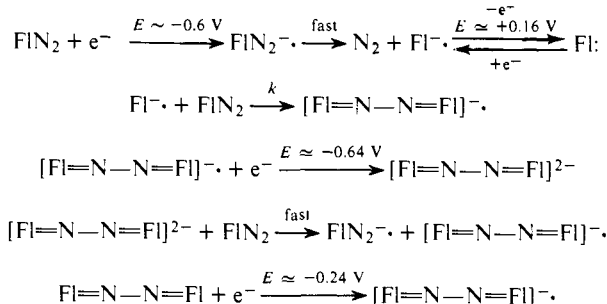


V. Since the results of separate single- and double-potential-step chronoamperometric experiments require that the reduction of  $\text{FIN}_2$  to product be an overall one-electron process and that all intermediates and products be reoxidized reversibly in a one-electron step per molecule of  $\text{FIN}_2$  reduced,<sup>9</sup> we conclude that the electroactive species of the couple is in the product-forming reaction channel.

The 9-fluorenyl anion ( $\text{FIH}^-$ ) was at first considered to be this intermediate since it could be formed by  $\text{FI}^-$  abstracting a hydrogen atom from a component of the solvent-electrolyte system.<sup>11,13</sup> However,  $\text{FIH}^-$  was rejected as being the electroactive intermediate when its oxidation was determined to occur slightly more readily ( $E_{p,a} = 0.08$  V) than that of the species in Figure 1 ( $E_{p,a} = 0.16$  V) and to be irreversible at all scan rates up to 100 V/s.<sup>14</sup>

In view of these considerations and our expectation that  $\text{FI}^-$  should be oxidized at a similar potential to that of  $\text{FIH}^-$ , we tentatively assign this redox couple to that of the carbene, fluorenylidene, and its anion radical,  $\text{FI}^-/\text{FI}^\cdot$  (Scheme I). If the assignment of this redox couple is correct, this requires a significantly longer lifetime of the carbene  $\text{FI}^-$  compared with that of the 9-fluorenyl radical ( $\text{FIH}^\cdot$ ) under these reaction conditions since the  $\text{FIH}^-/\text{FIH}^\cdot$  couple was not shown to be reversible in this solvent-electrolyte system.

#### Scheme I



Two features of these results should be stressed. The first, of course, is the possibility that we now have a method for measuring carbene/carbene anion radical redox potentials. Such data are important for understanding the structures and chemistry of these classes of reactive intermediates. The second feature is the increased production of the corresponding azine and concomitant decrease in the amount of hydrocarbon products from  $\text{FI}^-$  compared with  $\text{Ph}_2\text{C}^-$ .<sup>1a</sup> We believe that this may be related to the structures and, therefore, the relative reactivities of the two carbene anion radicals. Efforts are presently underway to elaborate further on these and other features in a number of hypovalent radical systems both in solution and in the gas phase.

**Acknowledgments.** This research was supported by the National Science Foundation (MPS-7502795 and CHE-7601410). The assistance of Dr. R. L. Krieger, K.-W. Lin, and F. Treibe is gratefully acknowledged.

#### References and Notes

- (1) (a) R. N. McDonald, J. R. January, K. J. Borhani, and M. D. Hawley, *J. Am. Chem. Soc.*, **99**, 1268 (1977). (b) A minor product of electroreduction of  $\text{Ph}_2\text{CN}_2$ , benzophenone, was mistakenly identified as diphenylmethylamine.<sup>1a</sup>
- (2) (a) P. F. Zittel, G. B. Ellison, S. V. O'Neil, E. Herbst, W. C. Lineberger, and W. R. Reinhardt, *J. Am. Chem. Soc.*, **98**, 3732 (1976). (b) R. B. Davidson and M. L. Hudak, *ibid.*, **99**, 3918 (1977);  $\theta_{\text{HCH}} = 99^\circ$ ,  $r_{\text{CH}} = 1.145$  Å.
- (3) This work:  $\theta_{\text{HCH}} = 99.9^\circ$ ,  $r_{\text{CH}} = 1.144$  Å,  $\Delta H_f = 100.6$  kcal/mol.
- (4) (a) We wish to thank Professor S. D. Worley, Auburn University, for making this program written for an IBM-370 computer available to us, and Professor Keith Purcell for his efforts to get it running on our machine. (b) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1285, 1294, 1302, 1307 (1975).
- (5) MINDO/3 calculations of the electronic ground state of the ( $^2A_1$ ) cation radical  $\text{H}_2\text{C}^+$  give  $\theta_{\text{HCH}} = 138.7^\circ$  and  $r_{\text{CH}} = 1.093$  Å (see also W. A. Lathan, W. J. Hehre, L. A. Curtiss, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 6377 (1971)). Structurally  $\text{H}_2\text{C}^-$  is that of singlet ( $^1A_1$ ) methylene with an electron added to the out-of-plane p orbital while  $\text{H}_2\text{C}^+$  is triplet ( $^3B_1$ ) methylene with the electron ionized from that p orbital.
- (6) R. Gleiter and R. Hoffmann, *J. Am. Chem. Soc.*, **90**, 5457 (1968), using EHT calculations reported that the  $p_y$  (in-plane) orbital of cyclopentadienylidene is "0.13 eV below the delocalized  $p_x$ " orbital.
- (7) O. W. Webster, *J. Am. Chem. Soc.*, **88**, 4055 (1966), considered the structure of the tetracyanocyclopentadienylidene anion radical to be a  $\pi$ -anion  $\sigma$  radical.
- (8) The yield of  $(\text{FI}=\text{N})_2$  was not affected by the addition of either 1% water or 90% tetrahydrofuran to solutions of a  $\text{FIN}_2$  in DMF. Typical  $n$  values were 0.25–0.50.
- (9) The sequence of reactions described by Scheme I (vide infra) was digitally simulated for the single- and double-potential-step chronoamperometric methods by procedures developed by Feldberg.<sup>10</sup> The model correctly predicts the  $\sim 10\%$  decrease which is seen in the single-potential-step chronoamperometric  $i^{1/2}c$  values in the 10-ms to 10-s time range ( $E_c = -1.20$  V) and the current-time behavior for the double-potential-step chronoamperometric experiment when all three anodic processes are made to occur ( $E_c = -1.20$  V and  $E_a = 0.40$  V). The deficiency in the model when only the  $[(\text{FI}=\text{N})_2]^{2-}$  and the  $[(\text{FI}=\text{N})_2]^-$  are reoxidized in the double-potential-step chronoamperometric experiment may be due to other reactions which occur at nearly the same rate as the coupling of  $\text{FI}^-$  with  $\text{FIN}_2$  (e.g., electron transfer from  $[(\text{FI}=\text{N})_2]^{2-}$  to  $\text{FIN}_2$ , and disproportionation of  $[(\text{FI}=\text{N})_2]^-$ ). Since these additional reactions would greatly increase the complexity of the simulations, and since the rates of these reactions are not known, additional attempts to model the system do not appear justified.
- (10) S. W. Feldberg in "Electroanalytical Chemistry", Vol. 3, A. J. Bard, Ed., Marcel Dekker, New York, N.Y., 1969, pp 199–296.
- (11) The anion  $\text{FIH}^-$  was prepared electrochemically by exhaustive controlled potential electrolysis of fluorene<sup>12</sup> and chemically by reaction of fluorene with sodium hydride or *n*-butyllithium. The method of  $\text{FIH}^-$  preparation had no effect upon its redox behavior. Although the products of  $\text{FIH}^-$  oxidation were not examined in detail, a cyclic voltammetric peak was observed for the reduction of 9,9'-bifluorenyl near  $-1.9$  V on the reverse, negative-going sweep.
- (12) (a) J. R. Jezorek, A. Lagu, T. M. Seigel, and H. B. Mark, *J. Org. Chem.*, **38**, 788 (1973); (b) A. Lagu and H. B. Mark, *ibid.*, **42**, 1063 (1977).
- (13)  $\text{FIH}^-$  was considered since this anion was shown in separate experiments to react with  $\text{FIN}_2$  to give azine dianion and fluorene.
- (14) The lack of reversibility of the  $\text{FIH}^-/\text{FIH}^\cdot$  couple also precludes  $\text{FIH}^\cdot$ , the assumed oxidation product of  $\text{FIH}^-$ , as being the electroactive species in this most positive redox couple.

Richard N. McDonald,\* K. J. Borhani, M. Dale Hawley\*

Department of Chemistry, Kansas State University  
Manhattan, Kansas 66506

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## Transition Metal Initiated Cationic Photopolymerization

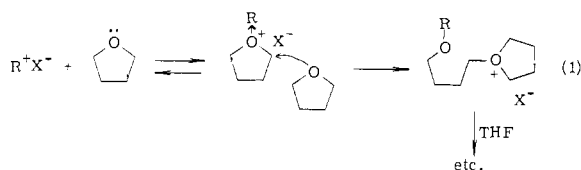
Sir:

Photochemical activation of electron transfer within organic donor-acceptor complexes is a useful method for initiating a variety of ionic polymerization reactions.<sup>1,2</sup> Such a concept has not been applied to complexes of transition metal ion acceptors with organic donors. The intrinsic coordinative preferences of the metal ion might be expected to impart reaction selectivity both in terms of organic substrate binding (type, number, and relative orientation of ligands) and the photochemical behavior of the complex.<sup>3</sup> We wish to report that efficient cationic photopolymerization of tetrahydrofuran (THF) can be initiated by small quantities of copper and silver salts.<sup>4</sup> This report constitutes the first example of a transition metal ion mediated cationic photopolymerization<sup>5</sup> and also the first report of THF photopolymerization.

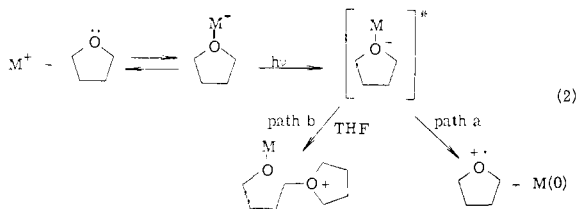
Solutions of the silver salts  $\text{AgBF}_4$ ,  $\text{AgPF}_6$ ,  $\text{AgSbF}_6$ , and  $\text{AgOTf}$ <sup>6</sup> in anhydrous<sup>7</sup> THF are stable indefinitely in the dark. However, upon irradiation with 254-nm light at 25 °C, degassed solutions of any of these silver salts in THF become increasingly viscous. Also formed is a black precipitate, shown by analysis to be silver metal.<sup>8</sup> Addition of water to the irradiated solutions produces a white precipitate, characterized as polytetrahydrofuran<sup>9</sup> by the infrared spectrum,<sup>10</sup> elemental analysis,<sup>11a</sup> and molecular weight.<sup>11b</sup> In a typical preparative reaction, irradiation of 0.24 g of  $\text{AgPF}_6$  in 8.9 g of THF for 13.5 h followed by 11.5 h in the dark yielded 4.5 g (50%) of

isolated dry polymer. Yields for preparative thermal THF polymerization are generally in the range of 30–80%.<sup>9</sup> The yield of polymer was found to increase with the duration of photolysis and also upon standing in the dark following photolysis. Several identical solutions of AgOTf (0.038 M) in THF were irradiated in a merry-go-round apparatus for 11.5 h and then stored in the dark for varying periods of time prior to precipitation of the polymer with water. Isolated yields increased from ~1% to a maximum value of ~10% during the first 10 h in the dark. A second series of AgOTf solutions was irradiated for varying times and analyzed for polymer formation after a constant total reaction time (light plus dark) of 19 h. Isolated yields increased linearly with irradiation time during the first hour, but then leveled off to a limiting conversion of ~6% after 12 h. Triethylamine (0.04 M) completely inhibits polymer formation but does not affect the formation of silver metal. Polymer yields also depend upon the anion, decreasing in the order AgPF<sub>6</sub> > AgOTf ~ AgBF<sub>4</sub> > AgSbF<sub>6</sub>. Silver salts which are insoluble in THF (AgNO<sub>3</sub>, AgOAc, AgF) are ineffective. Copper salts including (CuOTf)<sub>2</sub>·C<sub>6</sub>H<sub>6</sub> and Cu(OTf)<sub>2</sub> are active initiators of THF photopolymerization. In the Cu(I) system precipitation of copper metal was observed within the first few minutes of irradiation,<sup>12</sup> whereas with Cu(II) metal precipitate was only observed after several hours. Solutions of both copper salts in THF have absorption bands which extend to wavelengths longer than 300 nm, thus allowing large scale photopolymerization reactions to be conducted in Pyrex apparatus.

The mechanism of thermal cationic THF polymerization has been extensively investigated.<sup>9</sup> Considerable evidence suggests that cationic species (e.g., carbonium ions) or strong Lewis acids activate THF for nucleophilic attack at the  $\alpha$  position (eq 1), leading to ring opening of the intermediate oxo-



nium ion. In the metal ion mediated reaction we suggest that coordinated THF is activated for nucleophilic attack by ligand-to-metal charge-transfer excitation (eq 2).<sup>3,13</sup> That THF



coordination is a prerequisite for reaction is supported by the observation that the addition of olefins which form stable Cu(I) complexes<sup>14</sup> completely inhibits initiation by (CuOTf)<sub>2</sub>·C<sub>6</sub>H<sub>6</sub> (instead, olefin photodimerization<sup>14</sup> is observed). Thermal catalysis by finely divided metallic copper or silver<sup>15</sup> is inconsistent with two observations. First, thermal disproportionation of (CuOTf)<sub>2</sub>·C<sub>6</sub>H<sub>6</sub> in THF produces copper metal;<sup>12</sup> however, thermally induced THF polymerization is not observed. Second, irradiation of AgOTf in 1,2-dimethoxyethane (DME) produces finely divided silver, but no polymer. When excess THF is added to the previously irradiated DME solution in the dark, no polymer is formed; however, irradiation of AgOTf in a mixture of THF and DME does result in polymer formation, albeit in low yield. It is unclear from the information at hand whether expulsion of M(0) occurs immediately following excitation (path a), or following attack of the excited complex by ground state THF (path b). The THF cation

radical does not appear to be a likely candidate for the chain-initiating species, in view of the absence of polymer formation upon irradiation of the THF-tetracyanoethylene charge-transfer complex.<sup>16</sup> Attack of the excited complex by either a coordinated or free THF would yield a metal alkoxide (path b). Copper(I) alkoxides are known to be thermally unstable, decomposing to produce alkoxy radicals and copper metal.<sup>17</sup> Considerably less is known about Ag(I) and Cu(II) alkoxides.<sup>18</sup> Interestingly, monitoring of the Cu(OTf)<sub>2</sub> initiated reaction by EPR reveals the formation of one or more new Cu(II) species (possibly copper alkoxides<sup>18</sup>) during the early stages of irradiation. Prolonged irradiation results in complete disappearance of all Cu(II) signals.

Following the metal ion mediated photoinitiation, THF polymerization apparently proceeds via the normal cationic chain mechanism.<sup>9</sup> The observed effect of anion identity on polymer yield, the continued growth of the polymer in the dark, inhibition by triethylamine, and termination by water are all characteristic of the thermal cationic polymerization process. Free radical polymerization of THF has never been achieved.

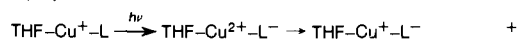
Metal ion initiated photopolymerization offers several unique features not available in either thermal or organic acceptor photoinitiated processes. In contrast to the former systems, the monomer-initiator mixture is completely stable with respect to polymerization until activated by ultraviolet light. Also, in many cases the reacted initiator (precipitated metal) can be easily separated from the polymer solution. Unlike photopolymerizations with organic acceptors, metal ions offer the possibility of greater variety, selectivity, and multiplicity in terms of substrate coordination and activation. Indeed, THF photopolymerization has never been initiated with an organic acceptor. Further studies of metal ion centered photoinitiated processes are in progress.

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## References and Notes

- (1) (a) M. Irie, Y. Yamamoto, and K. Hayashi, *Pure Appl. Chem.*, **49**, 455 (1977); (b) M. Irie and K. Hayashi, *Prog. Polym. Sci.*, **8**, 105 (1975); (c) S. Tazuke, *Pure Appl. Chem.*, **34**, 329 (1973).
- (2) (a) S. Tazuke, M. Asai, S. Ikeda, and S. Okamura, *J. Polym. Sci., Part B*, **5**, 453 (1967); (b) M. Sakamoto, K. Hayashi, and S. Okamura, *ibid.*, **3**, 205 (1965); (c) M. Irie, S. Tomimoto, and K. Hayashi, *ibid.*, **8**, 585 (1970).
- (3) (a) E. A. Koerner von Gustorf, L. H. Leenders, I. Fischer, and R. N. Perutz, *Adv. Inorg. Chem. Radiochem.*, **19**, 65 (1976); (b) M. S. Wrighton, *Top. Curr. Chem.*, **65**, 37 (1976); (c) C. R. Bock and E. A. Koerner von Gustorf, *Adv. Photochem.*, **10**, 221 (1977).
- (4) For reviews of cationic polymerization see (a) A. Ledwith and D. C. Sherrington in "Comprehensive Chemical Kinetics", Vol. 15, C. H. Bamford and C. F. H. Tipper, Ed., Elsevier, Amsterdam, 1976, Chapter 2; (b) A. Ledwith and D. C. Sherrington in "Reactivity, Mechanism, and Structure in Polymer Chemistry", A. D. Jenkins and A. Ledwith, Ed., Wiley, London, 1974, p 244; (c) A. Tsukamoto and O. Vogge, *Prog. Polym. Sci.*, **3**, 199 (1971).
- (5) For reviews of transition metal ion mediated free-radical photopolymerization, see ref 3a and (a) C. H. Bamford, *Pure Appl. Chem.*, **34**, 173 (1973); (b) C. Eastmond in "Comprehensive Chemical Kinetics", Vol. 14A, C. H. Bamford and C. F. H. Tipper, Ed., Elsevier, Amsterdam, 1976, p 46; (c) D. Phillips, *Spec. Period. Rep.: Photochem.*, **7**, 507 (1976).
- (6) OTf = O<sub>3</sub>SCF<sub>3</sub>.
- (7) Distilled from Na-K/benzophenone; all operations were carried out with rigorous exclusion of air.
- (8) Found: Ag, 99.2.
- (9) (a) P. Dreyfuss and M. P. Dreyfuss in "Comprehensive Chemical Kinetics", C. H. Bamford and C. F. H. Tipper, Ed., Vol. 15, Elsevier, Amsterdam, 1976; (b) P. Dreyfuss and M. P. Dreyfuss, *Adv. Polym. Sci.*, **4**, 528 (1967).
- (10) K. Imada, T. Miyakawa, Y. Chatani, H. Tadokoro, and S. Murahashi, *Makromol. Chem.*, **83**, 113 (1965).
- (11) (a) Calcd for (C<sub>4</sub>H<sub>8</sub>O)<sub>n</sub>: C, 65.5; H, 11.21. Found: C, 65.6; H, 11.2. (b) Osmometric molecular weights in benzene were in the range of 10 000–20 000 daltons.
- (12) (a) Some copper metal also arises from the known<sup>12b</sup> thermal disproportionation, Cu(I) → Cu(0) + Cu(II). (b) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed, Interscience, New York, N.Y., 1972, Chapter 25-H.

- (13) V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds", Academic Press, New York, N.Y., 1970, Chapters 13 and 19. A referee has suggested the possibility that metal-to-ligand charge-transfer excitation may initiate polymerization:



The absence of readily reducible ligands and the formation of reduced metal appear to be in better agreement with ligand-to-metal charge-transfer excitation. The identity of the reactive excited state is under continued investigation.

- (14) (a) R. G. Salomon and J. K. Kochi, *J. Am. Chem. Soc.*, **95**, 1889 (1973). (b) Instead the reported<sup>14c,d</sup> diene photocycloadditions are observed. (c) R. G. Salomon and J. K. Kochi, *J. Am. Chem. Soc.*, **96**, 1137 (1974). (d) R. G. Salomon, K. Folting, W. E. Streib, and J. K. Kochi, *ibid.*, **96**, 1145 (1974).  
 (15) Colloidal metals and organic halides can be used to initiate free radical polymerizations: G. Henrici-Olivé and S. Olivé, *Makromol. Chem.*, **88**, 117 (1965).  
 (16) Y. Achiba and K. Kimura, *Chem. Phys. Lett.*, **39**, 515 (1976).  
 (17) G. M. Whitesides, J. S. Sadowski, and J. Lilburn, *J. Am. Chem. Soc.*, **96**, 2830 (1974).  
 (18) (a) D. C. Bradley, *Adv. Inorg. Chem. Radiochem.*, **15**, 259 (1972); (b) D. C. Bradley, *MTP Int. Rev. Sci., Inorg. Chem. Ser. One*, **5**, 65 (1972).  
 (19) (a) Fellow of the Alfred P. Sloan Foundation; (b) Camille and Henry Dreyfus Teacher-Scholar.

Michael E. Woodhouse, Frederick D. Lewis\*<sup>19a,b</sup>  
 Tobin J. Marks\*<sup>19a,b</sup>

Department of Chemistry, and the Materials Research Center,  
 Northwestern University, Evanston, Illinois 60201

Received September 12, 1977

## Novel Iron Complexes from Cocondensations of Iron Vapor with Aminodifluorophosphines

Sir:

The dialkylaminodifluorophosphines form relatively stable homoleptic zerovalent nickel complexes (R<sub>2</sub>NPF<sub>2</sub>)<sub>4</sub>Ni by displacement of all four CO groups from Ni(CO)<sub>4</sub>.<sup>1,2</sup> However, no other homoleptic zerovalent dialkylaminodifluorophosphine metal complexes are known. This communication describes the first reported examples of the cocondensation of metal vapors<sup>3,4</sup> with aminodifluorophosphines. Such reactions are interesting since they provide routes to novel zerovalent metal complexes exhibiting relatively high stabilities and unusual structures.

About 0.5 g (8.93 mg-atoms) of iron metal was evaporated over a period of 30 min at 0.0001-mm pressure from an alumina coated tungsten wound crucible heated electrically. The resulting vapors were cocondensed at -196 °C with an excess (~8 mL) of dimethylaminodifluorophosphine. Excess ligand was then removed by pumping at -78 °C. The resulting black slurry was extracted with hexane and the resulting hexane solution chromatographed on a Florisil column. Elution of the yellow band with hexane gave 0.8 g (14% yield) of yellow [(CH<sub>3</sub>)<sub>2</sub>NPF<sub>2</sub>]<sub>5</sub>Fe. Anal. Calcd for C<sub>10</sub>H<sub>30</sub>F<sub>10</sub>FeN<sub>5</sub>P<sub>5</sub>: C, 19.3; H, 4.9; N, 11.3. Found: C, 19.6; H, 4.7; N, 11.1.

This iron(0) derivative [(CH<sub>3</sub>)<sub>2</sub>NPF<sub>2</sub>]<sub>5</sub>Fe is a yellow solid which appears indefinitely stable in air in contrast to many other iron(0) derivatives such as [(CH<sub>3</sub>O)<sub>3</sub>P]<sub>5</sub>Fe.<sup>5,6</sup> Its <sup>1</sup>H NMR spectrum exhibits the expected broad peak at τ 7.0. Its mass spectrum exhibits the complete sequence of ions [(CH<sub>3</sub>)<sub>2</sub>NPF<sub>2</sub>]<sub>n</sub>Fe<sup>+</sup> (n = 5, 4, 3, 2, and 1) indicating stepwise loss of (CH<sub>3</sub>)<sub>2</sub>NPF<sub>2</sub> ligands similar to the stepwise loss of carbonyl groups in the mass spectra of most metal carbonyls.<sup>7</sup>

The potentially bidentate ligand CH<sub>3</sub>N(PF<sub>2</sub>)<sub>2</sub> forms the relatively stable homoleptic complexes [CH<sub>3</sub>N(PF<sub>2</sub>)<sub>2</sub>]<sub>3</sub>M (M = Cr, Mo, and W) by ultraviolet irradiation with the corresponding metal hexacarbonyls.<sup>8</sup> However, all reactions of CH<sub>3</sub>N(PF<sub>2</sub>)<sub>2</sub> with iron carbonyls, even under photochemical

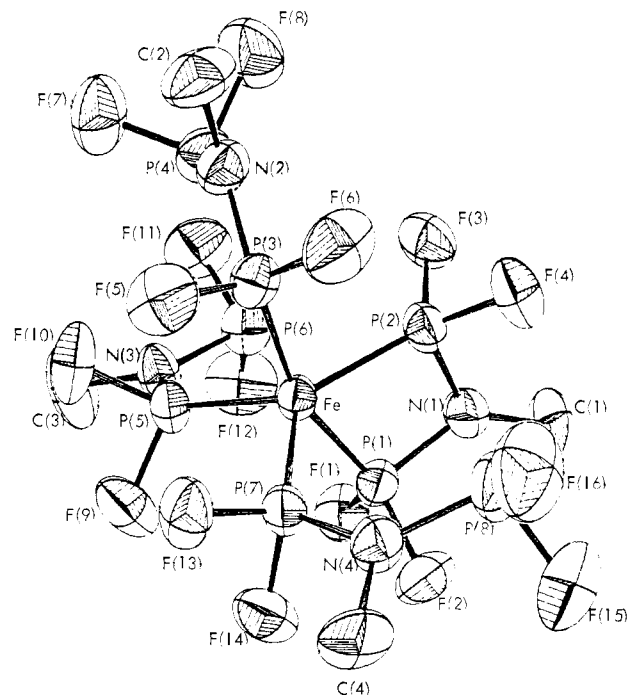


Figure 1. ORTEP drawing of the structure of [CH<sub>3</sub>N(PF<sub>2</sub>)<sub>2</sub>]<sub>4</sub>Fe.

conditions, give products still containing carbonyl groups.<sup>9,10</sup> In an attempt to prepare an iron(0) derivative containing only CH<sub>3</sub>N(PF<sub>2</sub>)<sub>2</sub> ligands, iron vapor was cocondensed with excess CH<sub>3</sub>N(PF<sub>2</sub>)<sub>2</sub> using a procedure completely analogous to that described above for the cocondensation of iron vapor with (CH<sub>3</sub>)<sub>2</sub>NPF<sub>2</sub>. Chromatography of the resulting reaction mixture on silica gel using hexane as solvent gave a yellow band. Elution of this yellow band followed by crystallization from *n*-hexane at -20 °C gave yellow crystals. The yield of this product was low (<1%) owing to the concurrent formation of iron particles and unidentified iron compounds which could neither be sublimed or chromatographed without decomposition. In view of the limited quantity of this yellow product for the usual characterization by elemental analyses and spectroscopic methods, the structure of this product was instead determined by single-crystal x-ray diffraction.

The iron complex [CH<sub>3</sub>N(PF<sub>2</sub>)<sub>2</sub>]<sub>4</sub>Fe forms monoclinic crystals by slow evaporation of an *n*-hexane solution at room temperature: space group *P*<sub>2</sub><sub>1</sub>/*n*; *a* = 16.777 Å, *b* = 10.486 Å, *c* = 15.538 Å, β = 117.048°, *Z* = 4. Least-squares anisotropic refinement using the 2656 observed reflections (*R* = 0.0391, *R*<sub>w</sub> = 0.0373) indicates the structure depicted in Figure 1. In this structure the iron(0) atom attains the expected coordination number of five since one of the CH<sub>3</sub>N(PF<sub>2</sub>)<sub>2</sub> ligands is bidentate whereas the remaining three CH<sub>3</sub>N(PF<sub>2</sub>)<sub>2</sub> ligands are only monodentate.

The coordination polyhedron of the five-coordinate iron(0) atom can be interpreted as a trigonal bipyramid which is severely distorted by the small-bite bidentate CH<sub>3</sub>N(PF<sub>2</sub>)<sub>2</sub> ligand. The ten angles around the five-coordinate iron atom are as follows: P(1)-Fe-P(3) = 161.96, P(1)-Fe-P(2) = 69.12, P(1)-Fe-P(7) = 93.07, P(1)-Fe-P(5) = 96.78, P(3)-Fe-P(2) = 93.61, P(3)-Fe-P(7) = 93.57, P(3)-Fe-P(5) = 97.85, P(2)-Fe-P(7) = 127.37, P(5)-Fe-P(7) = 104.03, P(5)-Fe-P(2) = 126.36°. The bidentate CH<sub>3</sub>N(PF<sub>2</sub>)<sub>2</sub> ligand (P(1) and P(2)) thus bridges an equatorial and an axial position of the iron(0) trigonal bipyramid and because of its small bite reduces the P<sub>ax</sub>-Fe-P<sub>eq</sub> angle from the idealized value of 90° to 69°. Part of this distortion involves bending the relevant Fe-P<sub>ax</sub> bond so that the P<sub>ax</sub>-Fe-P<sub>ax</sub> angle is no longer the ideal value of 180° but instead 162°. Thus the introduction of a