

## Metalloocene Electrochemistry. 4. Ferrocenylalkyl-Substituted Quaternary Ammonium Cations in Aqueous, Organic, and Molten Salt Phases

R. J. GALE,\*<sup>1a</sup> K. M. MOTYL, and R. JOB<sup>1b</sup>

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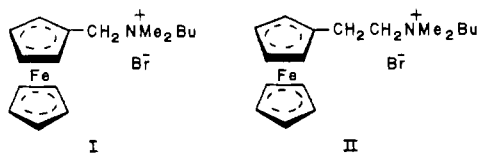
Reduction-oxidation, diffusion, and solubility properties of several ferrocenylalkyl quaternary ammonium derivatives have been determined in aqueous, acetonitrile, and room-temperature  $\text{AlCl}_3$ -1-butylpyridinium chloride melt electrolytes. Electrochemical evidence supports the premise that nucleophilic attack of ferrocenium ion charge-transfer products occurs in basic melts, the extent of which relates to anticipated electronic substituent effects. In acidic melts, the quaternary salt is shown to decompose and to undergo an intramolecular electron transfer from the carbonium ion to the metal center. Such behavior is consistent with earlier ideas concerning the reactivities and reaction pathways of these compounds. The yellow 1-COOH derivative of ferrocene dissolves in slightly acidic melts to produce a red color, and a reversible, one-electron wave is found at +0.726 V vs. Al (2:1) reference.

### Introduction

Earlier electrochemical studies of substituted metalloocene derivatives have been concerned primarily with attempts to correlate half-wave reduction-oxidation potentials with electronic, inductive effects. Results suggest that substitution of electron-donating groups on one cyclopentadienyl ring, or both, increases the ease of oxidation of the metal center, whereas electron-withdrawing groups have the opposite effect. Chronopotentiometric quarter-wave potentials of substituted ferrocenes best correlated with Hammett para  $\sigma$  constants, which indicates the importance of substituent resonance contributions to the carbocyclic ring of attachment.<sup>2-7</sup> The charge-transfer characteristics of metalloocene derivatives currently are of interest because of possible applications of such compounds to energy storage or conversion devices. We have synthesized several ferrocenylalkyl-substituted quaternary ammonium derivatives and studied their electrochemical behavior in aqueous, acetonitrile, and room-temperature molten salt electrolytes for two reasons: (i) they are ionic derivatives with high solubilities in polar solvents (see below), and in consequence they may be candidates for photoelectrochemical cell redox systems, and (ii) we wished to examine their feasibility as suitable components for room-temperature ionic melts of high charge storage capacity. Additional important practical considerations for photoelectrochemical cells are the thermal stabilities and photostabilities of both oxidation states of a redox couple.<sup>8</sup>

### Results and Discussion

**Voltammetric Investigations.** Cyclic voltammetric studies at vitreous carbon electrodes show that ferrocenylmethyl and ferrocenylethyl quaternary ammonium derivatives undergo 1e reversible charge-transfer reactions of the iron center in aqueous electrolytes, acetonitrile-based electrolytes, and acidic mixtures of  $\text{AlCl}_3$  and 1-butylpyridinium chloride (i.e., >1:1 molar ratio, respectively). Compounds I and II did not dissolve



- (1) (a) To whom correspondence should be addressed at the Chemistry Department, Louisiana State University, Baton Rouge, LA 70803. (b) Present address: Shell Development Co., Houston, TX 77001.  
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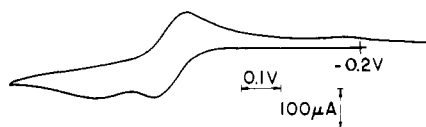
**Table I.** Half-Wave Potential Values for Ferrocenylalkyl Derivatives in Aqueous, Organic, and Molten Salt Phases<sup>a</sup>

compd	$E_{1/2}$ , V	solvent
$\text{C}_{10}\text{H}_{10}\text{Fe}^{12}$	0.146 (SCE)	aq 0.1 M $\text{Et}_4\text{NClO}_4$
$\text{C}_{10}\text{H}_9\text{FeCH}_2\text{-NMe}_2\text{BuBr}$ (I)	0.380 (SCE)	aq 0.2 M $\text{Me}_4\text{NCl}$
$\text{C}_{10}\text{H}_9\text{Fe}(\text{CH}_2)_2\text{-NMe}_2\text{BuBr}$ (II)	0.211 (SCE)	aq 0.2 M $\text{Me}_4\text{NCl}$
$\text{C}_{10}\text{H}_9\text{Fe}(\text{CH}_2)_2\text{-NMe}_2\text{BuBr}$ (II)	0.286 (SCE)	aq 0.1 M $\text{LiClO}_4$ -abs EtOH
$\text{C}_{10}\text{H}_9\text{FeCH}_2\text{-NMe}_2\text{BuBr}$ (I)	~0.277 (0.01 M $\text{Ag}^+\text{-Ag}$ )	0.2 M $\text{LiClO}_4\text{-CH}_3\text{CN}$
$\text{C}_{10}\text{H}_9\text{FeCH}_2\text{-NMe}_2\text{BzCl}$ (III)	0.279 (0.01 M $\text{Ag}^+\text{-Ag}$ )	0.2 M $\text{LiClO}_4\text{-CH}_3\text{CN}$
$\text{C}_{10}\text{H}_{10}\text{Fe}^{11}$	0.240 (Al (2:1 melt))	1:1 melt
$\text{C}_{10}\text{H}_9\text{FeCH}_2\text{-NMe}_2\text{BuBr}$ (I)	0.500 (Al (2:1 melt))	1.1:1 melt
$\text{C}_{10}\text{H}_9\text{Fe}(\text{CH}_2)_2\text{-NMe}_2\text{BuBr}$ (II)	0.305 (Al (2:1 melt))	1.1:1 melt

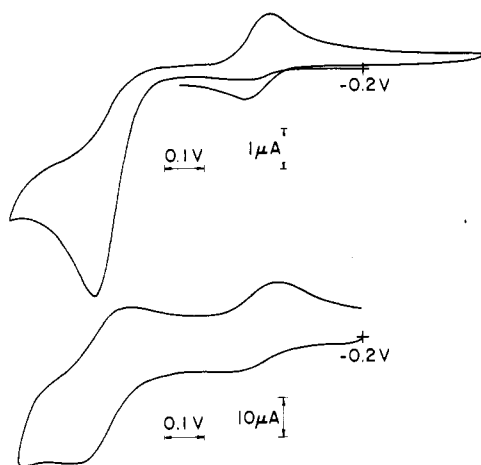
<sup>a</sup> Half-wave potentials are uncorrected for liquid-junction potentials. The butyl substituents are 1-butyl. Aqueous 0.1 M  $\text{LiClO}_4$ -absolute EtOH solutions are 50:50 (v/v).

satisfactorily in aqueous 0.2 M  $\text{LiClO}_4$ , but a solution of tetramethylammonium chloride proved to be a suitable supporting electrolyte. Half-wave potentials for the reversible charge-transfer processes are presented in Table I. The oxidation peak for compound I in acetonitrile was distorted slightly by the more positive bromide ion oxidation reaction, and the small peak in the return scan, at  $\sim -0.15$  V, is associated with bromine reduction (Figure 1). Compound III had a half-wave potential value indistinguishable from that of compound I. Each of the half-wave potentials for the three derivatives examined was positive of that for ferrocene, indicating that the influence of these substituent groups is to impede the oxidation processes by electron withdrawal from the cyclopentadienyl conjugate system. Perevalova and co-workers<sup>9</sup> have reported a potential difference between the  $(\text{C}_{10}\text{H}_9\text{FeCH}_2\text{NMe}_2\text{Et})^+$  ion and ferrocene of +0.234 V (75 vol %  $\text{CH}_3\text{COOH}$ , 25 vol % 0.033 M  $\text{HClO}_4$  solvent), which is identical with the corresponding difference value found in this work for compound I and ferrocene in aqueous solvent (Table I).

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**Figure 1.** Cyclic voltammogram of 7.54 mM  $C_{10}H_9FeCH_2NMe_2BuBr$  in 0.2 M  $LiClO_4-CH_3CN$  (100  $mV s^{-1}$ , reference 0.01 M  $Ag^+-Ag$ , vitreous C electrode of geometrical area 0.0573  $cm^2$ ).



**Figure 2.** Cyclic voltammogram of 3.83 mM  $C_{10}H_9FeCH_2NMe_2BuBr$  in 0.8:1 melt (40 °C, reference Al wire (2:1 melt), 0.0573  $cm^2$  vitreous C electrode): (top) scan rate 10  $mV s^{-1}$ ; (bottom) scan rate 1  $V s^{-1}$ .



**Figure 3.** Cyclic voltammogram of 2.50 mM  $C_{10}H_9Fe(CH_2)_2NMe_2BuBr$  in 0.8:1 melt (40 °C, Al (2:1) reference, 0.0573  $cm^2$  vitreous C electrode, scan rate 50  $mV s^{-1}$ ).

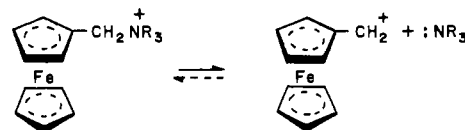
Interesting electrochemical behavior resulted for these ferrocenylalkyl derivatives in basic  $AlCl_3$ -1-butylpyridinium chloride melts. The ferrocenylmethyl compounds oxidize irreversibly in 0.8:1 molar ratio melts at slow scan rates, but at 1  $V s^{-1}$  sweep rate a reduction peak can be resolved (Figure 2). This behavior is consistent with diagnostic criteria for a rapid chemical follow-up reaction of the 1e ferrocenium ion product, possibly a nucleophilic attack by chloride ion. Voltammograms of compounds I and III contained a quasi-reversible redox process at  $E_{pc} \approx 0.035$  V and  $E_{pa} \approx 0.095$  V due to a product species. The voltammetry of the ferrocenylethyl derivative indicates almost reversible behavior upon oxidation, even at 10  $mV s^{-1}$ , and this evidence supports a premise that increasing the methylene chain length decreases the tendency for the follow-up reaction (Figure 3). The half-wave potentials of II, shown in Table I, are consistent with the concept of an increase in the alkyl character of the substituent group. In other words, electron withdrawal is diminished over that found in the case of a single  $-CH_2-$  group in the bridge. If suitable separation techniques could be developed, the nature of the decomposition product species of these ferrocenium ions (and other metallocenium rearrangements)<sup>15,16</sup> could be investigated.

**Table II.** Diffusion Coefficients for Ferrocenylmethyl Derivatives in Aqueous, Organic, and Molten Salt Phases

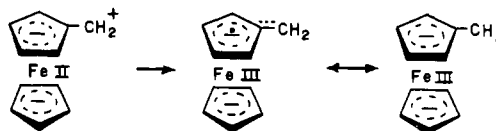
compd	$D$ , $cm^2 s^{-1}$	solvent
$C_{10}H_{10}Fe^3$	$2.4 \times 10^{-5}$	0.2 M $LiClO_4-CH_3CN$ (25 °C)
$C_{10}H_{10}Fe^{11}$	$5.4 \times 10^{-7}$	1:1 $AlCl_3$ -1-BPC (40 °C)
$C_{10}H_9FeCH_2NMe_2BuBr$	$1.1 \times 10^{-5}$	0.2 M $LiClO_4-CH_3CN$ (25 °C) <sup>a</sup>
$C_{10}H_9FeCH_2NMe_2BuBr$	$5.5 \times 10^{-6}$	aq 0.2 M $Me_4NCl$ (25 °C) <sup>a</sup>
$C_{10}H_9FeCH_2NMe_2BuBr$	$2.7 \times 10^{-7}$	1.1:1 $AlCl_3$ -1-BPC (40 °C)

<sup>a</sup> Approximate temperatures.

**Thermal Stability Studies.** Quaternary ammonium derivatives with the single methylene linkage decomposed thermally in acidic melts, over a period of days, to give a blue-green solution. Voltammetry showed that the reversible couple at  $E_{1/2} \approx 0.50$  V decreased and a new reversible couple appeared with  $E_{1/2} \approx 0.195$  V, comparable peak currents, and a rest potential positive to the couple. If an acidic melt containing partially decomposed compound was made basic, the new couple persisted and it was not identifiable with the follow-up product of the original ferrocenium ion; i.e., an irreversible transformation occurs. The experimental findings are consistent with an intramolecular electron transfer of a carbonium ion fragment to form a seemingly stable ferrocenium ion radical. The first step of such a mechanism might be the dissociation of the quaternary ammonium derivative, as postulated by Pennie and Bieber:<sup>12</sup>



Presumably, the free amine would be complexed with a Lewis acid species in the melt ( $AlCl_3$  or  $Al_2Cl_7^-$ ), and this may assist the completion of this dissociation. In the absence of a suitable nucleophilic base, the carbonium ion fragment could undergo intramolecular electronic rearrangement to form a tautomeric species:



The blue-green color of the melt and the electrochemical behavior reveal that the iron center has Fe(III) character. Rearrangements of this type have been proposed earlier to explain the stability of  $\alpha$ -ferrocenylcarbonium ions and the formation of dimer products.<sup>13</sup> Radical coupling might be expected to produce a bridged diferrocenylethylene species; however, in the acidic molten salts it is possible that the radical is stabilized to some extent and the dimerization reaction is slow. So far we have been unable to isolate the (possibly highly reactive) primary product for spectroscopic examination, partly because of experimental extraction difficulties of handling the molten salt solvent. The blue-green product can be reduced by stirring the melt with Al wire, and the addition of excess toluene induces the separation of an orange-yellow supernatant, which can be analyzed for uncharged product species. Both ferrocene and methylferrocene were identifiable by NMR as major products from thermal decomposition after workup. GC-mass spectroscopy confirmed the presence of a small amount of dimer product, supporting the idea that the uncoupled radical may be relatively stable in these media. Other

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**Table III.** Solubilities for Ferrocene and the Ferrocenylmethyl Derivatives in Aqueous, Organic, and Molten Salt Phases

compd	solubility, M	solvent
C <sub>10</sub> H <sub>10</sub> Fe <sup>10</sup>	1.7 × 10 <sup>-5</sup>	H <sub>2</sub> O (25 °C)
C <sub>10</sub> H <sub>10</sub> Fe	0.18	CH <sub>3</sub> CN (30 °C)
C <sub>10</sub> H <sub>10</sub> Fe	~0.25–0.60	(1.1:1)–(2:1) melt (30 °C)
C <sub>10</sub> H <sub>9</sub> FeCH <sub>2</sub> NMe <sub>2</sub> BuBr	>2.4	H <sub>2</sub> O (25 °C)
C <sub>10</sub> H <sub>9</sub> FeCH <sub>2</sub> NMe <sub>2</sub> BuBr	0.35	CH <sub>3</sub> CN (30 °C)

spectroscopic approaches have not been successful in providing more information of the primary decomposition product although visible and ESR spectroscopy have not been applied.

**Diffusion Coefficients.** The diffusion coefficients reported in Table II were calculated from the cyclic voltammetry data by using the expression

$$i_p = 602n^{3/2}AD^{1/2}v^{1/2}c_b\chi'$$

in which  $\chi'$  is the Nicholson and Shain constant (0.4463 at peak),  $i_p$  is in amperes, the scan rate  $v$  is in V s<sup>-1</sup>, the geometrical area  $A$  is in cm<sup>2</sup>, and the bulk concentration  $c_b$  is in moles per liter. The values for compound I are smaller than those for the ferrocene molecule and decrease consistently with increase of the solvent viscosities as expected from the Stokes–Einstein relation:

$$D = kT/6\pi\eta r$$

where  $\eta$  is the medium viscosity and  $r$  is the effective radius of the freely diffusing species. The  $\eta$  values for water, acetonitrile, and the 1:1 room-temperature melt are approximately 0.89 (25 °C), 0.35 (25 °C), and 23.5 cP (40 °C), respectively.<sup>11</sup>

**Solubilities.** Solubility values contained in Table III for ferrocene and the ferrocenylmethyl derivative were estimated from visible absorbance measurements of diluted samples of saturated solutions. A very large increase in solubility is obtained in aqueous electrolytes when ferrocene is derivatized with the quaternary ammonium side chain. Ferrocene, itself, is reasonably soluble in the AlCl<sub>3</sub>–1-butylpyridinium chloride molten salts presumably because of the like aromatic nature of the butylpyridinium cation. A yellow, ionic 1-COOH derivative of ferrocene dissolves in a 1.1:1 mole ratio melt to produce a red color and to give a reversible wave at  $E_{1/2} \approx +0.726$  V.

Attempts to form low-melting (room-temperature) liquid phases by mixing the ferrocenylalkyl derivatives and AlCl<sub>3</sub> were not successful. Our objective in this regard was to try to prepare room-temperature molten salt electrolytes with high mole fractions of electroactive species, thereby maximizing the storage capability of the electrolyte phase.

## Conclusions

In general, the electrochemical behavior of the quaternary ammonium substituted ferrocenes in room-temperature AlCl<sub>3</sub>–1-butylpyridinium chloride melts is consistent with our previous studies of metallocenes in these aprotic, highly anhydrous media.<sup>14–16</sup> Two types of behavior seem to predominate. First, in basic melts it is possible for nucleophilic chloride ion attack of metallocene oxidation charge-transfer products to ensue (e.g. nickelocenium, ruthenocenium) and such processes could be termed solvolyses. Difficulties in extraction of charged entities from the melts have so far prevented product analyses. Second, the melts appear to stabilize radical species and uncommon valence states of the metallocenes. In this particular study, evidence is presented that intramolecular electron transfer may occur as a result of the thermal dissociation of the quaternary ammonium side chain in acidic melts.

## Experimental Section

All syntheses and analyses were performed under an atmosphere of prepurified N<sub>2</sub> with use of standard inert-atmosphere techniques and equipment. Solvents were reagent grade (stored over molecular sieves) and were degassed and kept under N<sub>2</sub>. C<sub>10</sub>H<sub>9</sub>FeCH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub> was purchased from Pressure Chemicals and used without further purification. <sup>1</sup>H/<sup>13</sup>C spectra were obtained on either a Varian EM-360 or a JEOL FX-100 spectrometer. GC–MS and MS analyses were performed on a VG Micromass 16F spectrometer with a PDP 8a data system. Elemental analyses were made by Midwest Microlab, Ltd. Electrochemical methods and instrumentation were like those reported earlier.<sup>14–16</sup>

**Syntheses.** Compound III was prepared by the method of Perevalova et al.<sup>17</sup> The compound may be recrystallized from CH<sub>3</sub>CN, washed with Et<sub>2</sub>O, and vacuum-dried to mp 190–191 °C (500 torr N<sub>2</sub>) (lit.<sup>17</sup> mp 188.5–189.5 °C). The <sup>1</sup>H NMR spectrum (CD<sub>3</sub>CN) consisted of a broad singlet at 7.58 ppm (5 H, phenyl), a pair of multiplets at 4.52 and 4.41 ppm (2 H + 2 H, substituted cyclopentadienyl), a singlet at 4.27 ppm (5 H, unsubstituted cyclopentadienyl), a singlet at 2.82 ppm (6 H, methyls), and a pair of singlets at 4.41 and 4.61 ppm (2 H + 2 H, benzyl and ferrocenyl CH<sub>2</sub> groups, respectively) downfield from Me<sub>4</sub>Si.

Compound I was prepared by a variation of the above method. Anal. Calcd for C<sub>17</sub>H<sub>26</sub>BrFeN (fw 380.2): C, 53.7; H, 6.91. Found: C, 53.07; H, 6.86. The <sup>1</sup>H NMR spectrum (CD<sub>3</sub>CN) consisted of a multiplet at 4.53 ppm (4 H, substituted cyclopentadienyl + CH<sub>2</sub> adjacent to cyclopentadienyl), a 4.39-ppm multiplet (2 H, substituted cyclopentadienyl), a 4.31-ppm singlet (5 H, unsubstituted cyclopentadienyl), a 2.92-ppm singlet (6 H, methyl), and 3.2- and 1.8–0.9-ppm complex multiplets (2 H + 7 H, butyl) downfield from external Me<sub>4</sub>Si. The melting point was 137–144 °C dec (500 torr N<sub>2</sub>).

**Compound II.** The parent amine was prepared by a variation of the method of Hauser et al.<sup>18</sup> Solid C<sub>10</sub>H<sub>9</sub>FeCH<sub>2</sub>NMe<sub>2</sub>I (30.2 mmol), prepared from C<sub>10</sub>H<sub>9</sub>FeNMe<sub>2</sub> and MeI,<sup>18</sup> was added over 1 h to a stirred solution made from K (60 mmol) and 200 mL of liquid NH<sub>3</sub>. After an additional 3 h reaction time, NH<sub>4</sub>Cl (150 mmol) was added and the mixture allowed to warm to room temperature overnight. The residue was brought to dryness in vacuo, extracted with Et<sub>2</sub>O, and filtered, and the filtrate was distilled in vacuo. Once volatiles had been removed, at ≤90 °C and 0.35 torr, the pot residue proved to be essentially C<sub>10</sub>H<sub>9</sub>FeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> (>95%) by <sup>1</sup>H NMR and TLC (silica gel, 10% CH<sub>2</sub>Cl<sub>2</sub> in pentane). The <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) consisted of a multiplet centered at 4.12 ppm (9 H, cyclopentadienyl), a singlet at 2.25 ppm (6 H, methyls), and a deceptively simple singlet at 2.43 ppm (4 H, methylenes) downfield from Me<sub>4</sub>Si. The yield was 1.5 g (19%).

The amine prepared as above (5.8 mmol) was quaternized with *n*-butyl bromide (6.2 mmol) in CH<sub>3</sub>CN at 60 °C for 3 h. After removal of the volatiles in vacuo, the solid was recrystallized from CH<sub>3</sub>CN (or CH<sub>3</sub>CN–EtOAc) and washed with Et<sub>2</sub>O. The product dried in vacuo had a melting point of 182–184 °C (500 torr N<sub>2</sub>). The <sup>1</sup>H NMR spectrum (CD<sub>3</sub>CN) consisted of a multiplet at 4.21 ppm (9 H, cyclopentadienyl), a singlet at 3.07 ppm (6 H, methyls), a multiplet at 2.75 ppm (2 H, CH<sub>2</sub> adjacent to cyclopentadienyl), and 1.5-, 1.2-, and 1.0-ppm multiplets (7 H, butyl) downfield from Me<sub>4</sub>Si. Anal. Calcd for C<sub>18</sub>H<sub>28</sub>BrFeN (fw 394.2): C, 54.8; H, 7.17. Found: C, 55.5; H, 7.65.

**Thermolysis Studies.** Several analytical experiments were made on solutions of C<sub>10</sub>H<sub>9</sub>FeCH<sub>2</sub>NMe<sub>2</sub>BzCl dissolved in 1.5:1.0 molar ratio melts at 40 °C. Typical concentrations were 0.05–0.10 *m*. Generally, thermal degradation occurred over 1–4 days, whereupon Al wire was added to reduce the ferrocenium species. Excess toluene was added to obtain a partial separation of neutral species, and most analyses were attempted on the organic layer. (1) A sample of the N<sup>+</sup> compound stirred in a melt for 2 days at 40 °C that was reduced with Al was slowly warmed to 95 °C in vacuo (0.20 torr), and the volatile products were collected. The <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of the yellow-orange solids showed a singlet at 4.16 ppm, a multiplet at 4.10 ppm, and a singlet at 1.97 ppm downfield from Me<sub>4</sub>Si. The first is assignable to C<sub>10</sub>H<sub>10</sub>Fe, and the last two are assignable to C<sub>10</sub>H<sub>9</sub>–

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FeCH<sub>3</sub>. Separation by this technique is susceptible to additional thermolysis reactions. (2) A sample of the N<sup>+</sup> compound stirred in an acidic melt for 1 day at 40 °C was made basic with 1-BPC addition and quenched with MeOH. The MeOH was carefully removed by vacuum distillation (45 °C, 100 torr) to yield an oily solvolyzed melt, to which H<sub>2</sub>O is added. The resultant solution was extracted with Et<sub>2</sub>O, and the extracts were dried with K<sub>2</sub>CO<sub>3</sub> and these desolvated in vacuo. Comparative TLC (silica gel, 10% CH<sub>2</sub>Cl<sub>2</sub> in hexane) suggested that the major volatile product was C<sub>10</sub>H<sub>10</sub>Fe. Preparative TLC (silica gel, 5% isopropyl alcohol in toluene) gave two mobile bands (*R<sub>f</sub>* = 0.10 and 0.50), only the first of which (0.50) contained ferrocene compounds by <sup>1</sup>H NMR determinations: singlets at 4.25 and 4.19 ppm downfield from Me<sub>4</sub>Si (the latter due to C<sub>10</sub>H<sub>10</sub>Fe). A portion of the unsolvolyzed melt was subjected to <sup>1</sup>H NMR. In addition to the dominant melt components, solute protons at 7.72, 7.61, and 7.49 ppm (apparent multiplet, phenyls) and 4.34, 4.23, 4.18, and 4.11 ppm (apparent multiplet, cyclopentadienyl) downfield of the methyl triplet due to the solvent centered at 0.99 ppm<sup>19</sup> were resolved. (3) A sample of the N<sup>+</sup> compound stirred for 4 days in an acidic melt, reduced with Al wire, and converted to 0.8:1 basic melt was quenched with toluene. The toluene layer was analyzed by <sup>1</sup>H NMR, <sup>13</sup>C{<sup>1</sup>H} NMR, and GC-MS; identifiable components were toluene (*m/e* 91), BzNMe<sub>2</sub> (*m/e* 135, 91, 58), C<sub>10</sub>H<sub>10</sub>Fe (*m/e* 186, 121), C<sub>10</sub>H<sub>9</sub>FeCH<sub>3</sub> (*m/e* 200, 134, 121), and some C<sub>10</sub>H<sub>9</sub>FeEt (*m/e* 214, 199, 134), in which the last three components showed isotropic distribution characteristic of Fe-containing compounds. The <sup>1</sup>H NMR spectrum (benzene-*d*<sub>6</sub>) consisted of a singlet at 4.0 ppm (C<sub>10</sub>H<sub>10</sub>Fe), a multiplet around 3.97 ppm, and a singlet at 1.84 ppm (C<sub>10</sub>H<sub>9</sub>FeCH<sub>3</sub>) downfield from Me<sub>4</sub>Si. The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum showed a cluster of peaks 68–69 ppm downfield from Me<sub>4</sub>Si—C<sub>10</sub>H<sub>10</sub>Fe at 68.1 ppm and C<sub>10</sub>H<sub>9</sub>FeCH<sub>3</sub> at 69.2, 68.7, and 67.4 ppm with methyl at 45.2 ppm. (4) A sample

of the N<sup>+</sup> compound stirred in an acidic melt for 4 days was reduced with Al wire and quenched with toluene. The toluene layer was separated into three parts: (a) toluene, (b) volatile solids, and (c) nonvolatile residues. The last two were analyzed by MS and <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR. The proton NMR spectrum of the volatile solids consisted of resonances for C<sub>10</sub>H<sub>10</sub>Fe (singlet at 4.00 ppm), C<sub>10</sub>H<sub>9</sub>FeCH<sub>3</sub> (multiplet at 3.97 and singlet at 1.84 ppm), and some toluene (broad singlet at 7.08 ppm and singlet at 2.11 ppm) downfield from Me<sub>4</sub>Si. The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum also showed the expected resonances for C<sub>10</sub>H<sub>10</sub>Fe (68.1 ppm) and C<sub>10</sub>H<sub>9</sub>FeCH<sub>3</sub> (69.2, 68.7, and 67.4 ppm). The MS of the nonvolatile residues showed Fe-containing compounds at *m/e* 121 (Fe<sup>+</sup>Cp), 134 (Fe<sup>+</sup>C<sub>6</sub>H<sub>6</sub>), 186 (C<sub>10</sub>H<sub>10</sub>Fe<sup>+</sup>), and 200 (C<sub>10</sub>H<sub>9</sub>Fe<sup>+</sup>CH<sub>3</sub>). A peak at *m/e* 398 corresponding to some dimeric (C<sub>10</sub>H<sub>9</sub>FeCH<sub>2</sub>)<sub>2</sub><sup>+</sup> also was observed. The <sup>1</sup>H NMR spectrum (benzene-*d*<sub>6</sub>) for the nonvolatile residues showed only one broad resonance in the cyclopentadienyl region (4.0–4.2 ppm) centered at 4.16 ppm. The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum indicated only one resonance assignable to ferrocene species at 69.5 ppm downfield from Me<sub>4</sub>Si.

It is apparent that attempts to separate the possibly highly reactive radical species from an acidic melt have been an unsuccessful approach to analysis. Although not identifiable by electrochemical methods as the major products in the melt, ferrocene and 1-methylferrocene were frequently encountered products after workup. In situ analyses may be more successful in establishing a definitive structure to the ferrocenium product, if suitable procedures can be found.

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**Registry No.** I, 83527-56-4; II, 83511-13-1; III, 53248-56-9; C<sub>10</sub>H<sub>9</sub>FeCH<sub>2</sub>NMe<sub>3</sub>I, 12086-40-7; C<sub>10</sub>H<sub>9</sub>FeNMe<sub>2</sub>, 67251-69-8; MeI, 74-88-4; C<sub>10</sub>H<sub>9</sub>FeCH<sub>2</sub>NMe<sub>2</sub>, 1271-86-9; *n*-butyl bromide, 109-65-9.

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Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843, and the Laboratoire de Chimie Minérale Moléculaire, Equipe de Recherche Associée au CNRS, Parc Valrose, 06034, Nice Cedex, France

## Structure, Bonding, and Chemistry of *closo*-Tetraphosphorus Hexakis(methylimide), P<sub>4</sub>(NCH<sub>3</sub>)<sub>6</sub>, and Its Derivatives. 4. Spectroscopic Studies and General Conclusions

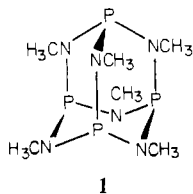
F. ALBERT COTTON,\*<sup>1a</sup> JEAN G. RIESS,\*<sup>1b</sup> and B. RAY STULTS<sup>1a</sup>

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Carbon-13 nuclear magnetic resonance spectra and valence-shell photoionization spectra have been measured for representative compounds of the type X<sub>n</sub>P<sub>4</sub>(NMe)<sub>6</sub> with X = O, S and *n* = 0–4. The <sup>13</sup>C spectra for the series P<sub>4</sub>(NCH<sub>3</sub>)<sub>6</sub>, S<sub>4</sub>P<sub>4</sub>(NMe)<sub>6</sub>, O<sub>4</sub>P<sub>4</sub>(NCH<sub>3</sub>)<sub>6</sub> indicate increasing positive charge on the nitrogen atoms in that order. The PE spectra for the compounds S<sub>n</sub>P<sub>4</sub>(NMe)<sub>6</sub> with *n* = 0, 1, 3, 4 show a steady increase in the stability of the nitrogen pπ electrons. These results together with previously reported structural data are used to discuss electron distribution in these molecules with particular regard to the extent of P–N π bonding, which is judged to be small but real. The softness and deformability of these molecules appear to be prominent characteristics of *closo* phosphorus compounds and to provoke various types of disorder; as a consequence, the electron distributions more probably adapt to the geometric structures rather than determining them.

### Introduction

Several years ago<sup>2a</sup> we began a program of physical studies of *closo*-tetraphosphorus hexakis(methylimide) (**1**) and some



of its derivatives to see whether evidence for a significant amount of N–P pπ→dπ bonding could be obtained. It had initially been our hope that structural data alone would provide strong evidence on this point, and in three earlier papers<sup>2b–4</sup> we have reported structures for **1** and the following derivatives of the type X<sub>n</sub>P<sub>4</sub>(NCH<sub>3</sub>)<sub>6</sub>: **2**, X = O, *n* = 4; **3**, X = S, *n* = 1; **4**, X = S, *n* = 2; **5**, X = S, *n* = 3; **6**, X = S, *n* = 4. For reasons that we shall consider later, the uncertainties in the structural results were much greater than we expected and the structures did not form a basis for unambiguous conclusions about bonding. We have, therefore, also obtained some NMR

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