A Diphosphaferrocene as a Chelating Ligand for Silver(I)

David A. Atwood, Alan H. Cowley,* and Sean M. Dennis

Department of Chemistry and Biochemistry,
The University of Texas at Austin, Austin, Texas 78712

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Introduction

Interesting cooperative magnetic properties have been observed for electron-transfer salts of decamethylferrocene, e.g.[1]

$$(\eta^5\text{-}C_5Me_5)_2Fe + TCNE \rightarrow [(\eta^5\text{-}C_5Me_5)_2Fe]^+[TCNE]^-$$

However, to our knowledge, the reactivity of heteroatom-substituted ferrocenes toward tetracyanoethylene (TCNE) and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) has not been explored. In terms of phosphaferrocenes, the closest analogue of $(\eta^5\text{-}Me_5C_5)_2Fe$ is 2,2′,3,3′,4,4′,5,5′-octamethyl-1,1′-diphosphaferrocene (**1**). We therefore attempted the reactions of **1** with TCNE and TCNQ.

Experimental Section

Methods and Materials. All operations were performed by using standard Schlenk techniques under an atmosphere of dry, oxygen-free dinitrogen. All solvents were freshly distilled over the appropriate drying agents immediately prior to use. Tetracyanoethylene (TCNE) and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) were procured commercially and used after sublimation; 2,2′,3,3′,4,4′,5,5′-octamethyl-1,1′-diphosphaferrocene was prepared and purified according to the literature method.[2] ^{31}P NMR spectra were recorded on a General Electric QE 300 instrument operating at a spectrometer frequency of 121.5 MHz.

Electrochemical Synthesis of $[Ag\{(\eta^5\text{-}Me_4C_4P)_2Fe\}_2]^+[TCNQ]^-$ (2). This experiment was carried out in a two-compartment cell of conventional design equipped with a silver anode and platinum cathode. The two compartments were separated by a glass frit. A solution of 0.50 g (0.15 mmol) of **1** in 30 mL of THF was placed in the anode compartment. The cathode compartment was charged with 0.306 g (1.5 mmol) of TCNQ in 30 mL of THF. Dark blue crystals of the product (**2**) (mp 210–213 °C) formed at the anode. The crystals were suitable for X-ray analysis.

X-ray Structure Analysis of 2. Crystallographic data are summarized in Table I. A suitable single crystal of **2** (0.35 × 0.34 × 0.34 mm) was obtained as described above, mounted in a thin-walled glass capillary, and sealed under argon. Initial lattice parameters were obtained from a least squares fit to 25 reflections, $15° \le 2\theta \le 20°$, accurately centered on an Enraf-Nonius CAD-4 diffractometer and refined subsequently using higher angle data. The data were collected by utilizing Mo Kα radiation. The space group was triclinic $P\bar{1}$. A total of 7285 unique reflections were collected at 298 K using the $\theta/2\theta$ scan mode over the range $2° \le 2\theta \le 50°$. The data set was corrected for Lorentz and polarization effects. The structure of **2** was solved by a combination of Patterson and difference Fourier methods using 4931 reflections with $I > 3.0\sigma(I)$. All non-hydrogen atoms were refined anisotropically. The final R and R_w values were 0.0856 and 0.0998, respectively.

Results and Discussion

No charge-transfer complex formation took place upon mixing $(\eta^5\text{-}Me_4C_4P)_2Fe$ (**1**) with equimolar quantities of either TCNE or TCNQ in THF solution at room temperature as evidenced by the absence of color changes and the persistence of the ^{31}P NMR resonance for **1**. In view of this lack of reactivity under normal conditions, we decided to explore the reaction of **1** with TCNQ in an electrochemical cell. However, the product of electrocrystallization of TCNQ with **1** is the novel silver complex $[Ag\{(\eta^5\text{-}Me_4C_4P)_2Fe\}_2]^+[TCNQ]^-$ (**2**), rather than an electron-

Table I. Crystallographic Data for **2**

formula	$C_{48}H_{60}AgFe_2OP_4$	Z	1
MW	1052.49	V, Å^3	2401(22)
a, Å	13.547(2)	space group	$P\bar{1}$
b, Å	13.729(1)	D_c, g·cm^{-3}	0.732
c, Å	15.415(3)	2θ range, deg	2.0–50.0
α, deg	98.55(1)	data used ($F_o > 3\sigma(F_o)$)	4931
β, deg	106.23(1)	variables	541
γ, deg	113.92(1)	final R/R_w, %	8.56/9.98

Table II. Atomic Parameters for **2**

atom	x	y	z	U,^{a} Å^2	atom	x	y	z	U,^{a} Å^2
Ag	0.42334(11)	0.15852(11)	0.26086(10)	0.0544(6)	C(24)	0.576(2)	0.188(2)	0.0610(12)	0.072(10)
Fe(1)	0.1927(2)	–0.0339(2)	0.25227(13)	0.0339(9)	C(25)	0.5888(13)	0.4662(11)	0.3461(10)	0.040(8)
Fe(2)	0.6263(2)	0.3686(2)	0.25397(13)	0.0354(9)	C(26)	0.6529(12)	0.5310(11)	0.2991(10)	0.039(7)
P(1)	0.2417(4)	0.0119(3)	0.1243(3)	0.048(2)	C(27)	0.5949(14)	0.4879(13)	0.1969(11)	0.049(9)
P(2)	0.3609(3)	0.0871(3)	0.3872(3)	0.045(2)	C(28)	0.4924(12)	0.3903(11)	0.1690(11)	0.043(7)
P(3)	0.6179(3)	0.1951(3)	0.2574(3)	0.046(2)	C(29)	0.625(2)	0.492(2)	0.4532(11)	0.063(11)
P(4)	0.4524(3)	0.3536(3)	0.2644(3)	0.049(2)	C(30)	0.7622(13)	0.6432(12)	0.3494(11)	0.052(7)
C(1)	0.1180(13)	0.0124(11)	0.1373(9)	0.042(7)	C(31)	0.641(2)	0.5479(15)	0.1313(13)	0.062(10)
C(2)	0.0362(13)	–0.0943(14)	0.1350(11)	0.050(8)	C(32)	0.407(2)	0.325(2)	0.0654(11)	0.072(10)
C(3)	0.0826(13)	–0.1714(12)	0.1327(10)	0.047(7)	C(33)	0.7842(14)	0.0497(14)	1.2715(11)	0.056(9)
C(4)	0.1942(14)	–0.1276(13)	0.1317(10)	0.046(9)	C(34)	0.777(2)	0.0240(14)	1.3575(11)	0.058(9)
C(5)	0.092(2)	0.111(2)	0.1380(12)	0.073(12)	C(35)	0.693(2)	–0.0761(15)	1.3559(11)	0.060(9)
C(6)	–0.089(2)	–0.125(2)	0.1309(15)	0.085(11)	C(36)	0.612(2)	–0.158(2)	1.2672(11)	0.062(10)
C(7)	0.010(2)	–0.2966(14)	0.1237(13)	0.089(13)	C(37)	0.619(2)	–0.131(2)	1.1819(11)	0.063(10)
C(8)	0.263(2)	–0.189(2)	0.1262(13)	0.076(13)	C(38)	0.7015(15)	–0.034(2)	1.1808(13)	0.067(9)
C(9)	0.2992(13)	–0.0584(11)	0.3665(9)	0.039(7)	C(39)	0.8669(15)	0.1504(15)	1.2711(12)	0.055(9)
C(10)	0.1840(13)	–0.1025(12)	0.3632(10)	0.043(8)	C(40)	0.953(2)	0.236(2)	1.3592(15)	0.066(11)
C(11)	0.1389(14)	–0.0223(14)	0.3673(10)	0.050(9)	N(1)	1.0226(15)	0.302(2)	1.4289(12)	0.089(10)
C(12)	0.2273(14)	0.0863(12)	0.3753(10)	0.044(8)	C(41)	0.871(2)	0.1762(15)	1.189(2)	0.065(10)
C(13)	0.365(2)	–0.123(2)	0.3675(12)	0.066(10)	N(2)	0.874(2)	0.194(2)	1.1160(12)	0.084(11)
C(14)	0.109(2)	–0.2264(14)	0.3584(13)	0.070(11)	C(42)	0.524(2)	–0.2629(14)	1.2622(11)	0.056(9)
C(15)	0.024(2)	–0.046(2)	0.3722(14)	0.083(12)	N(3)	0.385(2)	–0.406(2)	1.1004(12)	0.081(10)
C(16)	0.211(2)	0.1892(15)	0.3841(13)	0.069(12)	C(43)	0.448(2)	–0.343(2)	1.1744(14)	0.066(11)
C(17)	0.7299(13)	0.3167(13)	0.3434(11)	0.045(8)	N(4)	0.511(2)	–0.314(2)	1.4169(11)	0.069(12)
C(18)	0.7980(12)	0.3903(12)	0.3018(10)	0.042(7)	C(44)	0.517(2)	–0.2928(14)	1.3527(14)	0.091(11)
C(19)	0.7484(12)	0.3548(12)	0.2019(10)	0.043(7)	O	0.833(2)	0.4321(14)	0.7791(14)	0.15(2)
C(20)	0.6459(13)	0.2505(12)	0.1648(10)	0.044(7)	C(45)	0.807(2)	0.476(2)	0.704(2)	0.11(2)
C(21)	0.765(2)	0.336(2)	0.4491(12)	0.082(13)	C(46)	0.795(2)	0.572(2)	0.736(2)	0.10(2)
C(22)	0.9126(14)	0.4977(14)	0.3593(14)	0.074(9)	C(47)	0.875(2)	0.512(2)	0.8641(14)	0.081(14)
C(23)	0.804(2)	0.415(2)	0.1382(14)	0.068(11)	C(48)	0.840(2)	0.598(2)	0.842(2)	0.089(14)

[a] For anistropic atoms, the U value is U_{eq}, calculated as $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}\, a_i{}^*a_j{}^*A_{ij}$ where A_{ij} is the dot product of the ith and jth direct space unit cell vectors.

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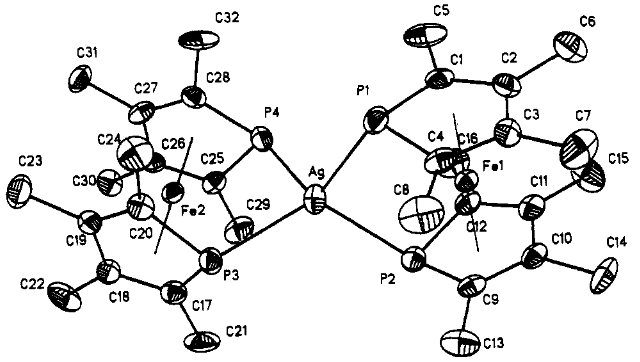

Figure 1. ORTEP diagram of the cation $[Ag\{(\eta^5\text{-}Me_4C_4P)_2Fe_2\}]^+$. The Me groups have been omitted for clarity.

Table III. Selected Bond Distances (Å) and Bond Angles (deg)[a]

Ag–P(1)	2.524(3)	P(1)–Ag–P(2)	95.39(14)
Ag–P(2)	2.507(5)	P(1)–Ag–P(3)	119.3(2)
Ag–P(3)	2.493(5)	P(1)–Ag–P(4)	111.6(2)
Ag–P(4)	2.534(5)	P(2)–Ag–P(3)	120.9(2)
		P(2)–Ag–P(4)	115.6(2)
		P(3)–Ag–P(4)	95.3(2)

[a] Estimated standard deviations are given in parentheses.

transfer salt. Presumably, the silver anode in the electrochemical cell serves as the source of Ag^+ ions.

The structure of **2** was established by X-ray crystallography. The solid state comprises $[Ag\{(\eta^5\text{-}Me_4C_5P)_2Fe\}_2]^+$ cations and $[TCNQ]^{\bullet-}$ radical anions, and there are no short interionic contacts. A diagram of the cation appears in Figure 1. Fractional atomic coordinates and selected interatomic distances and angles are assembled in Tables II and III, respectively.

Diphosphametallocenes have been shown previously to behave as normal phosphorus donor ligands toward a variety of transition metal moieties.[3] However, to our knowledge, this is the first Ag^+ complex involving this type of ligand. A further distinctive feature of **2** is that it represents the first instance in which a diphosphametallocene functions in a chelating fashion.

The overall arrangement of the four phosphorus atoms around the Ag^+ cation is distorted tetrahedral. The wide scatter of P–Ag–P bond angles (95.3(2)–120.9(2)°) is due to the "bite" angle of the diphosphaferrocene ligand. Counting the ring centroids as "quasi-atoms", each diphosphaferrocene ligand forms a six-membered chelate ring. The Ag–P bond distances for **2** range from 2.493(5) to 2.534(5) Å and are shorter than those observed for tetrahedral $[Ag(PPh_3)_4]^+$ (range 2.615(5)–2.746(5) Å.[4] This is perhaps due to the more modest steric requirements of the diphosphaferrocene ligand. The X-ray crystal structure of uncomplexed **2** has not been reported. However, the metric parameters for the diphosphaferrocene ligands of **2** are similar to those of, e.g., 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene.[5]

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Supplementary Material Available: Tables of anisotropic thermal parameters and selected bond distances, bond angles, and torsion angles and a unit cell diagram for **2** (9 pages). Ordering information is given on any current masthead page.

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(1) See, for example: Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Chem. Rev.* **1988**, *88*, 201. Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Acc. Chem. Res.* **1988**, *21*, 114. Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Science* **1988**, *240*, 40.

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