04-5; **6g**, 78791-05-6; **7**, 64424-68-6; **9a**, 26314-39-6; **9b**, 50615-12-8; **10b**, 78791-06-7; **11**, 360-91-8.

Supplementary Material Available: Listings of hydrogen atom coordinates and isotropic thermal parameters (Table S1) and structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

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(Trimethylsilyl)methylidene and (Trimethylsilyl)methylidyne Compounds of Molybdenum and Tungsten: $(Me_3SiCH_2)_3M{\equiv}CSiMe_3$ (M = Mo, W) and $(Me_3SiCH_2)_3Mo{=}CHSiMe_3$

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From the reaction between $MoCl_5$ and $LiCH_2SiMe_3$ (5 equiv) at 0 °C in hexane/ether solvent, a purple distillate (70 °C, 10^{-3} torr) has been obtained, in addition to the previously characterized $Mo_2(CH_2SiMe_3)_6$. The purple distillate has been shown to contain the carbene compound $(Me_3SiCH_2)_3Mo{=}CHSiMe_3$ and the carbyne compound $(Me_3SiCH_2)_3Mo{\equiv}CSiMe_3$ by analytical and spectroscopic studies. When the above reaction is carried out at -78 °C, a yellow distillate (70 °C, 10^{-3} torr) is obtained, which is the pure carbyne compound. Analogous reactions employing WCl_6 and $LiCH_2SiMe_3$ (6 equiv) at -78 °C lead to $(Me_3SiCH_2)_3W{\equiv}CSiMe_3$ as the sole volatile tungsten-containing product. The new compounds have been characterized by elemental analyses and IR, NMR (^1H and ^{13}C), and mass spectroscopy.

Introduction

The reactions between early-transition-metal halides and alkyllithiums or Grignard reagents, in which the alkyl groups lack β-hydrogen atoms, have allowed the syntheses of extensive series of homoleptic alkyl transition-metal complexes.[2,3]

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