(27) K. Yasufuku, K. Aoki, and H. Yamazaki, *J. Organomet. Chem.*, **84**, C28 (1975).

(28) R. J. Restivo, G. Ferguson, T. W. Ng, and A. J. Carty, *Inorg. Chem.*, **16**, 172 (1977).

(29) F. A. Cotton, J. D. Jamerson, and B. R. Stults, *J. Am. Chem. Soc.*, **98**, 1774 (1976).

(30) K. Nicholas, L. S. Bray, R. E. Davis, and R. Pettit, *Chem. Commun.*, 608 (1971).

(31) W. G. Sly, *J. Am. Chem. Soc.*, **81**, 18 (1959). A revised value of the acetylene C≡C distance appears in D. A. Brown, *J. Chem. Phys.*, **33**, 1037 (1960).

(32) V. W. Day, S. S. Abdel-Meguid, S. Dabestani, M. G. Thomas, W. R. Pretzer, and E. L. Muetterties, *J. Am. Chem. Soc.*, **98**, 8289 (1976).

(33) H. Hoberg, R. Krause-Going, C. Kruger, and J. C. Sekutowski, *Angew. Chem., Int. Ed. Engl.*, **16**, 183 (1977).

(34) R. D. Adams, F. A. Cotton, and R. A. Rusholme, *J. Coord. Chem.*, **1**, 275 (1971).

(35) The 0.016 Å difference between the two crystallographically independent Ni–Ni distances more than likely indicates that the esd's of 0.001 Å noted are underestimates. Since the two molecular units are chemically equivalent, one may independently derive the magnitude of the likely errors by direct comparison of the chemically equivalent bonds. Such a procedure suggests that the true uncertainty in the Ni–Ni distance is around 0.005 Å.

(36) A Bondi, *J. Phys. Chem.*, **68**, 441 (1964).

(37) J. D. Dunitz, H. C. Mez, O. S. Mills, and H. M. M. Shearer, *Helv. Chim. Acta*, **45**, 647 (1962).

(38) R. S. Dickson and P. J. Fraser, *Adv. Organomet. Chem.*, **12**, 323 (1974).

(39) (a) G. D. Andreeti, G. Bocelli, and P. Sgarabotto, *Cryst. Struct. Commun.*, **3**, 109 (1974); (b) T. S. Cameron and C. K. Prout, *Acta Crystallogr., Sect. B*, **28**, 2021 (1972); (c) B. Barnett, B. Bussemeier, P. Heimbach, P. W. Jolly, C. Kruger, I. T. Katchenko, and G. Wilke, *Tetrahedron Lett.*, 1457 (1972); (d) A. E. Smith, *Inorg. Chem.*, **11**, 165 (1972); (e) M. Zocchi and A. Albinati, *J. Organomet. Chem.*, **77**, C40 (1974).

(40) L. F. Dahl and W. E. Oberhansli, *Inorg. Chem.*, **4**, 629 (1965); (b) *ibid.*, **4**, 150 (1965); (c) R. F. Bryan, *J. Am. Chem. Soc.*, **86**, 733 (1964).

(41) "Tables of Interatomic Distances and Configuration in Molecules and Ions", *Chem. Soc., Spec. Publ.*, **No. 11** (1958).

(42) (a) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, C71 (1951); (b) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

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Crystal Structure at −35 °C of (π-Cyclopentadienyl)(bis(diphenylphosphino)ethane)(acetonitrile)iron Tetraphenylborate and Evidence for Cationic Iron–Methylene Complexes

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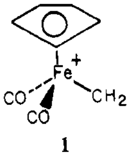
$(\pi\text{-}C_5H_5)[((C_6H_5)_2PCH_2)_2](CH_3OCH_2)Fe$ and $(\pi\text{-}C_5H_5)((C_6H_5)_3P)(CH_3OCH_2)Fe(CO)$ have been synthesized and their abilities to transfer CH_2 to cyclohexene have been examined. The structure of the compound $\{(\pi\text{-}C_5H_5)[((C_6H_5)_2PCH_2)_2]Fe(NCCH_3)\}B(C_6H_5)_4$, resulting from the acid treatment of the diphosphine complex has been determined by single-crystal x-ray diffraction techniques with intensity data gathered at −35 °C. Crystals form as deep red irregular blocks in monoclinic space group *Cc* with $a = 23.542$ (8) Å, $b = 11.494$ (3) Å, $c = 18.774$ (4) Å, $\beta = 112.26$ (2) Å. The calculated density of 1.248 g cm^{-3} for four formula weights of $\{(C_5H_5)[((C_6H_5)_2PCH_2)_2]Fe(NCCH_3)\}B(C_6H_5)_4$ per unit cell agrees with the measured value of 1.24 g cm^{-3}. Iron is bonded to the C_5H_5 ring in a symmetric π manner, to the two phosphorus atoms of the diphosphine ligand—thereby forming a five-membered chelate ring—and to the nitrogen atom of the CH_3CN molecule. The angle at the N atom of the Fe–N–C linkage is 171.9 (5)°. Four of the atoms of the C–P–Fe–P–C ring are essentially coplanar; one carbon atom lies ~0.7 Å from this plane, so that the ring has an envelope conformation. Full-matrix least-squares refinement of the structure has converged with an *R* index (on $|F|$) of 0.059 for the 4963 symmetry-independent reflections within the Mo Kα shell defined by $4 < 2\theta < 55°$ which have $I_o/\sigma(I_o) > 2.0$.

Introduction

Although transition-metal–methylene complexes have long been postulated as reaction intermediates, the first successful preparation and characterization of such a complex, $(\pi\text{-}C_5H_5)_2Ta(CH_3)(CH_2)$, was not reported until 1975.[1,2] Earlier, however, considerable evidence for the existence of the transitory iron–methylene complex **1** had been obtained in these laboratories.[3] In an attempt to isolate such a species, the two CO molecules of **1** were replaced with the chelating ligand bis(diphenylphosphino)ethane (dppe) in accordance with Scheme I. Compound **2** was prepared as previously reported.[3] It was hoped that the additional electron density (in comparison to that of **2**) at Fe resulting from its coordination with the strongly electron-donating/weakly electron-withdrawing diphosphine ligand[4] might be transferred to the CH_2 moiety, thereby stabilizing cation **4**.



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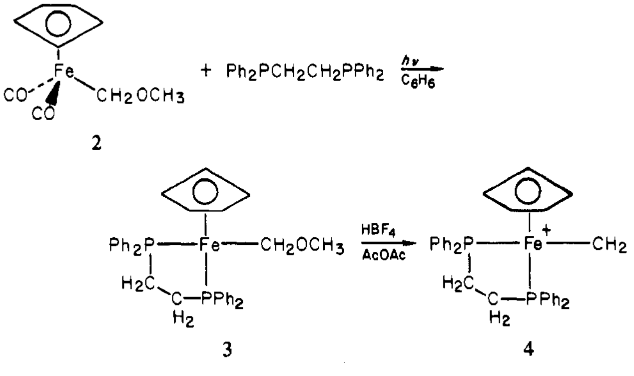
Treatment of the orange-red compound **3** with acid, as shown, gave a very dark solution, which upon addition of ether afforded a light brown precipitate **5** (subsequently found to liberate ethylene in both the dissolved and the solid states[5]). However, neither the ^1H nor the ^{13}C NMR spectrum (see Experimental Section) provided support for the formulation of the product as **4**. Thus, to establish the nature of the product of these reactions a single-crystal x-ray diffraction study has been carried out.

Scheme I



In addition to the diphosphine complex **3**, the corresponding (π-cyclopentadienyl)(triphenylphosphine)(methoxymethyl)iron carbonyl complex **6** was prepared by photolysis of **2** with

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triphenylphosphine in benzene. The capacity of complexes **2**, **3**, and **6** to function as cyclopropanating agents has been studied and will be discussed.

Experimental Section

Infrared Spectra. Infrared spectra were recorded on a Perkin-Elmer Model 257 grating infrared spectrophotometer. Absorptions are reported in cm^{-1} and were calibrated against the 1601- and 1583-cm^{-1} bands of polystyrene.

Nuclear Magnetic Resonance Spectra. Proton NMR spectra were recorded on a Perkin-Elmer R-12 NMR spectrophotometer. Me_4Si was used as an internal standard. Resonances are reported in τ units.

Elemental Analyses. Microanalyses were performed by Chemalytics, Inc., Tempe, Ariz.

Melting Points. Melting points were measured with a Fisher-Johns melting point apparatus and are uncorrected for stem exposure.

Preparation of $(\pi\text{-}C_5H_5)(dppe)(CH_3OCH_2)Fe$, 3. A solution of 17.793 g (0.0477 mol) of 1,2-bis(diphenylphosphino)ethane (Strem Chemical Co.), 10.030 g (0.0452 mol) of (π-cyclopentadienyl)-(methoxymethyl)iron dicarbonyl, **2**, bp 90.5–91.5 °C (4 mm), prepared by the method of Jolly and Pettit,[3] and 210 mL of reagent grade benzene was photolyzed for 8 h with a high-pressure 450-W Hanovia lamp. The reaction solution was cooled in an ice bath and argon was flushed through the system throughout the photolysis.

The solvent was removed successively on a rotoevaporator and a high-vacuum pump to afford 26.80 g of a red solid. Two recrystallizations from benzene and Skelly B afforded fine orange-red crystals, mp 150 °C (dec), in 19% yield (4.738 g). Infrared spectrum ($CDCl_3$): 3060 (s), 2920–2800 (s), 1960 (w), 1890 (w), 1805 (w), 1590 (w), 1480 (s), 1433 (vs), 1060 (vs) cm^{-1}. ^1H nuclear magnetic resonance spectrum ($CDCl_3$): τ 2.70 (m, 20), 6.08 (t), 6.20 (m, 7), 7.87 (s), 7.80 (broad, 7). Anal. Calcd for $C_{33}H_{34}FeOP_2$: C, 70.21; H, 6.08; P, 10.97. Found: C, 69.78; H, 6.01; P, 10.96.

Preparation of $(\pi\text{-}C_5H_5)((C_6H_5)_3P)(CH_3OCH_2)Fe(CO)$, 6. The same procedure as used for the synthesis of **3** was used here. A solution of 6.067 g (0.0273 mol) of $(\pi\text{-}C_5H_5)(CH_3OCH_2)Fe(CO)_2$, **2**, 7.172 g (0.0273 mol) of freshly recrystallized triphenylphosphine, and 225 mL of reagent grade benzene was photolyzed for 2.5 h. Removal of the solvent and recrystallization of the crude product from acetone afforded 5.209 g (42%) of orange needles, mp 150–152 °C. Infrared spectrum ($CHCl_3$): 1900 (vs), 1094 (s), 1050 (s) cm^{-1}. ^1H nuclear magnetic resonance spectrum (benzene-d_6): τ 2.35 (m), 2.88 (m, 15), 5.35 (m), 5.70 (m, 2), 5.65 (d, 5), 6.90 (s, 3). Anal. Calcd for $C_{26}H_{25}FeO_2P$: C, 68.42; H, 5.53; P, 6.79. Found: C, 68.25; H, 5.44; P, 6.60.

Preparation of $[(\pi\text{-}C_5H_5)(dppe)Fe(NCCH_3)]B(C_6H_5)_4$, 7. In a 50-mL round-bottom flask was placed a magnetic stirring bar, 1.002 g (0.001 77 mol) of complex **3**, and 16 mL of acetic anhydride. Upon addition of a cold solution of 0.002 86 mol of HBF_4 in 10 mL of acetic anhydride to this ice-bath-cooled, argon-saturated slurry, complex **3** dissolved. This dark solution was stirred for 11 min in an ice bath and then poured into 300 mL of anhydrous ether. The ether was decanted from the resulting precipitate, which was then washed 4 times with 250-mL portions of anhydrous ether. Approximately 1 g of a light brown solid (**5**) was isolated. The brown solid was dissolved in about 30 mL of acetonitrile and filtered. After two unsuccessful recrystallization attempts, the BF_4^- ions of the recovered red, glasslike material were exchanged in anhydrous methanol for $B(C_6H_5)_4^-$ ions. The resulting orange-red crystals (0.427 g, mp 190 °C (dec)) were then washed with methanol. Deep red irregular blocky crystals, suitable for single-crystal work, were subsequently grown from acetone by slowly cooling a warm (50 °C), concentrated solution to room temperature. Infrared spectrum (CH_2Cl_2): 2980 (s), 2300 (w), 2270 (w), 1950 (w), 1880 (w), 1810 (w), 1580 (s), 1420 (s), 1243 (m), 1100 (s), 1043 (m), 850 (m) cm^{-1}. ^1H nuclear magnetic resonance spectrum (acetone-d_6): τ 2.10 (m), 2.48 (m), 3.15 (m, 40), 5.60 (t, 5), 7.38 (m), 7.60 (m, 4), 8.60 (m, 3). ^{13}C nuclear magnetic resonance spectrum (acetone-d_6): δ 79.7 (C_5H_5); 133.7, 133.5, 132.5, 132.3, 131.5, 131.2, 129.9 (C_6H_5). Anal. Calcd for $C_{57}H_{52}BFeNP_2$: C, 77.81; H, 5.97; P, 7.04. Found: C, 77.57; H, 6.24; P, 6.32.

Further experimentation revealed that upon dissolution of the brown solid **5** in polar solvents such as methylene chloride, nitromethane, methanol, acetone, or acetonitrile, red to yellow solutions were formed which evolved ethylene. It was also noted that the undissolved brown solid liberated ethylene, even at temperatures as low as −25 °C, and that it failed to react with cyclohexene, ethyl vinyl ether, dimethyl fumarate, or p-methoxystyrene, suggesting that it probably does not contain the methylene group.

Table I. Experimental Summary for $[(C_5H_5)(dppe)Fe(NCCH_3)]B(C_6H_5)_4$

Crystal Data at -35 °C[a]			
a, Å	23.542 (8)	Systematic absences	hkl, $h + k = 2n + 1$
b, Å	11.494 (3)		
c, Å	18.774 (4)		$h0l$, $l = 2n + 1$
β, deg	112.26 (2)		
V, Å^3	4702 (5)		$0k0$, $k = 2n + 1$
d_{measd}, g cm^{-3} (flotation, aq $ZnCl_2$)	1.24	Crystal system	Monoclinic
d_{calcd}, g cm^{-3}	1.248	Space group	Cc (No. 9) or $C2/c$ (No. 15)[b]
Z	4		
$F(000)$, electrons	1848	Fw	879.70
		Empirical formula	$C_{57}H_{52}BFeNP_2$

Data Collection at -35 °C[d]	
Radiation (Mo Kα), Å	0.71069
Mode	ω scan
Scan range	Symmetrically over 1.0° about K$\alpha_{1,2}$ maximum
Background	Offset 1.0 and −1.0° in ω from K$\alpha_{1,2}$ maximum
Scan rate, deg min^{-1}	Constant for $4 < 2\theta < 35°$, 3.0; variable for $35 < 2\theta < 55°$, 1.5–5.0
Check reflections	4 remeasured after every 96 reflections; analysis[c] of these data indicated only random fluctuation in intensity for data crystal with all correction factors less than 0.3σ
2θ range, deg	4.0–55.0
Octants of reciprocal space examined	hkl, $\bar{h}kl$
Total reflections measured	5385
Data crystal dimensions, mm	0.31 × 0.50 × 0.54
Data crystal vol, mm^3	0.057
Data crystal faces	$(11\bar{1})$, $(1\bar{1}1)$, $(\bar{1}11)$, (111), $(\bar{1}\bar{1}1)$, $(\bar{1}1\bar{1})$, $(\bar{1}00)$, $(\bar{1}01)$, $(1\bar{1}2)$, (112), two other minor faces
Absorption coeff μ(Mo Kα), cm^{-1}	4.38
Transmission factor range	0.84–0.89

[a] Unit cell parameters were obtained by least-squares refinement of the setting angles of 43 reflections with $24 < 2\theta < 32°$. [b] Shown by successful refinement to be Cc (see text). [c] W. H. Henslee and R. E. Davis, *Acta Crystallogr., Sect. B*, 31, 1511 (1975). [d] Syntex $P2_1$ autodiffractometer equipped with graphite monochromator and Syntex LT-1 inert-gas low-temperature delivery system.

Cyclopropanation Reactions. Cyclopropanation experiments were conducted by the procedure of Jolly and Pettit.[3] An acetone solution of the iron complex and cyclohexene was treated under argon with a solution of HBF_4. Norcarane yields were determined by gas-chromatographic analysis of the solution on 3% SE-30. In some experiments, the product was further characterized by comparison of its mass spectrum to that of authentic norcarane.

Crystallographic Analysis. A single crystal of the unknown species obtained from the acidification of **3** was affixed to a glass fiber and then transferred to a Syntex $P2_1$ diffractometer, where it was maintained in a stream of cold (−35 °C), dry nitrogen during the course of all diffraction experiments. Preliminary examination of the crystal indicated the monoclinic symmetry of space group Cc (No. 9) or $C2/c$ (No. 15). Crystal data and x-ray diffraction data collection details are summarized in Table I. Processing of the diffraction data (with $p = 0.02$) was carried out as previously delineated.[6]

Table II

a. Fractional Coordinates and Anisotropic Thermal Parameters ($\times 10^3$) for Nongroup Nonhydrogen Atoms of $[(C_5H_5)(dppe)Fe(NCCH_3)]B(C_6H_5)_4$[a]

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe[b]		0.18650 (6)		259 (3)	268 (3)	307 (3)	27 (4)	91 (3)	−29 (3)
P(1)[b]	−0.09089 (7)	0.21390 (11)	0.00569 (9)	269 (6)	256 (6)	344 (7)	19 (5)	105 (5)	4 (5)
P(2)[b]	−0.00007 (7)	0.37394 (12)	−0.02223 (8)	271 (6)	293 (7)	298 (6)	−26 (5)	86 (5)	−21 (5)
N	0.0431 (2)	0.2278 (4)	0.1035 (3)	32 (2)	40 (3)	31 (2)	1 (2)	10 (2)	2 (2)
B	0.1900 (3)	−0.0719 (5)	0.3197 (3)	33 (3)	32 (3)	30 (3)	2 (2)	10 (2)	1 (2)
C(1)	0.0261 (3)	0.1416 (6)	−0.0906 (4)	50 (4)	46 (4)	46 (3)	6 (3)	25 (3)	−9 (3)
C(2)	0.0729 (3)	0.1091 (6)	−0.0211 (4)	36 (3)	52 (4)	54 (4)	8 (3)	22 (3)	−12 (3)
C(3)	0.0479 (4)	0.0269 (6)	0.0156 (4)	70 (5)	46 (4)	49 (4)	25 (3)	27 (3)	5 (3)
C(4)	−0.0146 (3)	0.0098 (6)	−0.0312 (5)	59 (5)	29 (3)	77 (5)	2 (3)	33 (4)	−11 (3)
C(5)	−0.0284 (3)	0.0815 (6)	−0.0973 (4)	42 (3)	44 (4)	56 (4)	0 (3)	17 (3)	−24 (3)
C(6)	−0.1104 (3)	0.3708 (5)	−0.0066 (4)	33 (3)	29 (3)	43 (3)	8 (2)	16 (3)	1 (2)
C(7)	−0.0501 (3)	0.4400 (5)	0.0221 (3)	37 (3)	27 (3)	40 (3)	1 (2)	17 (2)	−1 (2)
C(8)	0.0673 (3)	0.2660 (6)	0.1633 (4)	66 (4)	55 (4)	42 (4)	−18 (3)	27 (3)	−1 (3)
C(9)	0.1009 (4)	0.3128 (7)	0.2382 (4)	74 (5)	57 (4)	42 (3)	3 (4)	13 (3)	0 (3)

b. Fractional Coordinates and Isotropic Thermal Parameters (Å^2) for Nongroup Hydrogen Atoms of $[(C_5H_5)(dppe)Fe(NCCH_3)]B(C_6H_5)_4$[a]

Atom[c]	x	y	z	U, Å^2	Atom[c]	x	y	z	U, Å^2
H(1)	0.033 (3)	0.196 (6)	−0.124 (4)	0.05 (2)	H(6,2)	−0.131 (2)	0.393 (5)	0.022 (3)	0.02 (1)
H(2)	0.108 (3)	0.134 (5)	−0.010 (4)	0.04 (2)	H(7,1)	−0.030 (2)	0.432 (5)	0.075 (3)	0.02 (1)
H(3)	0.067 (3)	−0.005 (6)	0.062 (4)	0.04 (2)	H(7,2)	−0.052 (3)	0.528 (6)	0.009 (4)	0.06 (2)
H(4)	−0.049 (5)	−0.045 (8)	−0.026 (5)	0.11 (3)	H(9,1)[e]	0.073	0.328	0.265	0.08
H(5)	−0.069 (3)	0.106 (6)	−0.149 (4)	0.05 (2)	H(9,2)[e]	0.120	0.385	0.233	0.08
H(6,1)	−0.131 (2)	0.384 (5)	−0.054 (3)	0.02 (1)	H(9,3)[e]	0.132	0.261	0.267	0.08

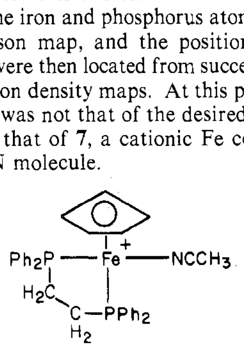
c. Group Parameters for $[(C_5H_5)(dppe)Fe(NCCH_3)]B(C_6H_5)_4$[a]

Group[d]	x_0	y_0	z_0	ϕ	θ	ρ
Ph(1)	−0.1560 (2)	0.1376 (3)	−0.0674 (2)	−0.903 (3)	−2.636 (2)	0.873 (3)
Ph(2)*	−0.1002 (2)	0.1719 (3)	0.0957 (2)	−1.678 (5)	2.073 (2)	0.934 (5)
Ph(3)	−0.0316 (2)	0.4333 (3)	−0.1203 (2)	−2.273 (3)	−2.225 (3)	−0.199 (4)
Ph(4)	0.0736 (1)	0.4473 (4)	0.0218 (2)	1.985 (3)	3.033 (3)	0.822 (3)
Ph(5)*	0.2046 (2)	−0.0349 (3)	0.2416 (2)	0.406 (7)	−1.941 (2)	−1.082 (7)
Ph(6)	0.2546 (1)	−0.1296 (3)	0.3862 (2)	1.133 (3)	2.688 (2)	1.858 (3)
Ph(7)	0.1690 (2)	0.0437 (3)	0.3599 (2)	−2.849 (2)	2.545 (2)	0.0936 (3)
Ph(8)	0.1326 (2)	−0.1702 (3)	0.2886 (2)	−0.862 (2)	−3.040 (3)	0.569 (3)

[a] See Figure 1 for identity of the atoms. Numbers in parentheses throughout the tables are estimated standard deviations in the units of the last significant digits for the corresponding parameter. The U_{ij} are the mean-square amplitudes of vibration in Å^2 from the general temperature factor expression $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. [b] For the Fe and P atoms the anisotropic thermal parameters are given $\times 10^4$. [c] The sequence number of a hydrogen atom corresponds to that of the carbon atom to which it is bound. [d] A description of these group parameters is provided elsewhere.[13] Angular coordinates are in radians. The internal coordinate system of a phenyl ring has been defined previously.[14] Groups marked with an asterisk were refined in accordance with ref 14 to avoid singularity of the transformation matrix.[13] [e] Hydrogen atom parameters of methyl carbon C(9) were not refined, as discussed in ref 8.

Solution and Refinement of the Structure. Because the density of these crystals (see Table I) indicated four formula weights of compound per unit cell and since the desired methylene species **4** (or the subsequently determined CH_3CN complex 7) cannot possess either C_i or C_2 symmetry as required for four molecules per unit cell in space group $C2/c$, the noncentrosymmetric space group Cc was assumed to be correct. Satisfactory refinement of the structure in this space group has corroborated this choice.

The positions of the iron and phosphorus atoms were located from a sharpened Patterson map, and the positions of the remaining nonhydrogen atoms were then located from successive electron density and difference electron density maps. At this point it was clear that the cation structure was not that of the desired methylene complex 4 but was probably that of 7, a cationic Fe complex containing a coordinated CH_3CN molecule.



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Following full-matrix least-squares refinement of these atomic positions, the hydrogen atomic positions were located from a difference electron density map. Continued least-squares refinement of a model structure using the 4963 reflections with $I_o/\sigma(I_o) > 2.0$, in which phenyl rings were treated as rigid groups of D_{6h} symmetry,[7] nongroup nonhydrogen atoms ultimately as anisotropic thermal ellipsoids and nongroup hydrogen atoms[8] as isotropic atoms converged with $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.060$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.064$. The function minimized in refinement is $\sum w(|F_o| - |F_c|)^2$, where the weight w is $\sigma(|F_o|)^{-2}$, the standard deviation of each observation $|F_o|$. Neutral-atom scattering factors for Fe, P, N, C, B[10] and H[11] were used in these calculations, and to this juncture only the real component ($\Delta f'$) of the anomalous scattering correction[10] had been applied to the Fe and P scattering curves.

To determine whether the proper enantiomorph (for this particular crystal) had been selected in this model, refinement was continued with the application of the imaginary components ($\Delta f''$) of anomalous scattering to the iron and phosphorus scattering curves; at convergence $R = 0.059$ and $R_w = 0.064$. Reversal of the signs of $\Delta f''$ for Fe and P, followed by additional cycles of refinement—the computational equivalent of refinement of the opposite enantiomorph—commencing with the atomic parameters obtained prior to the inclusion of the $\Delta f''$ effects, caused convergence with $R = 0.061$ and $R_w = 0.066$. Since these values were significantly higher than those obtained from the refinement of the initial model, the first model had to be the correct enantiomorph, and accordingly, the atomic and group coordinates presented in Table II are those of the original model. The standard deviation of an observation of unit weight, $[\sum w(||F_o| - |F_c||)^2/(m - s)]^{1/2}$, is 3.32 for $m = 4963$ observations ($|F_o|$) and $s = 329$ variables. At the conclusion of refinement a structure-factor calculation using

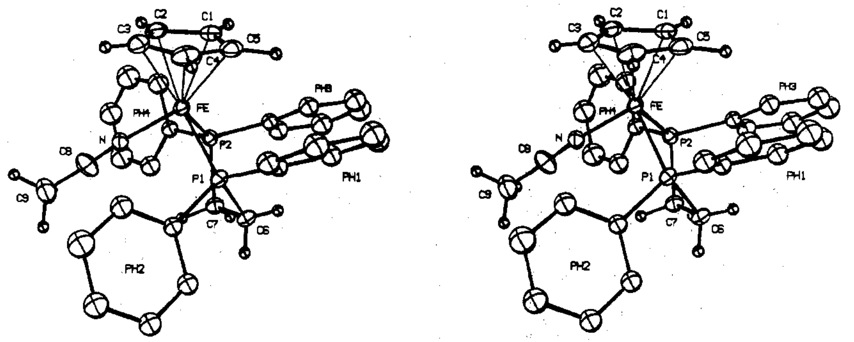


Figure 1. Stereoview of the $[(C_5H_5)(dppe)Fe(NCCH_3)]^+$ ion, illustrating the atom numbering scheme. Nonhydrogen atoms are shown as ellipsoids of 30% probability and hydrogen atoms as sphere of radius 0.1 Å.

all 5385 reflections measured during data collection gave R and R_w values of 0.065 and 0.064, respectively. Examination of the data showed no evidence of secondary extinction.

In the final cycle of least-squares refinement, the parameter shift/parameter esd ratios were less than 0.16 for nongroup nonhydrogen positional parameters, less than 0.34 for nongroup nonhydrogen thermal parameters, less than 0.30 for nongroup hydrogen parameters, and less than 0.48 for all rigid-group parameters. A final difference Fourier map showed several small peaks, all less than 0.7 e $Å^{-3}$, all of which were associated with phenyl rings. For comparison, the heights of typical carbon and hydrogen atoms from previous Fourier maps were 2.4–3.5 and 0.3–0.5 e $Å^{-3}$, respectively.

A listing of the principal computer programs used in this work is provided elsewhere.[6] Nongroup atomic positional and thermal parameters and rigid-group parameters with corresponding standard deviations, as estimated from the least-squares inverse matrix, are presented in Table II. Fractional crystallographic coordinates and isotropic thermal parameters (with standard deviations) for group atoms and a tabulation of observed and calculated structure factor amplitudes are available.[12]

Table III. Bond Lengths (Å) for $[(C_5H_5)(dppe)Fe(NCCH_3)]B(C_6H_5)_4$[a]

Fe–P(1)	2.206 (2)	C(6)–C(7)	1.535 (9)
Fe–P(2)	2.195 (1)	C(8)–N	1.139 (9)
Fe–C(1)	2.080 (7)	C(8)–C(9)	1.431 (10)
Fe–C(2)	2.100 (7)	C(1)–H(1)	0.94 (7)
Fe–C(3)	2.115 (8)	C(2)–H(2)	0.83 (7)
Fe–C(4)	2.106 (6)	C(3)–H(3)	0.89 (7)
Fe–C(5)	2.078 (7)	C(4)–H(4)	1.05 (10)
Fe–N	1.881 (5)	C(5)–H(5)	1.11 (7)
P(1)–C(6)	1.854 (6)	C(6)–H(6,1)	0.85 (6)
P(1)–C(11)*	1.846 (4)	C(6)–H(6,2)	0.90 (6)
P(1)–C(21)*	1.850 (4)	C(7)–H(7,1)	0.93 (6)
P(2)–C(7)	1.845 (6)	C(7)–H(7,2)	1.04 (7)
P(2)–C(31)*	1.837 (4)	C(9)–H(9,1)[b]	0.98
P(2)–C(41)*	1.821 (4)	C(9)–H(9,2)[b]	0.97
C(1)–C(2)	1.403 (10)	C(9)–H(9,3)[b]	0.94
C(2)–C(3)	1.423 (10)	B–C(11)*	1.683 (7)
C(3)–C(4)	1.413 (12)	B–C(21)*	1.696 (7)
C(4)–C(5)	1.420 (11)	B–C(31)*	1.693 (7)
C(5)–C(1)	1.421 (10)	B–C(41)*	1.687 (7)

[a] Numbers in parentheses are the estimated standard deviations in the last significant digits. See Figure 1 for identity of the atoms. Atoms marked with asterisks are rigid-group atoms. [b] The C–H distances of methyl carbon C(9) are unrefined values, as stated in the text.

Table IV. Bond Angles (deg) for $[(C_5H_5)(dppe)Fe(NCCH_3)]B(C_6H_5)_4$[a]

P(1)–Fe–P(2)	86.5 (1)	C(31)*–P(2)–C(41)*	103.7 (2)
P(1)–Fe–N	93.9 (2)	P(1)–C(6)–C(7)	108.0 (4)
P(2)–Fe–N	84.8 (2)	P(2)–C(7)–C(6)	106.9 (4)
Fe–P(1)–C(6)	109.4 (2)	C(5)–C(1)–C(2)	108.5 (6)
Fe–P(1)–C(11)*	116.4 (1)	C(1)–C(2)–C(3)	107.7 (6)
Fe–P(1)–C(21)*	117.4 (1)	C(2)–C(3)–C(4)	108.3 (7)
C(6)–P(1)–C(11)*	105.9 (2)	C(3)–C(4)–C(5)	107.7 (6)
C(6)–P(1)–C(21)*	105.0 (3)	C(4)–C(5)–C(1)	107.7 (6)
C(11)*–P(1)–C(21)*	101.7 (2)	N–C(8)–C(9)	176.9 (8)
Fe–P(2)–C(7)	105.8 (2)	C(51)*–B–C(61)*	108.5 (4)
Fe–P(2)–C(31)*	121.8 (1)	C(51)*–B–C(71)*	112.4 (4)
Fe–P(2)–C(41)*	115.9 (1)	C(51)*–B–C(81)*	108.2 (4)
Fe–N–C(8)	171.9 (5)	C(61)*–B–C(71)*	105.6 (4)
C(7)–P(2)–C(31)*	105.4 (2)	C(61)*–B–C(81)*	111.7 (4)
C(7)–P(2)–C(41)*	102.4 (2)	C(71)*–B–C(81)*	110.4 (4)

[a] Numbers in parentheses are the estimated standard deviations in the last significant digits. See Figure 1 for identity of the atoms. Angles involving hydrogen atoms vary as follows: P–C–H, 106 (4)–112 (3)°; C–C–H (C_5H_5), 114 (4)–138 (4)°; C–C–H (dppe), 107 (4)–118 (4)°; H–C–H, 108 (5) and 111 (5)°. Atoms marked with asterisks are rigid-group atoms.

Discussion

Description of the Structure. As mentioned above, this structural analysis has revealed that the unknown cationic complex isolated from the reaction sequence outlined in the Introduction is not methylene complex **4** but is instead acetonitrile complex **7**. The cation is composed of an Fe atom bonded to a C_5H_5 ring in a symmetric π manner, to the two phosphorus atoms of the dppe ligand (thereby forming a five-membered chelate ring), and to the nitrogen atom of a CH_3CN molecule. The crystal structure consists of well-separated $[(C_5H_5)(dppe)Fe(NCCH_3)]^+$ and $B(C_6H_5)_4^-$ ions with no unusual interionic contacts.

Figure 1 is a stereoview of the $[(C_5H_5)(dppe)Fe(NCCH_3)]^+$ ion and illustrates the atom numbering scheme used herein; a stereoview of the packing of the ions in the crystal is given in Figure 2. Selected interatomic distances and angles are presented in Tables III and IV. Features of the coordination geometry of $[(C_5H_5)(dppe)Fe(NCCH_3)]^+$ are normal and, as shown in Table V, are in good agreement with structural aspects of related complexes.

From Table VI it is clear that the $\overline{\text{C–P–Fe–P–C}}$ chelate ring exhibits an envelope conformation; i.e., the atoms Fe, P(1), P(2), and C(6) are essentially coplanar, while atom C(7)—the "flap atom" of the envelope—lies more than 0.7 Å from this plane. As shown in Figure 1, the nonplanarity of this conformation diminishes the contacts between the chelate-ring phenyl groups and the acetonitrile and cyclopentadienyl ligands. Table VII compares the torsion angles of the chelate ring in $[(C_5H_5)(dppe)Fe(NCCH_3)]^+$ to those of some other metal–dppe complexes. With the exception of the values for the Re and Pd complexes (which possess virtually ideal half-chair conformations) these angles are similar, and this, in conjunction with the additional torsion angle data for metal–diphosphine complexes provided elsewhere,[20] suggests that the envelope conformation with carbon at the "flap" may be preferred.

Few structural characterizations of the M–$NCCH_3$ linkage are available for comparison to that in $[(C_5H_5)(dppe)Fe(NCCH_3)]^+$. A summary of much of this data is given in Table VIII. It might be expected that the CH_3CN ligand would accept electron density from the metal much like CO

Table V. Some Mean Distances (A) in Selected Fe Complexes[a]

Compd	Fe-C(cp)	Fe-cp centroid	Fe-P	C-C(cp)	P-C	Ref
$[(C_5H_5)(dppe)Fe(NCCH_3)]^+$	2.096 (17)	1.715 (1)	2.200 (6)	1.416 (8)	1.842 (11)	This work
$[(C_5H_5)(dppe)Fe(CO)]^+$	2.094 (7)	1.717 (1)	2.210 (1)	1.408 (7)	1.833 (7)	15
$(C_5H_5)(dppe)FeMgBr(C_4H_8O)_2$	2.093 (20)	1.700 (1)	2.107 (1)	1.437 (56)	1.897 (27)	16
$(dppm)Fe(CO)_3$[b]			2.217 (8)		1.851 (74)	17
$((C_6H_5)_2PCCP(C_6H_5)_2C_2F_4CF_2)Fe(NO)_2$			2.244 (4)		1.827 (14)	18

[a] Numbers in parentheses are the estimated standard deviations in the last significant digits. A mean distance is given by $\bar{X} = \Sigma_i^n X_i/n$, and its standard deviation by $[\Sigma(X_i - \bar{X})^2/(n-1)]^{1/2}$, where n is the number of observations X_i. cp is an abbreviation for the C_5H_5 ring. [b] dppm is an abbreviation for the $[(C_6H_5)_2PCH_2P(C_6H_5)_2]$ ligand.

Table VI. Selected Mean Planes[a]

Atom	Dev from planes,[b] A	Atom	Dev from planes,[b] A
$-0.0693X - 0.1712Y - 0.9828Z + 0.3670 = 0$			
C(1)*	0.004 (7)	H(1)	−0.01 (7)
C(2)*	−0.003 (7)	H(2)	0.06 (6)
C(3)*	0.001 (8)	H(3)	−0.05 (7)
C(4)*	0.001 (7)	H(4)	0.03 (10)
C(5)*	−0.003 (7)	H(5)	−0.06 (7)
		Fe	−1.715 (1)
$0.4682X - 0.7461Y - 0.4735Z - 0.1154 = 0$			
Fe*	0	C(6)	−0.073 (6)
P(1)*	0	C(7)	−0.784 (6)
P(2)*	0		
$-0.0851X - 0.1555Y - 0.9842Z + 0.3155 = 0$			
Fe*	−0.0179 (1)	C(6)*	−0.017 (6)
P(1)*	0.022 (1)	C(7)	−0.736 (6)
P(2)*	0.014 (1)		

[a] Orthonormal (A) coordinate system with axes X, Y, and Z parallel to unit cell vectors a, b, and c^*. Coordinates of atoms marked with asterisks were used to define the planes. [b] Numbers in parentheses are the estimated standard deviations in the last significant digits. A negative deviation from the plane indicates that the atom with coordinates given in Table II lies between the plane and the origin.

and other simple unsaturated ligands which possess available empty π orbitals. However, as shown by crystallographic[28] and (IR) spectroscopic[30,31] studies, the N-C bond is apparently strengthened upon coordination through the N atom rather than weakened as in conventional metal carbonyl complexes. This is illustrated by an increase in the N-C stretching frequency by as much as 80 cm^{-1} [31] (see Table IX) and by a decrease of ~0.02 Å in the N-C bond lengths in X_3B-$(NCCH_3)$, X = F or Cl.[28] In $[(C_5H_5)(dppe)Fe(NCCH_3)]^+$, the N-C stretching frequency has increased by 10 cm^{-1} (see Table IX), in agreement with this phenomenon.

The M-N-C bond angle (172°) in $[(C_5H_5)(dppe)Fe(NCCH_3)]^+$ deviates significantly from 180°, as do the analogous angles for most of the other M-$NCCH_3$ complexes in Table VIII. The closest approaches to methyl carbon C(9) are made by $B(C_6H_5)_4^-$ hydrogen atoms at distances of 3.10 (1) and 3.25 (1) Å. Since the accepted values for the van der Waals radii of a CH_3 group and an H atom are 2.0[32] and 1.0 Å,[33] respectively, the nonlinearity of the Fe-N-C moiety is probably not due to steric effects but rather, as suggested previously,[25] to the use of orbitals of partial sp^2 character by the donor nitrogen atom.

Reactivity of Methylene Complexes. A broad spectrum in the chemical reactivity of the $[(C_5H_5)(CO)_2Fe(CH_2)]^+$ (**1**), $[(C_5H_5)((C_6H_5)_3P)(CO)Fe(CH_2)]^+$ (**8**) (the methylene-containing complex obtained by treatment of **6** with HBF_4), and $[(C_5H_5)(dppe)Fe(CH_2)]^+$ (**4**) ions has been discovered. Stepwise substitution of phosphine ligands for the coordinated carbon monoxide molecules produces unexpected and unusual chemical activity in the resulting iron-methylene complexes.

Table VII. Torsion Angles (deg) about Bonds in Some C-P-M-P-C Complexes[a]

Complex	τ(M-P)	τ(P-C)	τ(C-C)	τ(C-P)	τ(P-M)	Ref
$[(C_5H_5)(dppe)Fe(NCCH_3)]^+$	−2.4	−27.5	48.4	−50.3	26.2	This work
$[(C_5H_5)(dppe)Fe(CO)]^+$	−4.7	−22.3	42.8	−45.2	25.1	15
$(C_5H_5)(dppe)FeMgBr(C_4H_8O)_2$	−6.9	−11.1	25.4	−32.7	20.9	16
$[(dppe)_2Ir(CNCH_3)]^+$	2.1	−29.4	47.6	−43.7	19.6	19
	−8.5	39.5	−53.6	46.0	−17.5	19
$[(dppe)_2Ru(NO)]^+$	3.6	26	−48	49	−26	21
	5.2	25	−49	53	−29	21
$[(dppe)(P(C_6H_5)_3)_2ReH_3]$	14	−45	55	−46	14	22
$(dppe)PdCl_2$	−11.4	39.3	−50.1	40.7	−13.0	23

[a] M represents the appropriate transition metal.

Table VIII. Dimensions of Some Coordinated CH_3CN Ligands[a]

Compd	N-C, A	C-CH_3, A	M-N-C,[b] deg	Ref
$[(C_5H_5)(dppe)Fe(NCCH_3)]^+$	1.139 (9)	1.431 (10)	171.9 (5)	This work
$Cu_3Cl_6(CH_3CN)_2$	1.134	1.480	159	24
$Cu_2Cl_4(CH_3CN)_2$	1.17 (3)	1.45 (4)	165 (4)	24
$[ReBr_4O(CH_3CN)]^-$	1.22 (8)	1.46 (1)	170 (4)	25
$((C_2H_5OC(O)CH)_2)_2Ni(CH_3CN)$	1.129 (6)	1.46 (1)	178 (8)	26
$((C_2H_5OC(O)CH)_2)_2Co(CH_3CN)_2$	1.13 (1)	1.49 (1)	171.4 (3)	27
	1.14 (1)	1.47 (1)	167.8 (2)	27
$F_3B(CH_3CN)$	1.135 (5)	1.439 (5)		28
$Cl_3B(CH_3CN)$	1.122 (7)	1.437 (8)		28
CH_3CN[c]	1.157	1.458	180	29

[a] Numbers in parentheses are the estimated standard deviations, if available, in the last significant digits. [b] M represents the appropriate transition metal. [c] These dimensions of molecular CH_3CN were obtained from microwave spectroscopy.

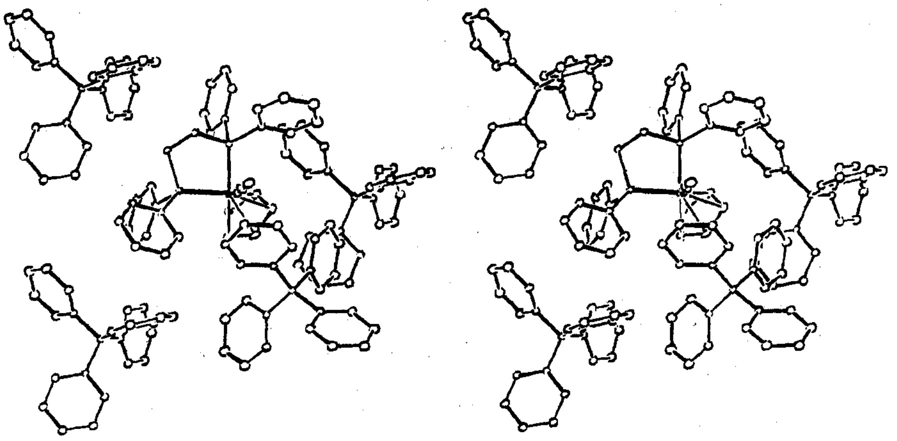


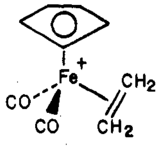
Figure 2. Stereoview of the immediate environment of a $[(C_5H_5)(dppe)Fe(NCCH_3)]^+$ ion. The closest approaches are made by four $B(C_6H_5)_4^-$ ions, as shown, at nonhydrogen atom contact distances of 3.5–3.6 Å. The next closest approaches (not shown) to the cation are made by two other cations at distances of 3.65 Å and then by another anion and two more cations at distances of 3.75 Å. Atoms are shown as ellipsoids of 10% probability; hydrogen atoms have been omitted for clarity.

Table IX. Infrared Stretching Frequencies (cm^{-1}) of the Carbon–Nitrogen Triple Bond of Some Acetonitrile Complexes

Complex	Freq	Medium	Ref
$[(C_5H_5)(dppe)Fe(NCCH_3)]^+$	2270	CH_2Cl_2	This work
$[(C_5H_5)((C_6H_5O)_3P)_2\text{-}Fe(NCCH_2Cl)]^+$	2271	Mull	34
$[(C_5H_5)((C_6H_5O)_3P)_2\text{-}Fe(NCCH_2CH_2Cl)]^+$	2278	Mull	34
cis-$[((C_6H_5)(CH_3)_2P)(CO)_4\text{-}Mn(NCCH_3)]^+$	2296	Nujol	35
$(CO)_5Cr(NCCH_3)$	2285	Hexane	36
$(CO)_5W(NCCH_3)$	2347	KBr	37
	2282	Hexane	36
	2292	Nujol	36
$((C_6H_5)_3P)_3(H)Co\text{-}(NCCH_3)$	2210		38
$[ReBrO_4(NCCH_3)]^-$	2280	Nujol	39
F_3BNCCH_3	2359		30
CH_3CN	2260	CH_2Cl_2	This work, 36

It was previously reported[3] that when dicarbonyl complex **2** and cyclohexene are treated with HBF_4 in acetone at 0 °C, norcarane is formed in 46% yield. Similar treatment of diphosphine complex **3** at room temperature failed to produce norcarane. When this reaction was carried out at −78 °C and the reaction mixture was then allowed to warm to room temperature, norcarane was detected, but only in 1.6% yield. However, if this reaction is conducted in acetic anhydride at −20 °C, the yield of norcarane is increased substantially, to 23%. When the same reaction is carried out with triphenylphosphine–carbonyl complex **6** at room temperature, norcarane is formed in 11% yield. But when this reaction is performed above −78 °C (but below room temperature), norcarane is produced in 63% yield. Thus, the production of norcarane with these complexes apparently is a function of solvent, temperature, and coordination environment of iron. In particular, the data for complex **6** clearly demonstrate the crucial dependence of norcarane formation on temperature.

The methylene complexes $[(C_5H_5)(CO)_2Fe(CH_2)]^+$ (**1**), $[(C_5H_5)((C_6H_5)_3P)(CO)Fe(CH_2)]^+$ (**8**), and $[(C_5H_5)(dppe)Fe(CH_2)]^+$ (**4**) all tend to form ethylene. Earlier[3] it was reported that the $[(C_5H_5)(CO)_2Fe(C_2H_4)]^+$ complex, **9**, was formed only in the absence of cyclohexene. Apparently cyclohexene is readily attacked by methylene complex **1** and the coupling of **1** to form ethylene complex **9** is not a significantly competitive reaction. Although the formation of ethylene from triphenylphosphine complex **8** may be suppressed by conducting the reaction at low temperatures, the liberation of ethylene by diphosphine complex **4** was not suppressed either by the reaction conditions described above or by isolation as brown solid **5**.



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Registry No. 2, 12108-35-9; **3**, 64913-43-5; **6**, 53521-55-4; **7**, 64913-45-7.

Supplementary Material Available: Listings of fractional coordinates and isotropic thermal parameters for group atoms and observed and calculated structure factors for the title compound (29 pages). Ordering information is given on any current masthead page.

References and Notes

(1) R. R. Schrock, *J. Am. Chem. Soc.*, **97**, 6577 (1975).
(2) L. J. Guggenberger and R. R. Schrock, *J. Am. Chem. Soc.*, **97**, 6578 (1975).
(3) P. W. Jolly and R. Pettit, *J. Am. Chem. Soc.*, **88**, 5044 (1966).
(4) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed, Interscience, New York, N.Y., 1972, p 719.
(5) This observation was made following the elucidation of the crystal structure of the title compound. The nature of the light brown solid **5** is currently under investigation.
(6) P. E. Riley and R. E. Davis, *Acta Crystallogr., Sect. B*, **32**, 381 (1976).
(7) The phenyl rings were constrained as follows: C–C = 1.392 Å; C–H = 1.00 Å; C–C–C = 120°. Each phenyl hydrogen atom was assigned an isotropic thermal parameter 1.0 Å^2 greater than the refined value of the carbon atom to which it is bonded.
(8) Since the hydrogen atoms of methyl carbon C(9) refined to geometrically unreasonable positions, they were placed at idealized locations (C–H = 0.95 Å[9]) with assigned thermal parameters of 6.0 Å^2 and so maintained during the concluding cycles of refinement.
(9) M. R. Churchill, *Inorg. Chem.*, **12**, 1213 (1973).
(10) "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974.
(11) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(12) Supplementary material.
(13) R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965).
(14) P. E. Riley and R. E. Davis, *Acta Crystallogr., Sect. B*, **31**, 2928 (1975).
(15) P. E. Riley and R. E. Davis, to be submitted for publication.
(16) H. Felkin, P. J. Knowles, B. Neunier, A. Mitschler, L. Ricard, and R. Weiss, *J. Chem. Soc., Chem. Commun.*, **44** (1974).

(17) F. A. Cotton, K. L. Hardcastle, and G. A. Rusholme, *J. Coord. Chem.*, **2**, 217 (1973).
(18) W. Harrison and J. Trotter, *J. Chem. Soc. A*, 1542 (1971).
(19) S. Z. Goldberg and R. Eisenberg, *Inorg. Chem.*, **15**, 58 (1976).
(20) M. C. Hall, B. T. Kilbourn, and K. A. Taylor, *J. Chem. Soc. A*, 2539 (1970).
(21) C. G. Pierpont and R. Eisenberg, *Inorg. Chem.*, **12**, 199 (1973).
(22) V. Albano, P. Bellon, and V. Scatturin, *Rend., Ist. Lomb. Accad. Sci. Lett. A*, **100**, 989 (1966).
(23) W. L. Steffen and G. J. Palenik, *Inorg. Chem.*, **15**, 2432 (1976).
(24) R. E. Willet and R. W. Rundle, *J. Chem. Phys.*, **40**, 838 (1964).
(25) F. A. Cotton and S. J. Lippard, *Inorg. Chem.*, **5**, 416 (1966).
(26) I. W. Bassi and M. Calcaterra, *J. Organomet. Chem.*, **110**, 129 (1976).
(27) G. Agnes, I. W. Bassi, C. Benedicenti, R. Inbrito, M. Calcaterra, and C. Santini, *J. Organomet. Chem.*, **129**, 401 (1977).
(28) B. Swanson, D. F. Shriver, and J. A. Ibers, *Inorg. Chem.*, **8**, 2182 (1969).
(29) C. C. Costain, *J. Chem. Phys.*, **29**, 864 (1958).
(30) H. J. Coerver and C. Curran, *J. Am. Chem. Soc.*, **80**, 3522 (1958); K. F. Purcell and R. S. Drago, *ibid.* **88**, 919 (1966); D. W. Hensley and R. P. Stewart, Jr., *Inorg. Chem.*, **15**, 2418 (1976).
(31) W. Gerrard, M. F. Lappert, H. Pyszora, and J. W. Wallis, *J. Chem. Soc.*, 2182 (1960).
(32) L. Pauling, "The Nature of the Chemical Bond", 3rd ed, Cornell University Press, Ithaca, N.Y., 1960, p 260.
(33) W. H. Baur, *Acta Crystallogr., Sect. B*, **28**, 1456 (1972).
(34) M. L. H. Green and R. N. Whitely, *J. Chem. Soc. A*, 1943 (1971).
(35) R. H. Reimann and E. Singleton, *J. Chem. Soc., Dalton Trans.*, 808 (1974).
(36) B. L. Ross, J. G. Grasselli, W. M. Ritchley, and H. D. Kaesz, *Inorg. Chem.*, **2**, 1023 (1963).
(37) I. W. Stolz, G. R. Dobson and R. K. Sheline, *Inorg. Chem.*, **2**, 323 (1963).
(38) A. Misono, Y. Uchida, M. Hidai, and T. Kuse, *Chem. Commun.*, 208 (1969).
(39) F. A. Cotton and S. J. Lippard, *Inorg. Chem.*, **5**, 9 (1966).

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Synthesis and Chemical and Structural Investigation of Molybdenum(IV) Thioxanthate Complexes. An Unusual Example of η^3 Coordination for a Dithio Acid Ligand

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The synthesis of the compounds $MoO(S_2CSR)_2$, R = i-C_3H_7 and t-C_4H_9, is reported. The electronic, IR, and proton NMR spectra are discussed and compared to those obtained for the parent dimers $[Mo_2O_3(S_2CSR)_2]$. The molecular structure of $MoO(S_2CS$-i-$C_3H_7)_2$ was revealed in a single-crystal x-ray diffraction study. The compound crystallizes in the triclinic crystal system, space group $P\bar{1}$, with $a = 6.14$ (1) Å, $b = 10.24$ (1) Å, $c = 12.924$ (8) Å, $\alpha = 109.71$ (1)°, $\beta = 93.25$ (1)°, and $\gamma = 99.80$ (1)°, giving a density of 1.76 g cm^{-3} on the basis of two molecules per unit cell, in agreement with the measured density of 1.74 (2) g cm^{-3}. The structure was solved using 1450 independent, statistically significant reflections collected on a full-circle automated diffractometer. The structure was solved by the usual Patterson and Fourier series methods to give a final value of the discrepency factor R_1 of 0.059. The molecule is a pseudo-square-pyramidal monomer with two distinct ligand coordination types: one thioxanthate group exhibits the usual bidentate geometry, with Mo–S distances of 2.438 (4) and 2.454 (5) Å and a chelate ring angle S–Mo–S of 72.2 (1)°, while the second thioxanthate group displays unusual nonclassic coordination, with the Mo significantly displaced from the S_2CS plane such that the Mo–central carbon bond distance is 2.25 (1) Å and the Mo–S distances are 2.375 (5) and 2.365 (4) Å, with a chelate ring angle S–Mo–S of 77.9 (2) Å. The oxo group completes the coordination about the Mo atom [Mo–O distance 1.66 (1) Å] which is displaced 0.86 Å from the plane generated by the four sulfur donors toward this approximately apical oxygen. Voltammetric studies of the monomers indicate an irreversible oxidation and a quasi-reversible reduction as the major electrode processes. Comparison of the voltammetric behavior of the monomers with that of the dimer complexes $[Mo_2O_3(S_2CSR)_4]$ establishes the importance of dimer disproportionation into monomeric species in determining the overall electrochemical characteristics of these complexes. Oxidation–reduction mechanisms are proposed on the bases of these electrochemical studies, spectroscopic measurements, and isolation of electrode reaction products.

Introduction

The coordination chemistry of molybdenum in the higher oxidation states (IV–VI) continues to draw a growing interest, in view of the possible relevance of these complexes to the redox-active molybdoenzymes.[1] In particular, the nitrogenase iron–molybdenum protein component from a number of bacterial sources[2–4] contains two molybdenum atoms per mole of enzyme. It has been proposed that the two molybdenum atoms are present at this enzyme-active site and function in a concerted fashion in the catalytic process.[5] The vital importance of molybdenum to the function of these enzymes and the speculation of a dimeric metal site involving coordination to sulfur-donor ligands have prompted a number of chemical,[5–7] electrochemical,[8] and structural studies[9–26] of molybdenum–oxo complexes enjoying some degree of coordination to sulfur-containing ligands. The chemical and structural aspects of the molybdenum dithiocarbamates have been extensively investigated, and the interrelationship of the dimeric and monomeric species has been established. The chemical[5,6] and electrochemical[8] behavior of these complexes is dictated by the disproportionation of the molybdenum(V) dimer into monomeric Mo(IV) and Mo(VI) species:

$$Mo_2O_3(dtc)_4 \rightleftarrows MoO(dtc)_2 + MoO_2(dtc)_2 \qquad (1)$$

In a series of parallel investigations[12,27,28] we have studied the chemistry of molybdenum with the analogous thioxanthate ligand. This choice was dictated by the ability of the ligand to stabilize redox-active complexes[29,30] and to produce unique structural types through ligand dissociation or rearrangement.[31] In this paper, we describe the synthesis of a new type of molybdenum(IV) dithio acid monomer $MoO(S_2Cs$-i-$C_3H_7)_2$ and its relationship to the previously reported dimers.[12] The infrared and visible spectra are presented and discussed. The structure of the complex, determined by x-ray crystallography, is contrasted to the geometry of other monomeric square-pyramidal molybdenum compounds.

In addition, the present investigation has attempted to elucidate the electrochemical properties of the oxomolybdenum

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