A subsidiary observation is that hydroxide ion (as 25% tetraethylammonium hydroxide in methanol) reacts rapidly with CCl_4 and $CHCl_3$ in aprotic solvents. For example, the reaction with CCl_4 is so rapid in Me_2SO that it can be titrated with a stoichiometry of 4 mol of OH^- per mol of CCl_4. The ultimate product presumably is CO_2, which probably cannot be further titrated to CO_3^{2-} in Me_2SO.

In the presence of a fourfold excess of OH^-, the rate of disappearance of $O_2^-\cdot$ by reaction with CCl_4 is measurably reduced. Analysis of the kinetics for such experiments indicates that the assumed second-order rate constant for the $OH^- + CCl_4$ reaction is 0.7 ± 0.3 of that for the $O_2^-\cdot + CCl_4$ reaction.

For the solution conditions of Table I, thiocyanate ion (SCN^-) does not react to a significant extent with CCl_4 in Me_2SO (second-order rate constant $<10^{-2}\ M^{-1}\ s^{-1}$). Hence, $O_2^-\cdot$ and OH^- appear to be unique, exceptionally strong nucleophiles with respect to their reactivity toward alkyl halides in aprotic media.

Although strong bases are known to eliminate HCl from $CHCl_3$ and *p,p'*-DDT via an S_N1cB mechanism to give dichlorocarbene and $(p\text{-}ClC_6H_4)_2C{=}CCl_2$,[16] there is not any evidence that such processes are competitive with the displacement reactions of Table I. However, the stoichiometry for the reaction of *p,p'*-DDT indicates that only two of the three alkylchloro atoms are removed. Hence, subsequent to the first step, there may be a dehydrohalogenation to give a chloro-substituted alkene. Such a product may have limited reactivity with $O_2^-\cdot$; for example, 1,1,2-trichloroethene (trichloroethylene) reacts extremely slowly.

That the rate constants for CCl_4 and $CHCl_3$ are much larger than that for CH_3Cl is surprising and in conflict with their extreme steric inhibition of an S_N2 process. Although a direct electron transfer is an attractive alternative mechanism (reaction 1), the

$$CCl_4 + O_2^-\cdot \rightarrow CCl_4^- + O_2 \qquad (1)$$

redox potentials for CCl_4 ($E^{\circ\prime}$, -1.3 V vs. SCE) and O_2 ($E^{\circ\prime}$, -0.9 V vs. SCE) in DMF do not favor a rapid and complete reaction. However, formation of an adduct, $CCl_4(O_2^-\cdot)$, as a transition state prior to concerted intramolecular electron transfer, displacement of Cl^-, and formation of $CCl_3O_2\cdot$ would facilitate a rapid reaction and overcome the thermodynamic inhibition of reaction 1. Hence, reasonable and self-consistent initial reactions for the $O_2^-\cdot$–CCl_4 system in DMF are

$$CCl_4 + O_2^-\cdot \rightarrow [CCl_4(O_2^-\cdot)]_{tr} \rightarrow CCl_3O_2\cdot + Cl^- \qquad (2)$$

$$CCl_3O_2\cdot + O_2^-\cdot \rightarrow CCl_3O_2^- + O_2 \qquad (3)$$

These are followed by additional rapid displacement and reduction steps to give the overall reaction of Table I. Analogous mechanistic pathways are proposed for the other substrates. There is not any evidence that the C–H bond of $CHCl_3$ is broken or that aromatic chlorides (*p,p'*-DDT) are displaced within the time frame of our experiments (less than 1 h).

The exceptional reactivity of $O_2^-\cdot$ with polychloro hydrocarbons in aprotic solvents provides a convenient means to their degradation and detoxification. For example, a controlled-potential electrolysis cell with an air-saturated Me_2SO–tetraalkylammonium chloride electrolyte could be used to generate $O_2^-\cdot$, which would convert CCl_4 wastes (added to the cell) to CO_3^{2-} and Me_2SO_2.

Slater[17] has suggested that the hepatotoxicity of CCl_4 is due to a CCl_4-stimulated peroxidation of unsaturated fatty acids via the $Cl_3CO_2\cdot$ radical. Because this species is believed to be the primary product for the reaction of $O_2^-\cdot$ with CCl_4 in aprotic media (eq 2), similar chemistry may occur with in vivo generated $O_2^-\cdot$ and represent the mechanism of CCl_4 toxicity.

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[15] During the course of the kinetic measurements 10–20% of the $O_2^-\cdot$ decomposed. Presumably, this was due to residual water and impurities in the aprotic solvents (Burdick and Jackson "Distilled in Glass" grade). Water would produce OH^- and HO_2^- via the net reaction

$$2O_2^-\cdot + H_2O \rightarrow O_2 + HO_2^- + OH^-$$

However, these nucleophiles (OH^- and HO_2^-), at most, would be present at a tenfold lower concentration than $O_2^-\cdot$. Their contribution to the total reaction rate with CCl_4 would be less than 5% (less than the experimental error of the measurements).

[16] March, J. "Advanced Organic Chemistry", 2nd ed.; McGraw-Hill: New York, 1977; pp 342–343.

[17] Slater, T. F. *Ciba Found. Symp.* 1979, *65*, 143–163.

Ferrocenyl-Stabilized Two-Coordinate Phosphorus Cations: Synthesis, Coordination Chemistry, and Mössbauer Spectroscopy

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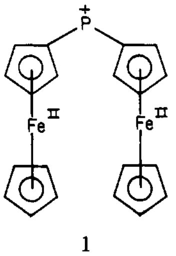
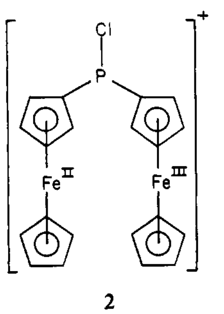
Halide abstraction from bis(dialkylamino)halophosphines with Lewis acids to form two-coordinate phosphorus cations (phosphenium ions) is well established,[1,2] but there are no unequivocal examples of phosphenium ions featuring two P–C bonds.[3] Since the remarkable ability of the ferrocenyl moiety (Fc) to stabilize carbenium ions is well documented,[6] it seemed appropriate to attempt the stabilization of phosphenium ions by using this substituent. The purpose of the present communication is to report the synthesis of $(Fc)_2P^+$ (**1**), the first example of a low-coordinate noncarbon main group cation stabilized by ferrocenyl groups. We also report initial results on the coordination chemistry of **1**.



1



2

Treatment of Fc_2PCl[7] with a stoichiometric quantity of Al_2Cl_6 in CH_2Cl_2 at -78 °C, followed by warming to room temperature, resulted in a deep red solution. The ^{31}P NMR spectrum of this

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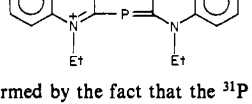
[1] (a) Maryanoff, B. E.; Hutchins, R. O. *J. Org. Chem.* 1972, *37*, 3475–3480. (b) Fleming, S.; Lupton, M. K.; Jekot, K. *Inorg. Chem.* 1972, *11*, 2534–2540. (c) Thomas, M. G.; Schultz, C. W.; Parry, R. W. *Ibid.* 1977, *16*, 994–1001.

[2] For a recent review, see: Cowley, A. H.; Cushner, M. C.; Lattman, M.; McKee, M. L.; Szobota, J. S.; Wilburn, J. C. *Pure Appl. Chem.* 1980, *52*, 789–797.

[3] On treatment with acid, the phosphamethinecyanines are protonated at the phosphorus center;[4] thus the predominant resonance form must be, e.g.,



This viewpoint is confirmed by the fact that the ^{31}P NMR chemical shifts (~25–50 ppm) fall well outside the range observed for phosphenium ions.[2] Interestingly, even though Gamon and Reichardt[5] regard their phosphatrimethinecyanine as a predominantly P=C bonded species, in fact, the ^{31}P chemical shift (+355.8 ppm) is indicative of the presence of appreciable positive charge on phosphorus.

[4] Dimroth, K.; Hoffmann, P. *Chem. Ber.* 1966, *99*, 1325–1331.

[5] Gamon, N.; Reichardt, C. *Angew. Chem., Int. Ed. Engl.* 1977, *16*, 404–405.

[6] (a) Cais, M. *Organomet. Chem. Rev.* 1966, *1*, 435–454. (b) Watts, W. E. *J. Organomet. Chem. Libr.* 1979, *7*, 399. (c) Hill, E. A.; Wiesner, R. *J. Am. Chem. Soc.* 1969, *91*, 509–510.

[7] Sollott, G. P.; Peterson, W. R. *J. Organomet. Chem.* 1969, *19*, 143–159.

Table I. ^{57}Fe Mössbauer Data for Ferrocenyl Phosphorus Compounds

compound	temp, K	isomer shift[a,b]	quadrupole splitting[a]
ferrocene[c]	300	0.454	2.396
Fc_2PCl	300	0.435	2.296
$[Fc_2P]^+[AlCl_4]^-$	60	0.525	2.328
$(Fc_2PCl)Fe(CO)_4$	60	0.534 (Fc) −0.103 $[Fe(CO)_4]$	2.323 (Fc) 2.474 $[Fe(CO)_4]$
$[(Fc_2P)Fe(CO)_4]^+[AlCl_4]^-$	60	0.524 (Fc) −0.103 $[Fe(CO)_4]$	2.259 (Fc) 2.322 $[Fe(CO)_4]$
$[(Me_2N)_2PFe(CO)_4]^+[AlCl_4]^-$	60	−0.031 $[Fe(CO)_4]$	1.896 $[Fe(CO)_4]$

[a] In mm/s. [b] Relative to metallic Fe. [c] Data derived from ref 14.

solution consisted of a singlet at +183 ppm compared to +82 ppm for Fc_2PCl, thus indicating the development of positive charge at phosphorus. The presence of the $AlCl_4^-$ anion was indicated by a sharp singlet ($W_h \sim 6$ Hz, δ 102.2) in the ^{27}Al NMR spectrum.[8]

Elegant work by Bock and co-workers[9] has shown that Al_2Cl_6 in CH_2Cl_2 can function as an oxidizing agent toward substrates possessing valence electrons less tightly bound than ~7.9 eV. Since the first ionization potential of ferrocene is ~6.9 eV[10] and it is known to react with Al_2Cl_6 in CH_2Cl_2,[11,12] the possibility of oxidation of Fc_2PCl to a mixed-valence[13] bridged ferrocene (**2**) was considered. Since ^{57}Fe Mössbauer spectroscopy can differentiate between ferrocenyl and ferricenyl moieties,[14,15] we have employed this technique for distinguishing between the chloride ion abstraction and one-electron oxidation reaction modes. Ferrocene and ferrocenyl groups are manifested spectroscopically by a well-resolved doublet with a quadrupole splitting of 2-2.5 mm/s, while ferricenyl groups are evidenced by a small or vanishing quadrupole splitting. If the rate of electron transfer between a ferrocenyl and a ferricenyl group in a mixed-valence bridged ferrocene (such as **2**) exceeds the inherent ^{57}Fe Mössbauer time scale, an averaged doublet will be observed. The Mössbauer spectra of Fc_2PCl and the product of its reaction with Al_2Cl_6 (Table I) are both typical of ferrocenyl compounds; hence it is clear that the phosphenium ion, **1**, is produced and not the ferricenyl substituted species, **2**.

Treatment of $(Fc_2PCl)Fe(CO)_4$ (**3**)[16] with a stoichiometric quantity of Al_2Cl_6 in CH_2Cl_2 at 0 °C produced a red-brown solution. The ^{31}P NMR spectrum of this solution consists of a singlet at +280 ppm, which falls in the region observed for other (phosphenium)$Fe(CO)_4$ complexes,[17] and represents an appreciable downfield shift from the starting material (+161 ppm). The ^{57}Fe Mössbauer spectrum of **3** (Table I) consists of two doublets, with an intensity ratio, as revealed by quantitative analysis,[18] of 1.8:1. The more intense doublet has isomer shift (IS) and quadrupole splitting (QS) values typical of those of ferrocenyl compounds,[14,15] and the less intense signal has Mössbauer parameters similar to those which have been reported for other $Fe(CO)_4$ complexes.[19] The reaction product of **3** and Al_2Cl_6 exhibited a ^{57}Fe Mössbauer spectrum similar to that of **3**, and, as in the case of **1**, these data are consistent only with the presence of a phosphenium ion, viz., $[(Fc_2P)Fe(CO)_4]^+[AlCl_4]^-$ (**4**).

Collins and Pettit[19] have demonstrated that for the ^{57}Fe Mössbauer spectra of $LFe(CO)_4$ complexes, a graph of IS vs. QS is linear and may be employed to estimate the relative σ-donor or π-acceptor capabilities of the ligand, L. This approach may be used to compare the bonding in **4** with that in other (phosphenium)$Fe(CO)_4$ tetracarbonyl complexes, and for this purpose, we have obtained the Mössbauer spectrum of the well-established complex, $(Me_2N)_2P^+Fe(CO)_4$.[17b] We find that the IS and QS values for the amino compound fall in the π-acceptor region of the Collins–Pettit graph. The conclusion that $(Me_2N)_2P^+$ is a good π acceptor is in excellent accord both with vibrational spectroscopic data[17] and with observations made by Bennett and Parry[20] concerning the facility of exchange of free CO with $(R_2N)_2P^+Fe(CO)_4$. This is not the case with **4**, which falls on the graph in the tertiary phosphine region, thus indicating that **1** is a poor π acceptor in comparison with $(Me_2N)_2P^+$. Thus, the position of **4** on the Collins–Pettit graph would seem to imply that ferrocenyl substitution disperses the positive charge from the phosphorus more effectively than dimethylamino substitution. This view is supported by the ^{31}P chemical shifts of **1** and **4**, which are upfield from their dimethylamino counterparts (264[1c] and 311 ppm,[17] respectively).

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(12) Under anhydrous conditions treatment of ferrocene with Al_2Cl_6 in CH_2Cl_2 gives a dark green solution, and the ^{57}Fe Mössbauer spectrum (60 K) indicated ferricenium formation (broad singlet which can be computer resolved into a doublet with IS = 0.474 and QS = 0.235 mm/s).

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Thermal Rearrangement of 1,1-Difluorospiropentane

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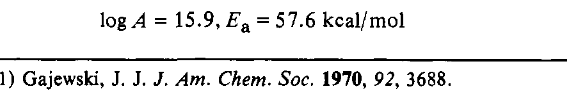
The thermal unimolecular rearrangement of spiropentane to methylenecyclobutane is an interesting and complex reaction, the mechanism of which has been investigated in detail.

Initial cleavage of the peripheral C_1–C_2 bond, rather than the C_1–C_3 bond, was demonstrated by Gajewski,[1] while reversibility of this step was detected by Gilbert.[2] Activation parameters for



log A = 15.9, E_a = 57.6 kcal/mol

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