complete for Ia but still continued for Ib. The initial rates of the reaction measured from the slope of the evolution curve were 6.9 ± 10^{-3} and 1.9×10^{-3} mol of O_2/s for Ia and Ib, respectively, and these compare with a value of 8.4×10^{-2} mol of O_2/s for an effective catalase model compound of iron(III)[24] under the same conditions. Clearly, the manganese complexes are efficient disproportionation catalysts, but their rate of reaction is much slower than that of iron(III) catalase analogues.

In the case of iron(III) catalase models, or iron(III) heme units in general, catalase activity is frequently coupled with peroxidase activity either via generation of free oxy radical species during disproportionation or through the intermediacy of a high oxidation state iron oxo species.[24] Since the present manganese species display slow catalase activity, they were tested for peroxidase behavior by introducing an oxidizable substrate, phenol or 2,6-dimethylphenol, to the catalase experiments. In all cases, after workup of the reaction mixture, the only organic species recovered and detected was unreacted phenol in almost quantitative yield. This result is in marked contrast to results with the corresponding iron(III) complexes of structure I, where in addition to catalase activity catalytic conversion of phenol to quinone proceeds with moderate efficiency. It therefore appears that, if the disproportionation of peroxide does proceed via a high oxidation state metallo-oxo species, then in the case of manganese this species is incapable of phenol oxidation, and this may indicate that it has enhanced stability over the more reactive iron species.[18] As such, the manganese systems may offer a fruitful line of investigation toward elucidation of the potent oxidizing species of the natural heme oxygenases such as peroxidase or cytochrome P-450. This and experiments related to oxene atom transfer from reagents such as iodosylbenzene or metaperiodate are topics of continuing investigation in these laboratories.

Acknowledgment. The support of the National Institutes of Health is gratefully acknowledged.

Registry No. Mn(III)-Ia, 87306-40-9; Mn(II)-Ia, 87306-44-3; Mn(III)-Ib, 87306-42-1; Mn(II)-Ib, 87306-46-5; $[H_4((CH_2)_6(MeNEthi)_2Me_2[16]tetraeneN_4)]Cl(PF_6)_3$, 87318-57-8; $[H_4((m\text{-xylylene})(MeNEthi)_2Me_2[16]tetraeneN_4)]Cl(PF_6)_3$, 87306-47-6; tris(2,4-pentanedionato)manganese(III), 14284-39-0; oxygen, 7782-44-7; hydrogen peroxide, 7722-84-1; potassium superoxide, 12030-88-5.

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Ferrocenyl-Substituted Phosphenium Cations and Phosphide Anions

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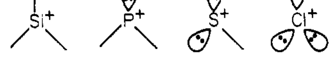
Received February 16, 1983

The phosphorus(III) chloride $Fc(Me_2N)PCl$ (**6**) (Fc = ferrocenyl) was prepared by the reaction of Me_3SiNMe_2 with $FcPCl_2$ (**5**). Treatment of Fc_2PCl (**4**), **6**, or **5** with a stoichiometric quantity of Al_2Cl_6 in CH_2Cl_2 solution results in tetrachloroaluminate salts of the phosphenium ions $[Fc_2P]^+$ (**7**), $[Fc(Me_2N)P]^+$ (**8**), or $[Fc(Cl)P]^+$ (**9**), respectively. ^{31}P, ^{27}Al, and ^1H NMR data are reported for all three salts, and the formulation of **7** as a ferrocenyl compound was confirmed by ^{57}Fe Mössbauer spectroscopy. No evidence for $[FcP]^{2+}$ formation was found when **5** was treated with excess Al_2Cl_6. The Lewis acidity of **7** was demonstrated by reaction with $n\text{-}Bu_3P$, which results in the adduct $[n\text{-}Bu_3PPFc_2]^+[AlCl_4]^-$ (**10**). The iron carbonyl complex $(Fc_2PCl)Fe(CO)_4$ (**11**) was prepared by the reaction of **4** with $Fe_2(CO)_9$ in *n*-hexane. Treatment of **11** with a stoichiometric quantity of Al_2Cl_6 in CH_2Cl_2 solution affords the coordinated phosphenium ion complex $[Fc_2PFe(CO)_4]^+[AlCl_4]^-$ (**12**). ^{57}Fe Mössbauer data for **12** suggest that the phosphenium ion occupies an axial site of the iron trigonal bipyramid. Reduction of **4** with $LiAlH_4$ in Et_2O affords the secondary phosphine Fc_2PH (**13**), which can be lithiated to Fc_2PLi (**14**) with *n*-BuLi. Treatment of **14** with D_2O produced Fc_2PD (**15**). The diphosphine Fc_2PPFc_2 (**16**) can be prepared via the reaction of **4** with K, Mg, or sodium naphthalenide in THF.

Introduction

Two-coordinate phosphorus cations (phosphenium ions) represent a relatively new class of compounds that have attracted significant recent attention.[1] Featuring six valence electrons, phosphenium ions constitute part of an isoelectronic series that extends from silicenium[2] to chloronium[3] ions:



At the inception of this work, all isolable unligated phosphenium ions featured at least one conjugatively stabilizing amido substituent.[1,4] Our primary goal was to synthesize phosphenium ions with only P–C bonds. Since the ferrocenyl (Fc) group has proved to be highly effective for stabilizing positive charge, particularly in the realm of carbocation chemistry,[5] we were encouraged to undertake the synthesis of ferrocenyl-substituted phosphenium ions.[6] In passing, we note thate since starting this program, we have discovered $[(Me_5C_5)PR]^+$, R = *t*-Bu, and $(Me_3Si)_2CH$, a different class of carbon-based phosphenium ion.[7] Furthermore, in a historical vein we should note the pioneering work of Dimroth and co-workers[8] on the

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(1) For early work in this area, see: (a) Fleming, S.; Lupton, M. K.; Jekot, K. *Inorg. Chem.* **1972**, *11*, 2534. (b) Hutchins, R. O.; Maryanoff, B. E. *J. Org. Chem.* **1972**, *37*, 3475. (c) Schultz, C. W.; Parry, R. W. *Inorg. Chem.* **1976**, *15*, 3046. (d) Thomas, M. G.; Schultz, C. W.; Parry, R. W. *Ibid.* **1977**, *16*, 994. For a review, see: (e) Cowley, A. H.; Cushner, M. C.; Lattman, M.; McKee, M. L.; Szobota, J. S.; Wilburn, J. C. *Pure Appl. Chem.* **1980**, *52*, 789. For developments since 1980, see: (f) Baxter, S. G.; Cowley, A. H.; Mehrotra, S. K. *J. Am. Chem. Soc.* **1981**, *103*, 5572. (g) Cowley, A. H.; Lattman, M.; Wilburn, J. C. *Inorg. Chem.* **1981**, *20*, 2916.

(2) Silicenium ions have so far defied all attempts at isolation. For reviews, see: (a) Corriu, R. J. P.; Henner, M. *J. Organomet. Chem.* **1974**, *74*, 1. (b) O'Brien, D. H.; Hairson, T. J. *Organomet. Chem. Rev., Sect. A* **1971**, *7*, 95. See also: (c) Cowley, A. H.; Cushner, M.; Riley, P. E. *J. Am. Chem. Soc.* **1980**, *102*, 624. (d) Olah, G. A.; Field, L. D. *Organometallics* **1982**, *1*, 1485.

(3) For a thorough discussion of halonium ions, the reader is referred to: Olah, G. A. "Halonium Ions"; Wiley: New York, 1975.

(4) There is one instance of a ligated MeO-substituted phosphenium ion (however, free phosphenium ions of the type $(RO)_2P^+$ have not been isolated): (a) Muetterties, E. L.; Kirner, J. F.; Evans, W. J.; Watson, P. L.; Abdel-Meguid, S. S.; Tavanaiepour, I.; Day, V. W. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 1056. (b) Choi, H. W.; Gavin, R. M.; Muetterties, E. L. *J. Chem. Soc., Chem. Commun.* **1979**, 1085. (c) Day, V. W.; Tavanaepour, I.; Abdel-Meguid, S. S.; Kirner, J. F.; Goh, L.-Y.; Muetterties, E. L. *Inorg. Chem.* **1982**, *21*, 657.

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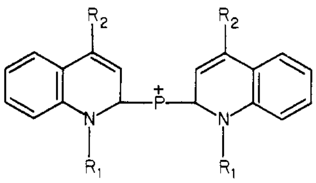
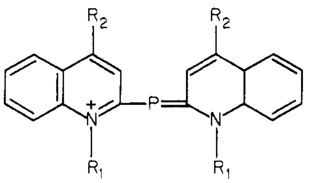
phosphamethinecyanines. Although one of the chemical forms for these intriguing species (**1**) features cationic phosphorus, the other form (**2**) is ylidic and places the positive charge at heterocyclic nitrogen. However, the ^{31}P NMR chemical shifts and reactivity of these compounds suggest very little if any phosphenium in character.[9] Somewhat similar compounds (**3**) have been reported by Gamon and Reichardt.[10]



1



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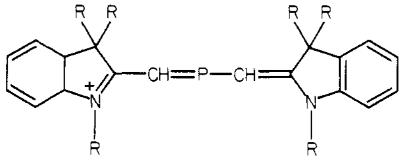

3

A further objective of the present work was to explore the possibility that the ferrocenyl substituent might permit the generation of unknown dications of the genre RP^{2+}. The final point to be explored was the possibility that the appending of ferrocenyl residues might also stabilize negative charge, thereby permitting unprecedented access to one-electron oxidation–reduction sequences such as

$$[R_2P]^+ \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [R_2P]\cdot \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [R_2P]^-$$

Experimental Section

General Procedures. Since most of the reagents employed and products generated in this investigation are oxygen and/or moisture sensitive, all procedures, unless otherwise indicated, were carried out under an atmosphere of dry nitrogen or argon. All solvents were dried and distilled immediately prior to use. Ferrocene, PCl_3, Me_2HN, Et_3N, $LiAlH_4$, $Fe(CO)_5$, Me_3SiCl, *n*-BuLi, D_2O, and *n*-Bu_3P were procured commercially and used as received. Aluminum chloride was triply sublimed in vacuo from aluminum metal. Diiron enneacarbonyl was prepared by ultraviolet irradiation of $Fe(CO)_5$ in a solution of glacial acetic acid,[11] and Me_2NSiMe_3 was prepared by the reaction of Me_2NH with Me_3SiCl.[12] Elemental analyses were performed by Canadian Microanalytical Services, Ltd.

Spectroscopic Measurements. IR spectra were recorded on a Perkin-Elmer Model 337 or a Model 1330 grating spectrophotometer. Low-resolution mass spectral data (70 eV) were obtained on a Du Pont-Consolidated Electrodynamics Corp. Model 21-491 spectrometer. ^1H NMR spectra were recorded on a Varian EM 390 spectrometer at 90.0 MHz. ^{13}C and ^{27}Al NMR spectra were obtained on a Nicolet NT-200 spectrometer operating in the FT mode at spectrometer frequencies of 50.313 and 52.131 MHz, respectively. In general, the ^1H and ^{13}C NMR chemical shifts were measured relative to the internal solvent (usually CH_2Cl_2; $\delta_H = 5.32$, $\delta_C = 54.2$) but are reported relative to tetramethylsilane (Me_4Si). ^{27}Al NMR chemical shifts are reported relative to external aqueous $Al(H_2O)_6{}^{3+}$. ^{31}P NMR spectra were obtained in the FT mode on a Varian FT-80 (32.384 MHz) spectrometer. ^{31}P NMR chemical shifts are reported relative to external 85% H_3PO_4. All resonances occurring at lower magnetic field (higher frequency) than the stated reference are assigned positive chemical shift values.

The ^{57}Fe Mössbauer spectrometer was of local manufacture and employed a γ-ray source of ^{57}Co embedded in Pd metal and featured an automatic laser stabilization system. Low-temperature spectra were accumulated with the aid of a closed-cycle helium cryostat. Isomer shift (IS) data are given in mm/s relative to metallic iron. Quadrupole splitting (QS) parameters are likewise given in units of mm/s.

Diferrocenylchlorophosphine (4) and Ferrocenyldichlorophosphine (5). Diferrocenylchlorophosphine, Fc_2PCl (**4**), and $FcPCl_2$ (**5**) were prepared according to the method of Sollott and Peterson.[13] However, these authors reported only IR spectroscopic data. ^1H NMR (90 MHz);[14] **4** (CD_2Cl_2), H_α (m, 2 H, δ 4.39), H_β (m, 2 H, δ 4.44), $H_{1'}$ (s, 5 H, δ 4.22); **5** (C_6D_6), H_α (m, 2 H, δ 4.21), H_β (m, 2 H, δ 4.38), $H_{1'}$ (s, 5 H, δ 4.03). $^{31}P\{^1H\}$ NMR (32.384 MHz): **4**, δ 82.5 (s); **5**, δ 163.0 (s). Mass spectra (*m/e*, fragment): **4**, 436 (M^+), 401 ($M^+ - Cl$), 371 ($M^+ - C_5H_5$), 336 ($M^+ - Cl - C_5H_5$), 280 ($M^+ - Cl - C_5H_5Fe$), 216 (FcP^+), 186 (FcH^+), 121 ($C_5H_5Fe^+$); **5**, 286 (M^+), 251 ($M^+ - Cl$), 215 ($M^+ - 2Cl$), 186 (FcH^+), 156 ($(C_5H_5)FeCl^+$), 150 ($Fe(C_5H_4)P^+$), 121 ($C_5H_5Fe^+$), 95 ($C_5H_4P^+$).

Preparation of Ferrocenyl(dimethylamino)chlorophosphine, Fc-(Me_2N)PCl (6), (Trimethylsilyl)dimethylamine (0.41 g, 3.5 mmol) was added via a syringe to a stirred solution of $FcPCl_2$ (0.90 g, 3.1 mmol) in 10 mL of CH_2Cl_2 at 0 °C. The orange solution became slightly darker and evolved Me_3SiCl (as evidenced by precipitation of AgCl from aqueous $AgNO_3$). After the mixture was warmed to room temperature, the solvent and Me_3SiCl were removed in vacuo, leaving a crude orange solid. Recrystallization from 2:1 ether–*n*-hexane afforded pure **6** (0.82 g, 2.8 mmol) as an orange, microcrystalline solid in 90% yield. Anal. Calcd for $C_{12}H_{15}ClFeNP$: C, 48.77; H, 5.12; N, 4.74. Found: C, 48.02; H, 5.70; N, 4.41. Mass spectrum (*m/e*, fragment): 295 (M^+), 260 ($M^+ - Cl$), 251 ($M^+ - NMe_2$), 230 ($M^+ - C_5H_5$), 217 ($M^+ - Cl - NMe_2$), 186 (FcH^+), 121 ($(C_5H_5)Fe^+$), 96 ($C_5H_5P^+$), 65 ($C_5H_5{}^+$). ^1H NMR (90.0 MHz, CD_2Cl_2): Me_2N (d, 6 H, δ 2.60, $J_{PNCN} = 13.5$ Hz), $H_{\alpha,\beta}$ (m, 4 H, δ 4.2–4.6), $H_{1'}$ (s, 5 H, δ 4.24). $^{31}P\{^1H\}$ (32.384 MHz): δ 144.9 (s).

Preparation of Diferrocenylphosphenium(1+) Tetrachloroaluminate, $[Fc_2P]^+[AlCl_4]^-$ (7). Aluminum chloride (0.285 g, 2.14 mmol, $AlCl_3$ units) was added to a stirred solution of **4** (0.933 g, 2.14 mmol) in 10 mL of CH_2Cl_2 at −78 °C. As the reaction mixture was allowed to warm to 25 °C, the color changed from orange to a deep, blood red. The solvent was removed in vacuo, and the crude product was washed with *n*-hexane to remove unreacted **4**. Recrystallization from CH_2Cl_2–*n*-hexane afforded pure **7** as a dark red solid in 90% yield. Anal. Calcd for $C_{20}H_{18}AlCl_4Fe_2P$: C, 42.16; H, 3.18. Found: C, 41.43; H, 3.51. ^1H NMR (90.0 MHz, CD_2Cl_2): H_α (m, 2 H, δ 4.39), H_β (m, 2 H, δ 4.44), $H_{1'}$ (s, 5 H, 4.22). $^{31}P\{^1H\}$ NMR (32.384 MHz): δ 180.7 (s). $^{27}Al\{^1H\}$ NMR (52.131 MHz): δ 103 (s).

Preparation of Ferrocenyl(dimethylamino)phosphenium(1+) Tetrachloroaluminate, $[Fc(Me_2N)P]^+[AlCl_4]^-$ (8). A chilled (−78 °C) solution of $Fc(Me_2N)PCl$ (0.27 g, 0.91 mmol) in 2 mL of CH_2Cl_2 was treated with an equimolar quantity of Al_2Cl_6 as described in the preceding experiment. When it was warmed to 25 °C, the initially orange solution turned deep red. Prolonged cooling to −20 °C caused precipitation of **8** as a dark red solid, which was collected by filtration and dried in vacuo. Anal. Calcd for $C_{12}H_{15}AlCl_4FeNP$: C, 33.61; H, 3.53; N, 3.27. Found: C, 33.32; H, 3.86; N, 3.09. ^1H NMR (90 MHz): Me_2N (d, 6 H, δ 3.20, $J_{PNCH} = 10.0$ Hz), $H_{\alpha,\beta}$ (m, 4 H, δ 4.6–5.0), $H_{1'}$ (s, 5 H, δ 4.37). $^{31}P\{^1H\}$ NMR (32.384 MHz): δ 258.5

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(5) (a) Corriu, M. *Organomet. Chem. Rev.* **1966**, *1*, 435. (b) Hill, E. A.; Wiesner, R. *J. Am. Chem. Soc.* **1969**, *91*, 509. (c) Hill, E. A. *J. Organomet. Chem.* **1970**, *24*, 457. (d) Watts, W. E. *J. Organomet. Chem. Libr.* **1979**, *7*, 399.

(6) For a preliminary account of this work, see: Baxter, S. G.; Collins, R. L.; Cowley, A. H.; Sena, S. F. *J. Am. Chem. Soc.* **1981**, *103*, 715.

(7) Cowley, A. H.; Mehrotra, S. K. *J. Am. Chem. Soc.* **1983**, *105*, 2074.

(8) For a review of this chemistry, see: Dimroth, K. *Top. Curr. Chem.* **1973**, *38*, 1.

(9) The ^{31}P chemical shifts of the phosphamethinecyanines are ~+25 to +50 ppm and thus significantly outside the range anticipated for phosphenium ions[1] (>+200 ppm).

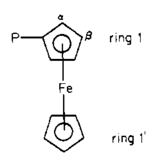
(10) Gamon, N.; Reichardt, C.: (a) *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 404. (b) *Liebigs Ann. Chem.* **1980**, 2072.

(11) Braye, E. H.; Hübel, W. *Inorg. Synth.* **1966**, *8*, 178.

(12) Stober, M. R.; Michael, K. W.; Speier, J. L. *J. Org. Chem.* **1967**, *32*, 2740.

(13) Sollott, G. P.; Peterson, W. R. *J. Organomet. Chem.* **1969**, *19*, 143.

(14) Labeling scheme for ring positions:



(s). $^{27}Al\{^1H\}$ NMR (52.131 MHz): δ 103 (s).

Preparation of Ferrocenylchlorophosphenium(1+) Tetrachloroaluminate, $[Fc(Cl)P]^+[AlCl_4]^-$ (9). A stirred solution of **5** (0.78 g, 2.7 mmol) in 5 mL of CH_2Cl_2 was treated with Al_2Cl_6 (0.38 g, 2.8 mmol) at −78 °C. When it was warmed to 25 °C, the reaction mixture turned dark brown. After filtration, the filtrate was treated with 2 mL of dry *n*-hexane and chilled (−20 °C) overnight. The dark brown solid that precipitated was collected by filtration and dried in vacuo, affording **9** in 85% yield. Anal. Calcd for $C_{10}H_9AlCl_5FeP$: C, 28.58; H, 2.16. Found: C, 28.36; H, 2.30. ^1H NMR: H_α (m, 2 H, δ 4.55), H_β (m, 2 H, δ 4.93), $H_{1'}$ (s, 5 H, δ 4.28. $^{31}P\{^1H\}$ NMR: (32.384 MHz): δ 239.5 (s). The same cation was formed when excess Al_2Cl_6 was employed, and no evidence for FcP^{2+} formation was obtained.

Reaction of $[Fc_2P]^+[AlCl_4]^-$ (7) with *n*-Bu_3P. A solution of 1.47 mmol of **8** (prepared in situ as described earlier) in 10 mL of CH_2Cl_2 was treated with an equimolar quantity of *n*-Bu_3P. The blood red color was immediately discharged, yielding a clear, orange solution. The formation of the adduct $[n\text{-}Bu_3PPFc_2]^+[AlCl_4]^-$ (**10**) was followed by $^{31}P\{^1H\}$ NMR (32.384 MHz): P_B (d, −35.3, $J_{P_AP_B}$ = 336 Hz), P_A (d, δ 20.3, $J_{P_AP_B}$ = 336 Hz). $^{27}Al\{^1H\}$ NMR (52.131 MHz): δ 103.2 (s).

Preparation of (Diferrocenylchlorophosphine)tetracarbonyliron, $(Fc_2PCl)Fe(CO)_4$ (11). The chlorophosphine **4** (4.36 g, 10.0 mmol) and $Fe_2(CO)_9$ (3.64 g, 10.0 mmol) were combined in *n*-hexane (100 mL) and heated at 50 °C with stirring for 2 h. The reaction mixture proceeded through an intermediate dark green color before finally turning blood red. After cooling to room temperature and filtering, the *n*-hexane and $Fe(CO)_5$ byproduct were removed in vacuo, leaving a red-orange solid. Recrystallization from *n*-hexane afforded pure **11** as a dark orange powder in 94% yield. Anal. Calcd for $C_{24}H_{18}ClFe_3O_4P$: C, 47.70; H, 3.00; Cl, 5.87. Found: C, 47.58; H, 3.08; Cl, 7.23. Mass spectrum (*m/e*, fragment): 604 (M^+), 492 (M^+ − CO), 457 (M^+ − CO − Cl), 436 (Fc_2PCl^+), 401 (Fc_2P^+), 336 ($Fc(Fe(C_5H_4))PCl^+$), 280 ($Fc(C_5H_4)PCl^+$), 216 ($FcPCl^+$), 186 (FcH^+), 121 ($C_5H_5Fe^+$), 65 ($C_5H_5^+$). ^{13}C NMR (50.313 MHz): C_{IPSO} (d, δ 85.3, J_{PC} = 51.5 Hz), C_α (d, 71.9, J_{PCC} = 12.6 Hz and d, δ 73.4, J_{PCC} = 17.6), C_β (d, δ 70.5, J_{PCCC} = 9.0 Hz and d, δ 71.0, J_{PCCC} = 9.9 Hz). $C_{1'}$ (s, δ 69.7), CO (d, δ 212.1, J_{PFeC} = 19.3 Hz. $^{31}P\{^1H\}$ NMR (32.384 MHz): δ 160.6 (s). IR: ν_{CO} = 2050, 1975, and 1940 cm^{-1}.

Preparation of (Diferrocenylphosphenium)tetracarbonyliron(1+) Tetrachloroaluminate, $[Fc_2PFe(CO)_4]^+[AlCl_4]^-$ (12). Freshly sublimed Al_2Cl_6 (0.22 g, 0.8 mmol) was added to a solution of **11** (0.99 g, 1.6 mmol) in 10 mL of CH_2Cl_2 at −78 °C. The reaction mixture was allowed to warm slowly to room temperature, during which time it assumed a dark, red-brown color. Filtration, followed by removal of solvent in vacuo from the filtrate, afforded **12** as a dark red solid. Since this compound decomposed at room temperature, it was not possible to obtain analytical data. Therefore, its identification is based on the following spectroscopic data. $^{31}P\{^1H\}$ NMR (32.384 MHz): δ 280 (s). The low-temperature solubility of **8** was not sufficient to obtain $^{13}C\{^1H\}$ NMR data. IR: ν_{CO} = 2095, 2060, and 2020 cm^{-1}. Mössbauer data for **12** are presented in the Results and Discussion section.

Preparation of Diferrocenylphosphine, Fc_2PH (13). The chlorophosphine **4** in 50 mL of Et_2O was added slowly to a slurry of $LiAlH_4$ (0.356 g, 9.38 mmol) in 50 mL of Et_2O at 0 °C via a transfer needle. After the reaction mixture was warmed to room temperature and stirred for 1 h, the unreacted $LiAlH_4$ was allowed to settle to the bottom of the flask. The supernatant orange solution was then quenched carefully by dropwise addition to another flask containing 100 mL of deoxygenated H_2O at 0 °C via a transfer needle. The organic layer was separated, washed with deoxygenated H_2O, and dried over Na_2SO_4. Removal of Et_2O in vacuo afforded pure **13** as a yellow-orange solid in 72% yield. Anal. Calcd for $C_{20}H_{19}Fe_2P$: C, 59.75; H, 4.76. Found: C, 59.63; H, 5.05. Mass spectrum (*m/e*, fragment): 402 (M^+), 336 ($(M{-}H - C_5H_5)^+$), 216 (FcP^+), 186, (FcH^+), 121 ($C_5H_5Fe^+$), 65 ($C_5H_5^+$). ^1H NMR (90.0 MHz) ($CDCl_3$): H_α (m, 2 H, δ 4.23), H_β (m, 2 H, δ 4.44), $H_{1'}$ (s, 5 H, δ 4.12). ^{31}P NMR (32.384 MHz): δ −79.3 (d, J_{PH} = 220.6 Hz).

Preparation of Diferrocenyllithiophosphide, Fe_2PLi (14). A 0.43-mL amount of a 1.6 M solution of *n*-BuLi was added to a stirred solution of **14** (0.275 g, 0.683 mmol) in 20 mL of Et_2O at 0 °C. As the last few drops of *n*-BuLi were added, the initially orange solution assumed a rosy red color. The mixture was allowed to warm to room temperature to expel the *n*-butane side product. ^{31}P NMR spectroscopy revealed the absence of any Fc_2PH (δ_P = −79.3) and the appearance of a new signal at −90.3 ppm, which was assigned to Fc_2PLi (**14**). This assignment was confirmed in the following experiment.

Preparation of Diferrocenyldeuteriophosphine, Fc_2PD (15). A solution of 0.87 mmol of Fc_2PLi in 4 mL of Et_2O (prepared in situ as described above) was treated with 0.02 g (1.0 mmol) of D_2O. The rosy red color was discharged immediately and replaced by an orange color. The exclusive presence of **15** was confirmed by NMR spectroscopy. ^{31}P NMR (32.384 MHz): δ −82.1 (t, J_{PD} = 33.3 Hz).

Preparation of Tetraferrocenyldiphosphine, Fc_2PPFc_2 (16). (a) From Fc_2PCl and K. The chlorophosphine **4** (0.44 g, 1.0 mmol) and freshly cleaned potassium metal (0.045 g, 1.1 mmol) were combined in 30 mL of THF, and the reaction mixture was refluxed with stirring for 6 h. During this time, the solution slowly assumed a dark orange color. The ^{31}P NMR spectrum of an aliquot withdrawn from this solution showed two signals—one corresponding to unreacted Fc_2PCl (δ_P = 82.5) and a new signal assignable to **16** at −31 ppm, with relative intensities of approximately 2:1, respectively. An additional 0.2 mmol of K metal was added to the reaction mixture, and reflux was continued for an additional 4 h. After this time, ^{31}P NMR showed the signal at −31 ppm for **16**, a small signal at −79 ppm corresponding to **13**, and a third unassigned signal at −50 ppm.

(b) From Fc_2PCl and Mg. The chlorophosphine **4** (0.592 g, 1.36 mmol) and magnesium turnings (0.0203 g, 0.835 mmol) were combined in 30 mL of THF and refluxed with stirring for 2 days, after which time most of the Mg appeared to have reacted and a red-orange solution was produced. After filtration a preliminary assay of the filtrate by ^{31}P NMR revealed the presence of only the desired diphosphine together with unreacted **4**. The solvent was removed in vacuo, and the resulting crude orange solid was subjected to prolonged Soxhlet extraction boiling *n*-heaxane. This was effective in removing unreacted **4** from the *n*-hexane-insoluble diphosphine, affording the latter as a powdery orange solid in 60% yield. Anal. Calcd for $C_{40}H_{36}Fe_4P_2$: C, 59.90; H, 4.52. Found: C, 59.62, H, 4.61. Mass spectrum (*m/e*, fragment): 802 (M^+), 617 ($(M - Fc)^+$, 401 (Fc_2P^+), 336 ($Fc(FeC_5H_4)P^+$), 280 ($Fc(C_5H_4)P^+$), 216 (FcP^+), 186 (FcH^+), 121 ($C_5H_5Fe^+$).

(c) From Fc_2PCl and Sodium Naphthalenide. A 1.15-mL amount of a 0.79 M solution of sodium naphthalenide[15] was aded via a syringe to a stirred slurry of **4** (0.396 g, 0.91 mmol) in 10 mL of THF at −78 °C. The dark green color of the sodium naphthalenide was discharged immediately. After the mixture was warmed to room temperature and stirred for ~2 h, ^{31}P NMR assay to the orange solution indicated that essentially quantitative conversion of **4** to **16** had taken place. After the solvent was removed in vacuo, the naphthalene side product was removed by prolonged sublimation (50 °C (0.005 torr)), affording pure **16** as a bright orange solid in excellent yield. The mass spectrum was identical with that obtained in the preceding experiment.

Reaction of Fc_2PPFc_2 with K in THF. Potassium metal (0.10 g, 2.6 mmol) and **16** (0.80 g, 1.0 mmol) were combined in 50 mL of dry THF and refluxed for 48 h. During this time, most of the potassium appeared to have reacted and the orange color of the solution darkened somewhat. ^{31}P NMR spectroscopy revealed the presence of a small amount of unreacted **16**, a small peak at −79 ppm (Fc_2PH), and a large unassigned peak at −50 ppm.

Results and Discussion

Synthesis of Ferrocenyl-Substituted Phosphenium Ions. As stated in the Introduction, the remarkable ability of the ferrocenyl substituent (Fc) to stabilize carbenium ions prompted our efforts to synthesize phosphenium ions featuring this moiety. Treatment of a CH_2Cl_2 solution of Fc_2PCl (**4**) with a stoichiometric quantity of Al_2Cl_6 followed by warming to room temperature resulted in a deep red solution from which a dark red solid was isolated. The ^{31}P NMR spectrum of the

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(15) The sodium naphthalenide–THF solution was prepared from 0.1 mol each of freshly cleaned Na metal and reagent grade naphthalene and 125 mL of dry, degassed THF under strictly oxygen- and moisture-free conditions. The concentration of sodium naphthalenide was determined by quenching an aliquot of the dark green solution with H_2O and titrating the resulting NaOH solution to the phenolphthalein end point with standardized HCl. See: Scott, N. D.; Walker, J. F.; Hansley, V. L. *J. Am. Chem. Soc.* **1936**, *58*, 2442. See also: Coates, G. E.; Green, M. L. H.; Wade, K. "Organometallic Compounds", 3rd ed.; Methuen: London, 1967; Vol. 1, pp 3, 50, 59–66.

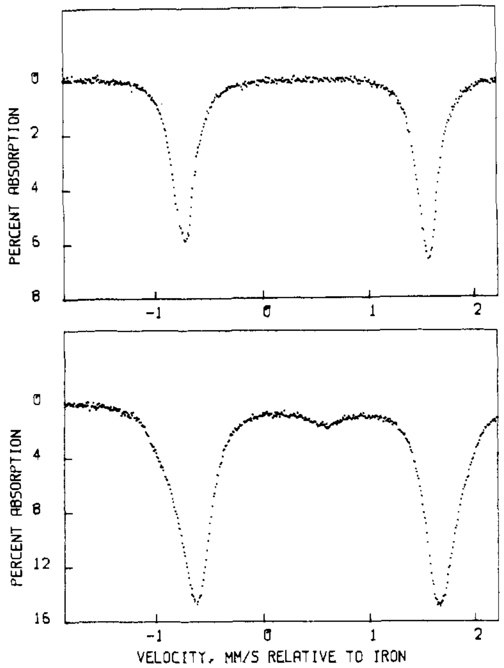
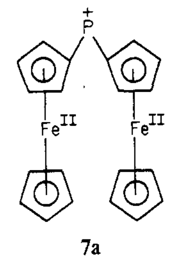
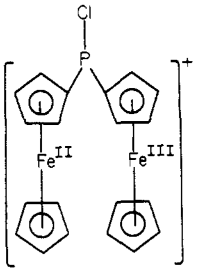


Figure 1. ^{57}Fe Mössbauer spectra for Fc_2PCl (4) (top) and $[Fc_2P]^+[AlCl_4]^-$ (7) (bottom).

red solution exhibited a singlet at +186.00 ppm compared to +84.8 ppm for the starting chlorophosphine **4**, indicating the development of positive charge at phosphorus. The presence of the $AlCl_4^-$ anion as the sole aluminum-containing species was evidenced by a sharp singlet (δ 102.2, w_h = 6 Hz) in the $^{27}Al\{^1H\}$ spectrum.[16] In addition, the ^1H NMR spectrum revealed a downfield shift (Experimental Section) for the ferrocenyl protons relative to those of **4**. Comparable shifts have also been observed in the ^1H NMR spectra of ferrocenyl carbocations[5d] and are indicative of the delocalization of positive charge from the cationic center onto the ferrocenyl substituents. The NMR and analytical data supported the formulation of the $Fc_2PCl-Al_2Cl_6$ reaction product as the ferrocenyl-substituted phosphenium ion **7a**. The Mössbauer spectra of Fc_2PCl and its reaction product with $AlCl_3$ were recorded and appear in Figure 1. For both Fc_2PCl (300 K; IS = 0.435 mm/s, QS = 2.296 mm/s) and its reaction product with Al_2Cl_6 (60 K; IS = 0.525 mm/s, QS = 2.328 mm/s) the Mössbauer parameters are typical of ferrocenyl compounds,[17] thus confirming the reaction of Fc_2PCl and Al_2Cl_6 proceeds via chloride abstraction to yield the phosphenium ion **7a** rather than the mixed-valence species 7b.[18]



7a



7b

Now that it was established that two ferrocenyl groups are capable of stabilizing a phosphenium ion, the next goal was to attempt the stabilization of such cations with only one Fc group. The requisite precursor chlorophosphine, $Fc(Me_2N)PCl$ (**6**), was prepared by the reaction of **4** with Me_3SiNMe_2. The reaction of **6** with Al_2Cl_6 in CH_2Cl_2 solution results in the amido-substituted phosphenium salt $[Fc(Me_2N)P]^+[AlCl_4]^-$ (**8**), which was characterized by elemental analysis and NMR spectroscopy. As expected, there is a pronounced downfield shift in the ^{31}P NMR in proceeding from the precursor chloride **6** (144.9 ppm) to the cation **8** (+258.5 ppm) and a sharp singlet for $AlCl_4^-$ ($w_h \approx$ 13 Hz) was detected by $^{27}Al\{^1H\}$ NMR spectroscopy. Treatment of $FcPCl_2$ with a stoichiometric quantity of Al_2Cl_6 in CH_2Cl_2 solution resulted in the formation of the chloro-substituted phosphenium ion $[Fc(Cl)P]^+[AlCl_4]^-$ (**9**). When excess quantities of Al_2Cl_6 were employed, no evidence for $[FcP]^{2+}$ formation was obtained.

The diferrocenyl cation **7** exhibits the highest field (least deshielded) ^{31}P chemical shift (+183.7 ppm) of any phosphenium ion reported so far.[1] Replacement of one Fc group of **7** by an Me_2N group leads to considerable deshielding and brings the ^{31}P chemical shift of $[Fc(Me_2N)P]^+$ (258.5 ppm) close to that of $[(Me_2N)_2P]^+$ (+264 ppm).[1d] This observation suggests that the ferrocenyl substituent is more effective than an amido group at dispersing positive charge. Several models have been proposed to explain the charge delocalization in ferrocenyl-substituted carbocations.[19] It is not clear which mechanism predominates in the case of phosphenium ions.

Reactivity of the Diferrocenylphosphenium Cation. The amphoteric nature of phosphenium ions was recognized first by Parry and co-workers. It was found that these species can behave as Lewis acids toward tertiary phosphines[1c] and as Lewis bases toward metal carbonyls.[20] The Lewis acid behavior of **7** was demonstrated in its reaction with n-Bu_3P, in which formation of the acid-base adduct $[n\text{-}Bu_3PPFc_2]^+[AlCl_4]^-$ (**10**) was followed by $^{31}P\{^1H\}$ NMR spectroscopy. The spectrum consisted of a second-order AB pattern similar to the one reported by Parry et al.[1c] for the related diphosphorus cation $(Me_2N)_3P-P^+(NMe_2)_2$. The doublet at +20.3 ppm was assigned to the ferrocenyl-substituted phosphorus and the upfield doublet at −35.3 ppm to the n-Bu_3P moiety. Interestingly, *both* phosphorus nuclei of **10** are more shielded than those of the individual components, Fc_2P^+ (183.7 ppm) and n-Bu_3P (−31.6 ppm). This was also the case for $(Me_2P)_3P-P^+(NMe_2)_2$ and was attributed by Parry et al.[1c] to the increase in coordination number of both phosphorus centers upon formation of the P–P bond. The $^1J_{PP}$ value of ~336 Hz

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(16) Akitt, J. W. *Annu. Rep. NMR Spectrosc.* **1972**, *5*, 465.

(17) (a) Wertheim, G. K.; Herber, R. H. *J. Chem. Phys.* **1963**, *38*, 2106. (b) Collins, R. L. *Ibid.* **1965**, *42*, 1072. (c) Fluck, E.; Hausser, F. *Z. Anorg. Allg. Chem.* **1973**, *396*, 257. (d) Kramer, J. A.; Herbstein, F. H.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1980**, *102*, 2293.

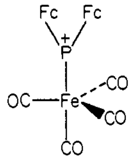
(18) For a discussion of mixed-valence bridged ferrocenes, see e.g.: (a) Cowan, D. O.; LeVanda, C.; Park, J.; Kaufman, F. *Acc. Chem. Res.* **1973**, *6*, 1. (b) Morrison, W. H., Jr.; Hendrickson, D. N. *Inorg. Chem.* **1975**, *14*, 2331.

(19) At least three models have been proposed to explain the special stability of α-ferrocenylcarbenium ions: (i) interaction of the central metal with a "fulvene" π system with concomitant shift of the metal toward the exocyclic carbon, (ii) conjugation between the 2p orbital of the exocyclic carbon with the π system of the substituted ring, and (iii) distortion and bending of bonds in the substituted ring, thus bringing the exocyclic carbon closer to the metal atom. See ref 5a and: (a) Hill, E. A.; Richards, J. H. *J. Am. Chem. Soc.* **1961**, *83*, 3480. (b) Cais, M.; Dannenburg, J. J.; Eisenstadt, A.; Levenburg, M. I.; Richards, J. H. *Tetrahedron Lett.* **1966**, 1695. (c) Traylor, T. G.; Ware, J. C. *J. Am. Chem. Soc.* **1967**, *89*, 2304. (d) Traylor, T. G.; Hanstein, W.; Berwin, H. J.; Clinton, N. A.; Brown, R. S. *Ibid.* **1971**, *93*, 5715. (e) Fitzpatrick, J. D.; Watts, L.; Pettit, R. *Tetrahedron Lett.* **1966**, 1299. (f) Davis, R. E.; Simpson, H. D.; Grice, N.; Pettit, R. *J. Am. Chem. Soc.* **1971**, *93*, 6688.

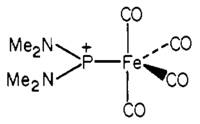
(20) (a) Montemayer, R. C.; Sauer, D. T.; Fleming, S.; Bennett, D. W.; Thomas, M. G.; Parry, R. W. *J. Am. Chem. Soc.* **1978**, *100*, 2231. For examples of coordinated phosphenium ions, see: (b) Light, R. W.; Paine, R. T. *Ibid.* **1978**, *100*, 2230. (c) Cowley, A. H.; Kemp, R. A.; Wilburn, J. C. *Inorg. Chem.* **1981**, *20*, 4289. Paine et al. have prepared numerous interesting neutral compounds by treatment of phosphenium ions with organometallic anions, some of which have an accumulation of positive charge at phosphorus. For a summary of this work, see: Hutchins, L. D.; Duesler, E. N.; Paine, R. T. *Organometallics* **1982**, *1*, 1254 and references therein.

is also similar to that reported by Parry et al.[1c] for their $(Me_2N)_3P$ adduct (340 Hz).

Now that the Lewis acid behavior of **7** was established, the next goal was to investigate its Lewis basicity toward a metal carbonyl by preparing $[Fc_2PFe(CO)_4]^+$. The requisite precursor complex $(Fc_2PCl)Fe(CO)_4$ (**11**) was prepared by the reaction of **4** with $Fe_2(CO)_9$ and characterized by elemental analysis and mass, IR, and NMR spectroscopy (Experimental Section). Treatment of **11** with a stoichiometric quantity of Al_2Cl_6 in CH_2Cl_2 produced a red-brown solution. The ^{31}P NMR spectrum of this solution consisted of a singlet at +280 ppm, which falls in the region observed for other (phosphenium)$Fe(CO)_4$ complexes[20] and represents an appreciable downfield shift from the starting material. Additional evidence for the formation of the phosphenium ion complex $[Fc_2PFe(CO)_4]^+[AlCl_4]^-$ (**12**) came from infrared spectroscopy, which revealed that the CO stretching frequencies of **12** (ν_{CO} = 2095, 2060, and 2020 cm^{-1}) are higher than those of **11** (ν_{CO} = 2050, 1975, and 1940 cm^{-1}). Such shifts have been observed for other (phosphenium)$Fe(CO)_4$ compounds[20] and can be ascribed to the reduction in Fe→CO back-bonding due to the presence of a positively charged ligand. The ^{57}Fe Mössbauer spectrum of **11** consisted of two doublets, with an area ratio, as revealed by quantitative analysis,[21] of 1.8:1. The more intense doublet has IS and QS values typical of ferrocenyl compounds[17] (60 K; IS = 0.534 mm/s, QS = 2.323 mm/s) and the less intense doublet has Mössbauer parameters (60 K; IS = −0.103 mm/s, QS = 2.474 mm/s) similar to those which have been reported for other $Fe(CO)_4$ compounds.[22] The reaction product of **11** and Al_2Cl_6 exhibited a Mössbauer spectrum very similar to that of **11** (60 K; IS = 0.524 (Fc), −0.103 ($Fe(CO)_4$) mm/s; QS = 2.259 (Fc), 2.322 ($Fe(CO)_4$) mm/s), and as in the case of Fc_2P^+, these data are consistent only with the presence of a phosphenium ion, viz., $[Fc_2PFe(CO)_4]^+[AlCl_4]^-$ (**12**). Sosinsky et al.[22] have recently drawn attention to the dichotomy in Mössbauer parameters for $Fe(CO)_4$ compounds. These authors have suggested that the QS/IS trends on whether the site of substitution about trigonal-bipyramidal Fe is axial or equatorial. If the criteria of Sosinsky et al.[22] is used, **12** is predicted to be an axially substituted phosphenium ion, while $[(Me_2N)_2PFe(CO)_4]^+[AlCl_4]^-$ (60 K, IS = −0.031 mm/s, QS = 1.896 mm/s)[6] is predicted to be equatorially substituted. Presumably in **12** σ-donation dominates, while in $[(Me_2N)_2PFe(CO)_4]^+$ σ-donation diminishes and π-acceptance assumes a role of major importance.



12



As mentioned in the Introduction, phosphenium cations, phosphinyl radicals, and phosphide anions are interrelated by one-electron oxidation–reduction steps. We were thus prompted to attempt the synthesis of $[Fc_2P]^-$ and $[Fc_2P]\cdot$.

The new secondary phosphine Fc_2PH (**13**) was prepared by the reaction of **4** with $LiAlH_4$ in Et_2O and characterized by elemental analysis and mass, IR, and NMR spectroscopy. The ^1H NMR data were indicative of a monosubstituted ferrocene, and the ^{31}P chemical shift and ^{31}P–^1H coupling are consistent with a P^{III}–H moiety.[23] Like most secondary arylphosphines, **13** is hydrolytically stable but moderately oxygen sensitive. Treatment of **13** with equiv of n-BuLi in Et_2O or THF solution at low temperature produced a red-orange solution. The $^{31}P\{^1H\}$ NMR spectrum of this solution revealed the absence of **13** and a new singlet resonance at −90.3 ppm, representing an upfield shift of 11 ppm relative to the starting compound. The formation of the lithiophosphide Fc_2PLi (**14**) was confirmed by quenching a solution of **14** with a stoichiometric quantity of D_2O. Quantitative conversion to Fc_2PD (**15**) was indicated by the ^{31}P NMR spectrum, which exhibited a 1:1:1 triplet with J_{PD} = 33.3 Hz, which is characteristic for the P^{III}–D bond.[23] The observation of only a small change of ^{31}P chemical shift accompanying the transformation $Fc_2PH \rightarrow [Fc_2P]^-$ is not unexpected. In fact, previous studies[24,25] have shown that the ^{31}P chemical shifts of RR′PLi species can be upfield or downfield of the precursor secondary phospines. Other studies[26] have revealed significant covalent metal–phosphorus interactions in alkali-metal phosphides.

Our initial approach to the phosphinyl radical $[Fc_2P]\cdot$ involved treatment of Fc_2PCl with an active metal (e.g. potassium or magnesium) or with a strong reducing agent such as sodium naphthalenide. However, each of these reactions resulted in the new diphosphine Fc_2PPFc_2 (**16**). Attempts to generate $[Fc_2P]\cdot$ by treatment of **16** with K in THF were not successful.

Acknowledgment. Generous financial support from the National Science Foundation (Grant CHE 8205871) and the Robert A. Welch Foundation is gratefully acknowledged.

Registry No. **4**, 1292-40-6; **5**, 1291-31-2; **6**, 87371-44-6; **7**, 76370-54-2; **8**, 87371-46-8; **9**, 87371-48-0; **10**, 87371-50-4; **11**, 76370-55-3; **12**, 76468-82-1; **13**, 39385-09-6; **14**, 87393-23-5; **15**, 87371-51-5; **16**, 87393-24-6; $AlCl_3$, 7446-70-0; $Fe_2(CO)_9$, 15321-51-4; Me_2NSiMe_3, 18135-05-2.

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(21) (a) The quantitative analysis determination entailed the collection of Mössbauer data at several temperatures between 15 and 150 K. The data analysis procedure has been described elsewhere: Collins, R. L. *J. Phys. Colloq.* (*Orsay, Fr.*) **1979**, *No. 3*, C2-36. (b) Collins, R. L.; Eakin, T.; Clemlow, J., paper presented at the 176th National Meeting of the American Chemical Society, Houston, TX, March 23–28, 1980.

(22) Sosinsky, B. A.; Norem, N.; Shong, R. G. *Inorg. Chem.* **1982**, *21*, 4229.

(23) Emsley, J.; Hall, D. "The Chemistry of Phosphorus"; *Wiley*: New York, 1976; Chapter 3.

(24) See, for example: Grim, S. O.; Molenda, R. P. *Phosphorus Relat. Group V Elem.* **1974**, *4*, 189.

(25) There is an upfield shift of 14.2 ppm upon dilithiation of $FcPH_2$ ($FcPH_2$, δ(P) = −147.6, J_{PH} = 220.6 Hz; $FcPLi_2$, δ(P) = −161.8 ppm): Sena, S. Ph.D. Dissertation, The University of Texas at Austin, Dec 1982.

(26) (a) Fluck, E.; Issleib, K. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1965**, *20B*, 1123. (b) Colquhoun, I. J.; McFarlane, H. C. E.; McFarlane, W. *J. Chem. Soc., Chem. Commun.* **1982**, 220.