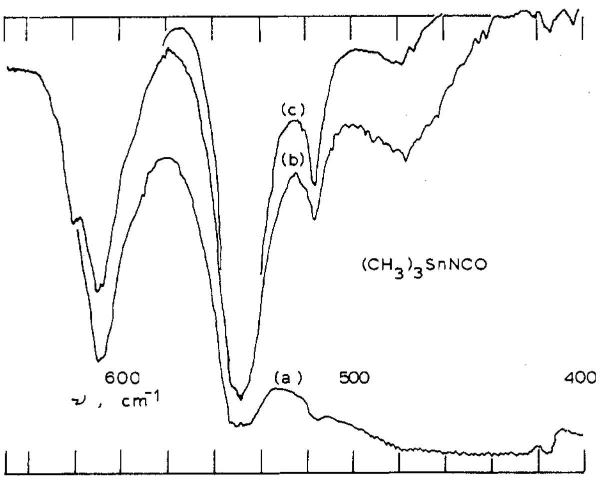


Figure 5.—Portion of the infrared spectrum of $(CH_3)_3SnNCO$ from 650 to 400 cm^{-1}. (a) Nujol mull spectrum using NaCl plates; (b) KBr pellet spectrum; (c) Nujol mull spectrum using CsI plates. The band at ~550 cm^{-1} is due to the Sn–C_3 asymmetric stretch, while that at 517 cm^{-1} is assigned to the Sn–C_3 symmetric mode. All data are at ~40°.

the basis of the infrared spectra of related molecules, such as $[(CH_3)_3Sn]_2SO_4$,[45] $[(CH_3)_3Sn]_2CrO_4$,[45] $[(CH_3)_3Sn]_2SeO_4$,[46] and $[(C_2H_5)_3Sn]_2$,[47] this band can be assigned with some confidence to the $Sn(CH_3)_3$ symmetric vibration. Its presence in the infrared spectrum rules out a planar trimethyltin moiety such as would be expected if the NCO group were acting as a strongly bridging ligand and is in consonance with the formulation of trimethyltin cyanate as having a distorted pyramidal structure with only weakly bridging cyanate moieties.

Acknowledgments.—The authors are indebted to Messrs. D. Headley and R. Levy for their assistance in the synthetic aspects of this work and for their initial Mössbauer data on $(C_6H_5)_3SnNCO$, $(C_6H_5CH_2)_3SnNCO$, $(C_6H_5CH_2)_2Sn(NCO)_2$, and the two hexacyanato complexes. We are especially grateful to Dr. S. Chandra, who carried out the temperature dependence measurements on $(CH_3)_3SnNCO$ and handled the computer analysis of the Mössbauer data. This research has been generously supported by the U. S. Atomic Energy Commission (Document NYO-2472-70), the Petroleum Research Fund administered by the American Chemical Society, and the Research Council of Rutgers University. In addition the award of an NSF undergraduate research fellowship to K. L. L. is gratefully acknowledged.

(45) H. C. Clark and R. Goel, *Inorg. Chem.*, **4**, 1428 (1965).

(46) J. R. Sams, private communication.

(47) D. H. Lohman, *J. Organometal. Chem.*, **4**, 382 (1965).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF NORTH CAROLINA, CHAPEL HILL, NORTH CAROLINA 27514

The Electrochemical Oxidation of Bis(π-cyclopentadienyldicarbonyliron)

BY JOHN A. FERGUSON AND THOMAS J. MEYER*[1]

Received September 14, 1970

Bis(π-cyclopentadienyldicarbonyliron) can be oxidized at carbon and platinum electrodes in acetone, acetonitrile, and dichloromethane using a variety of supporting electrolytes. Three general routes have been used for the preparation of complexes of the types $(\pi\text{-}C_5H_5)Fe(CO)_2L^+$ and $(\pi\text{-}C_5H_5)Fe(CO)_2X$ [L = neutral ligand; X = anionic ligand] by electrochemical oxidation of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$.

Introduction

It was recently reported[2] that chemical oxidation of bis(π-cyclopentadienyldicarbonyliron) by anhydrous ferric perchlorate in acetone or acetonitrile gives solutions of the corresponding solvento complexes, $(\pi\text{-}C_5H_5)Fe(CO)_2(OC(CH_3)_2)^+$ and $(\pi\text{-}C_5H_5)Fe(CO)_2(NCCH_3)^+$. The reactions involve the oxidative fissioning of the metal–metal bond in $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$. The overall stoichiometry for both reactions is 2:1 suggesting that the net reaction is

$$2S + 2Fe^{3+} + [(\pi\text{-}C_5H_5)Fe(CO)_2]_2 \longrightarrow 2Fe^{2+} + 2(\pi\text{-}C_5H_5)Fe(CO)_2S^+$$

where S = acetone or acetonitrile. It was also reported that acetone was easily displaced from the acetone complex by a variety of neutral or anionic ligands giving complexes of the types $(\pi\text{-}C_5H_5)Fe(CO)_2L^+$ and $(\pi\text{-}C_5H_5)Fe(CO)_2X$.

Here we report that bis(π-cyclopentadienyldicarbonyliron) can be oxidized electrochemically in a variety of media and that complexes of the types $(\pi\text{-}C_5H_5)Fe(CO)_2L^+$ (L = $S(C_2H_5)_2$, $NCCH_3$) and $(\pi\text{-}C_5H_5)Fe(CO)_2X$ (X^- = Cl^-) can be isolated in good yield either directly or indirectly using electrochemical techniques. The acetone complex has been prepared *in situ* and not isolated as a solid.

Experimental Section

All manipulations were carried out under nitrogen in deaerated solvents. Infrared spectra were obtained in KBr pellets using a Perkin-Elmer 421 spectrophotometer. Ultraviolet–visible spectra were obtained on a Cary 14 spectrophotometer.

A. **Materials.**—Bis(π-cyclopentadienyldicarbonyliron) (Alfa Inorganics) was purified by successive recrystallization from benzene–petroleum ether and dichloromethane–pentane. Ammonium hexafluorophosphate (Alfa Inorganics) was purified by three recrystallizations from acetone–dichloromethane and finally

---

(1) Author to whom inquiries should be addressed.

(2) E. C. Johnson, T. J. Meyer, and N. Winterton, *Chem. Commun.*, 934 (1970); E. C. Johnson, T. J. Meyer, and N. Winterton, submitted for publication.

TABLE I

ELECTROCHEMICAL OXIDATION OF $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$

Solvent	Supporting electrolyte	Electrode	$E_{1/2}$,[a] V	n	Product
CH_3CN	0.2 *M* NH_4PF_6	C	0.19	1.95	$(\pi\text{-}C_5H_5)Fe(CO)_2NCCH_3{}^+$
CH_3CN	0.2 *M* NH_4PF_6	Pt	~1.0[b]	...	$(\pi\text{-}C_5H_5)Fe(CO)_2NCCH_3{}^+$
CH_3CN	0.1 *M* $(C_2H_5)_4NCl$	C	0.42	1.97	5% $(\pi\text{-}C_5H_5)Fe(CO)_2NCCH_3{}^+$ 70% $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$
CH_3CN	0.1 *M* $(C_2H_5)_4NCl$	Pt	>0.88	...	$2Cl^- \rightarrow Cl_2$
$(CH_3)_2CO$	0.2 *M* NH_4PF_6	C	0.48	1.98	$(\pi\text{-}C_5H_5)Fe(CO)_2OC(CH_3)_2{}^+$
$(CH_3)_2CO$	0.2 *M* NH_4PF_6	Pt	~0.55[b]	...	$(\pi\text{-}C_5H_5)Fe(CO)_2OC(CH_3)_2{}^+$
$(CH_3)_2CO$	0.1 *M* $(C_4H_9)_4NCl$	C	>0.30[c]	>2.0	43% $(\pi\text{-}C_6H_5)Fe(CO)_2Cl$
CH_3Cl_2	0.2 *M* $(C_4H_9)_4NPF_6$	C	...	1.98	

[a] *Vs.* the saturated sodium chloride calomel electrode. [b] Wave ill defined because of adsorption. [c] Oxidation begins at 0.3 V but never reaches a limiting current. The current *vs.* time curve does not approach zero.

dried for 10 hr in a vacuum oven at 30°. Tetraethylammonium chloride was recrystallized from dichloromethane and dried for 10 hr in a vacuum oven at 30°. Spectrograde acetonitrile was treated with activated alumina before use, and reagent grade acetone was dried over anhydrous magnesium sulfate. All other chemicals were either reagent or polarographic grade and used without further purification.

B. Electrochemistry.—For all electrochemical experiments, conventional three-electrode operational amplifier circuitry was employed.[3] Voltammetric data were obtained at a rotated platinum bead electrode (1200 rpm). The carbon electrode used in this study was a carbon cloth made by Union Carbide and kindly provided by Professor Ralph Adams. All potentials are *vs.* the saturated sodium chloride calomel electrode (ssce) uncorrected for junction potentials.[4]

The n values, where n is the number of electrons transferred during the oxidation, represent an averaged value obtained from at least two experiments. n was calculated from the area under a current *vs.* time curve measured with a planimeter. Adsorption of the oxidation products of bis(π-cyclopentadienyldicarbonyliron) at platinum precludes the use of this metal for n determinations. In some instances this product adsorption yielded ill-defined voltammetric waves; such results are so indicated. Each measurement made at the carbon electrode involved a fresh electrode surface.

C. Preparations. 1. $[(\pi\text{-}C_5H_5)Fe(CO)_2S(C_2H_5)_2]PF_6$.—A 100-mg sample of bis(π-cyclopentadienyldicarbonyliron) was dissolved in 0.2 *M* ammonium hexafluorophosphate–acetone solution and oxidized for 2 hr at +0.70 V *vs.* the ssce at a carbon electrode. The solution was filtered and evaporated to 5 ml and 1 ml of diethyl sulfide was added. The mixture was stirred for 30 min, 15 ml of acetone was added to dissolve all reaction products, and stirring was continued for an additional 30 min. A 150-ml portion of water was added and the yellow water-insoluble crystals were collected and air dried. A 58-mg amount (27% yield) of $[(\pi\text{-}C_5H_5)Fe(CO)_2S(C_2H_5)_2]PF_6$ was obtained; ν_{CO} 2063, 2018 cm^{-1}.[2] *Anal.* Calcd for $FeC_9H_{15}O_2SPF_6$: C, 32.03; H, 3.66; S, 7.77. Found: C, 31.72; H, 3.70; S, 7.50.

2. $[(\pi\text{-}C_5H_5)Fe(CO)_2NCCH_3]PF_6$.—A 127-mg sample of bis(π-cyclopentadienyldicarbonyliron) was dissolved in a 0.2 *M* ammonium hexafluorophosphate–acetonitrile solution and oxidized for 2.5 hr at +0.80 V *vs.* the ssce at a carbon electrode. Spectrophotometric analysis (ϵ 737 at 370 nm) indicated that the oxidation was quantitative. The solution was filtered and evaporated to a small volume and then chromatographed on a 30 cm × 1 cm 60–100 mesh Florisil column. Elution with acetonitrile, followed by evaporation of the eluate, gave a 19% yield (52 mg) of $[(\pi\text{-}C_5H_5)Fe(CO)_2NCCH_3]PF_6$. A noticeable amount of material adhered to the column and could not be eluted; ν_{CO} 2038, 2020 cm^{-1}. *Anal.* Calcd for $FeC_9H_8O_2NPF_6$: C, 29.75; H, 2.20; N, 3.80. Found: C, 28.90; H, 2.30; N, 3.81.

3. $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$.—(i) A 122-mg sample of bis(π-cyclopentadienyldicarbonyliron) was dissolved in a 0.1 *M* tetraethylammonium chloride–acetonitrile solution and oxidized for 2 hr at +0.75 V *vs.* the ssce at a carbon electrode. The solution was filtered and evaporated to a small volume and chromatographed on a 40 cm × 1 cm 60–100 mesh Florisil column, eluting with dichloromethane. Two reaction products were observed: $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ and $(\pi\text{-}C_5H_5)Fe(CO)_2NCCH_3{}^+$. In previous experiments it had been observed that solutions of the acetonitrile complex undergo some decomposition when they are concentrated and chromatographed on Florisil.[5] The yellow band corresponding to the acetonitrile complex was not eluted but instead was removed mechanically. Both species were determined spectrophotometrically indicating a 70% yield of $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ (ϵ 977 at 340 nm in dichloromethane) and a 5% yield of $(\pi\text{-}C_5H_5)Fe(CO)_2NCCH_3{}^+$ (ϵ 1167 at 370 nm in acetonitrile). The solution containing the eluted chloride complex was evaporated to small volume, and the complex was precipitated by adding a mixture of hexane–pentane. The red crystals were collected and air dried giving 51.4 mg (35% yield) of $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$; ν_{CO} 2051, 1991 cm^{-1}. *Anal.* Calcd for $FeC_7H_5O_2Cl$: C, 39.6; H, 2.4; Cl, 16.7. Found: C, 39.5; H, 2.4; Cl, 16.9.

(ii) A 122-mg sample of bis(π-cyclopentadienyldicarbonyliron) was added to a 0.25 *M* tetrabutylammonium chloride–acetone solution and oxidized for 3 hr at +0.50 V *vs.* the ssce at a carbon electrode. The current reached a limiting value not close to zero. The solution was filtered and evaporated to a small volume and chromatographed on a 30 cm × 1 cm Florisil column using dichloromethane as the eluent. A red band was eluted and identified as the chloride complex by its ultraviolet spectrum (λ_{max} at 340 and 280 nm) and its infrared dichloromethane solution spectrum (ν_{CO} at 2058 and 2017 cm^{-1}). Spectrophotometric analysis indicated that the chloride complex was obtained in a 43% yield. A significant amount of unidentified material could not be eluted from the column.

(iii) A 40-mg sample of bis(π-cyclopentadienyldicarbonyliron) was dissolved in a 0.2 *M* tetrabutylammonium hexafluorophosphate–dichloromethane solution and electrolyzed at a carbon electrode. Excess tetra-*n*-butylammonium chloride was added, and the solution was stirred for 0.5 hr. The solution was filtered, evaporated to a small volume, and chromatographed on a 15 cm × 1 cm 60–100 mesh Florisil column, eluting with dichloromethane. Spectrophotometric analysis at 340 nm (ϵ 977) indicated an 86% yield of $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$.

4. $(\pi\text{-}C_5H_5)Fe(CO)_2(OC(CH_3)_2)$.—A 140-mg sample of bis(π-cyclopentadienyldicarbonyliron) was dissolved in a 0.2 *M* ammonium hexafluorophosphate–acetone solution and oxidized at a potential of +0.70 V *vs.* the ssce at a carbon electrode. The electrolysis was complete in 3 hr. The solution was filtered, evaporated to dryness under nitrogen, and extracted with dichloromethane. The dichloromethane solution infrared and ultraviolet–visible spectra were identical with those for the complex as prepared by Meyer, *et al.*[5]

Results

Data for the electrochemical oxidation of bis(π-cyclopentadienyldicarbonyliron) at carbon and platinum electrodes are given in Table I. The electrochemical oxidations are totally irreversible in all media studied since no reverse peak corresponding to the reduction of the oxidized product was observed to the cathodic limits of dichloromethane and acetone. In 1,2-dimethoxyethane $(\pi\text{-}C_5H_5)Fe(CO)_2(NCCH_3)^+$ has been reported to reduce to $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ at −1.2 V.[6] Therefore, $E_{1/2}$ is only an indication of the ease of oxidation in a particular medium. The oxidation was studied in acetone, acetonitrile, and dichloromethane, using perchlorate and hexafluorophosphate salts as supporting

---

(3) W. L. Underkofler and I. Shain, *Anal. Chem.*, **35**, 1778 (1963).

(4) J. B. Headridge, "Electrochemical Techniques for Inorganic Chemists," Academic Press, London and New York, 1969, p 71.

(5) T. J. Meyer and N. Winterton, unpublished results.

(6) R. E. Dessy, R. B. King, and M. Waldrop, *J. Amer. Chem. Soc.*, **88**, 5115 (1966).

electrolytes. Both coulometric and voltammetric techniques were employed in each medium. Single-sweep E_p values from cyclic voltammograms at 500 mV/sec were at +0.75 V in dichloromethane (0.2 M $(C_4H_9)_4NClO_4$ as the supporting electrolyte), at +0.62 V in acetone (0.2 M NH_4PF_6), and at +0.53 V in acetonitrile (0.2 M NH_4PF_6).

As indicated by Table I, for a given electrode, $E_{1/2}$ varies significantly with the solvent and supporting electrolyte used. In acetonitrile an even more dramatic change in $E_{1/2}$ is observed when the electrode material is changed from platinum to carbon. The preparations described in the Experimental Section were carried out after the $E_{1/2}$ and n values had been determined in the appropriate medium. A sufficient quantity of material was used to ensure isolation of characterizable amounts of products.

Discussion

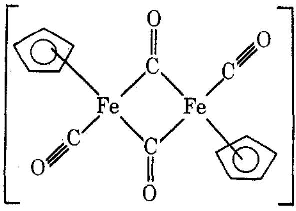
From the experiments described here, three general synthetic routes for the electrochemical preparation of $(\pi\text{-}C_5H_5)Fe(CO)_2L^+$ and $(\pi\text{-}C_5H_5)Fe(CO)_2X$ complexes can be identified. In the first, the metal–metal bond in $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ is oxidatively broken in a weakly coordinating solvent (acetone or dichloromethane) to give the solvento complex $(\pi\text{-}C_5H_5)Fe(CO)_2OC(CH_3)_2^+$. In the case of dichloromethane, that the solvent is coordinated has not been established, but some labile intermediate does exist. Subsequent addition of an appropriate ligand, $S(C_2H_5)_2$ or Cl^-, results in the displacement of the solvent from the inner coordination sphere, and the corresponding ligand complex $(\pi\text{-}C_5H_5)Fe(CO)_2S(C_2H_5)_2^+$ or $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ can be isolated. For such reactions to be successful, the anion of the supporting electrolyte must itself be weakly coordinating; therefore, either perchlorate or hexafluorophosphate salts are used as the supporting electrolyte. This electrochemical route should be as general as the ferric perchlorate oxidation of bis(π-cyclopentadienyldicarbonlyiron) in acetone as described by Johnson, Meyer, and Winterton.[2]

In the second route the electrochemical oxidation is carried out in a potentially coordinating solvent (acetonitrile) again using the salt of a noncoordinating or weakly coordinating anion as the supporting electrolyte. The coordination position made vacant by the oxidative fission of the metal–metal bond is taken up by solvent and the solvento complex $(\pi\text{-}C_5H_5)Fe(CO)_2NCCH_3^+$ is formed. Limitations to this preparative route would appear to be (A) the starting complex must not react with the solvent itself, (B) the solvento complex once formed must be stable, and (C) the solvent must be sufficiently coordinating to compete with or actually displace the anion of the supporting electrolyte in the labile coordination position.

In the third method, the oxidation is carried out in a weakly coordinating solvent like acetone. As the supporting electrolyte, a salt of an anionic ligand which is to be coordinated is used. If $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ is electrochemically oxidized in acetone at a carbon electrode using tetra-n-butylammonium chloride as the supporting electrolyte, $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ is obtained in 43% yield. However, for this oxidation an unresolved limiting current is obtained. This indicates that either a catalytic or a secondary Faradaic process is occurring concurrently with the normal oxidation of the metal–metal bond.[7] The n values for the overall reaction are greater than 2 and the electrolysis does not yield $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ exclusively. In general, the method is restricted to anions whose oxidation potential is lower than the potential needed to oxidize $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ (*e.g.*, see entry four in Table I).

Oxidation of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ was also carried out in acetonitrile with tetraethylammonium chloride as the supporting electrolyte. The products were analyzed spectrophotometrically after separation on a Florisil column and found to be 70% $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ and 5% $(\pi\text{-}C_5H_5)Fe(CO)_2NCCH_3^+$. Mass balance was not obtained because, as reported in the Experimental Section, a portion of the acetonitrile complex could not be removed from the column, apparently because of decomposition. This product distribution is remarkable since the stable product under these conditions appears to be the acetonitrile complex. In a blank experiment, using conditions identical with those in the electrolysis, it was found that $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ is partially solvolyzed. In fact, the presence of the acetonitrile complex as a product of the electrochemical oxidation can be entirely accounted for by the slow solvolysis of the chloride complex once formed. Under the same conditions, anation of the acetonitrile complex does not occur. The preferential formation of the chloride complex indicates that either the electron transfer occurs *via* a chloride bridge in the electrode double layer[8] or that, kinetically, chloride ion competes very effectively with acetonitrile for the initial product of oxidation.

In nearly all the media studied the n values obtained for the oxidation of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ are 2. The electrochemical stoichiometry verifies that two electrons are transferred from the metal–metal bond to the electrode upon oxidation. Attempts to observe possible intermediates such as $(\pi\text{-}C_5H_5)Fe(CO)_2^+$ (I) or



II

as initial products of the oxidation using fast-scan (100 V/sec) cyclic voltammetry at platinum were unsuccessful.

Successive-sweep E_p values obtained by cyclic voltammetry were ill defined due to adsorption of either the oxidized products or some decomposition product at the electrode surface and subsequent passivation of the reaction. The $E_{1/2}$ values for the oxidation of bis(π-cyclopentadienyldicarbonyliron) vary considerably with solvent and supporting electrolyte. In 0.2 M ammonium hexafluorophosphate in acetonitrile the oxidation takes place +0.8 V higher at platinum than at carbon. Both observations imply the importance of surface effects which may arise from the adsorption of products at the electrode surface.

A systematic shift to more negative potentials (making the oxidation more favorable) for the single-sweep cyclic voltammetry E_p values is observed as the solvent

---

(7) A. Vlcek, *Advan. Inorg. Chem. Radiochem.*, **5**, 211 (1963).

(8) C. N. Reilley, "Treatise on Analytical Chemistry," Vol. 4, M. Kolthoff and P. J. Elving, Ed., Interscience, New York, N. Y., 1963, Part I, p 2127.

is changed from dichloromethane to acetone to acetonitrile which is the order of increasing coordinating ability. This may mean either that the solvent is intimately involved in the electron transfer act or that the initial oxidation of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ gives a short-lived intermediate such as I or II which is rapidly attacked by solvent (in an EC step) to give $(\pi\text{-}C_5H_5)Fe(CO)_2S^+$ (S = solvent).

Acknowledgments.—Acknowledgments are made to the University of North Carolina Materials Research Center through Contract SD-100 with the Advanced Research Projects Agency, the National Science Foundation through Grant No. GP 17083, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Contribution from the Department of Chemistry,
State University of New York at Albany, Albany, New York 12203

Synthesis and Transformations of Phosphorus Imidazolidines (1,3-Diaza-2-phospholidines)

By M. K. Das and J. J. Zuckerman*[1]

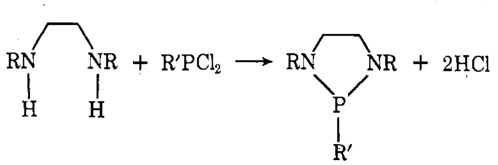
Received September 23, 1970

Four new derivatives of the phosphorus imidazolidine ring system have been prepared by amination of dichlorophosphines with variously *N,N'*-disubstituted ethylenediamines. The nmr spectra of the N-CH_3 substituted rings show a sharp doublet for these protons and a multiplet for the methylene bridge protons, while the *N*-phenyl derivatives show a sharp doublet for the methylene bridge protons at 60 and 100 MHz contrary to expectations on the basis of the pyramidal stereochemistry of phosphorus(III). These observations are interpreted in terms of the stereochemistry and dynamics of the diazaphospholidine heterocycles. The phosphorus imidazolidines are transformed to their boron analogs in an exothermic reaction with phenylboron dichloride with the release of dichlorophosphine, but the reaction is not reversible. Treatment of the phosphorus ring with arsenic trichloride yields a solid whose mass spectrum shows a peak at the highest mass corresponding to the ten-membered ring dimer of the known arsenic imidazolidine.

We have extended the previous studies in this laboratory on silicon[2] and germanium[2a,c–f,h–i] imidazolidines to phosphorus and boron.[3] This paper describes the synthesis and transformation reactions of phosphorus(III) imidazolidines.

Results and Discussion

Syntheses and Spectra.—Amination is the only method of synthesis extensively used to prepare phosphorus imidazolidines.[4] Lewis bases such as triethylamine facilitate the reactions, which are exothermic and rapid when the N substituent is small. We have prepared five simple derivatives by this route



(1)

I, R = CH_3, R' = CH_3
II,[5] R = CH_3, R' = C_6H_5
III, R = C_6H_5, R' = C_6H_5
IV, R = p-$CH_3C_6H_5$, R' = C_6H_5
V, R = p-$CH_3OC_6H_5$, R' = C_6H_5

Where R = CH_3, the reactions were carried out at room temperature in dilute media with slow addition. With larger groups, refluxing for 4–6 hr served to drive the reactions to completion. Yields were essentially quantitative. The *N*-alkyl derivatives are thermally stable liquids which hydrolyze rapidly in air; the solid aryl analogs are much more stable to atmospheric moisture. Hydrolysis regenerates the starting diamine and releases $R'P(OH)_2$.

The nmr spectra of I–V were measured at 60 and 100 MHz, and the data are gathered in Table I. The resonances in I assigned to the N-CH_3 and P-CH_3 protons appear as sharp doublets arising from ^{31}P coupling, but it was noted that $J(^{31}P\text{–N–C–}^1H) > J(^{31}P\text{–C–}^1H)$ in this compound (14.7 *vs.* 6.7 Hz). The methylene bridge protons in I and II appear as multiplets, while in III they give a sharp doublet signal both at 60 and at

Table I
Nmr Data (Hz)[a]

	N-CH_3			N-CH_2-			P-R'			N-C_6H_4-R''
	τ	J(P–H)	M[b]	τ	J(P–H)	M[b]	τ	J(P–H)	M[b]	τ
I	7.45	14.7[c]	d	6.95	...	m	9.25	6.7[c]	d	...
II	7.50	14.3[c,d]	d	7.15	...	m	2.77	...	m	...
III	...	...	...	6.11	7.3[c]	d	*e*	...	...	*e*
IV	...	...	...	6.35	5.0[c]	d	*e*	...	...	7.76
V	...	...	...	6.11	7.5[f]	d	*e*	...	...	6.33

[a] Measured at 60 MHz as neat liquids for I and II and as saturated solutions in $CDCl_3$ for the rest *vs.* tetramethylsilane as the internal standard at ambient temperature. [b] Multiplicity: d, doublet; m, multiplet. [c] Coupling constants verified at 100 MHz. [d] Reported as 14.5 Hz in ref 5. [e] P–R resonances of the compounds with three phenyl groups are not included here because of the complex nature of the overlapped *P*-phenyl and *N*-phenyl signals. [f] Multiplet at 100 MHz.

---

(1) To whom all inquiries should be addressed.

(2) (a) C. H. Yoder and J. J. Zuckerman, *Inorg. Chem.*, **3**, 1329 (1964); (b) *ibid.*, **4**, 116 (1965); (c) *J. Amer. Chem. Soc.*, **88**, 2170 (1966); (d) *ibid.*, **88**, 4831 (1966); (e) *Inorg. Chem.*, **5**, 2055 (1966); (f) *ibid.*, **6**, 103 (1967); (g) *Chem. Commun.*, 694 (1966); (h) *Prep. Inorg. React.*, in press; (i) E. W. Randall, C. H. Yoder, and J. J. Zuckerman, *Inorg. Chem.*, **6**, 744 (1967).

(3) M. K. Das, P. G. Harrison, and J. J. Zuckerman, *ibid.*, **10**, 1092 (1971).

(4) Tetrahydroimidazoles or imidazolidines where the 2 carbon is replaced by phosphorus are named as 1,3-diaza-2-phospholidines or 1,3-diaza-2-phosphacyclopentanes or simply as phosphorus imidazolidines.

(5) L. Siekmann, H. O. Hoppen, and R. Appel, *Z. Naturforsch. B*, **23**, 1156 (1968).