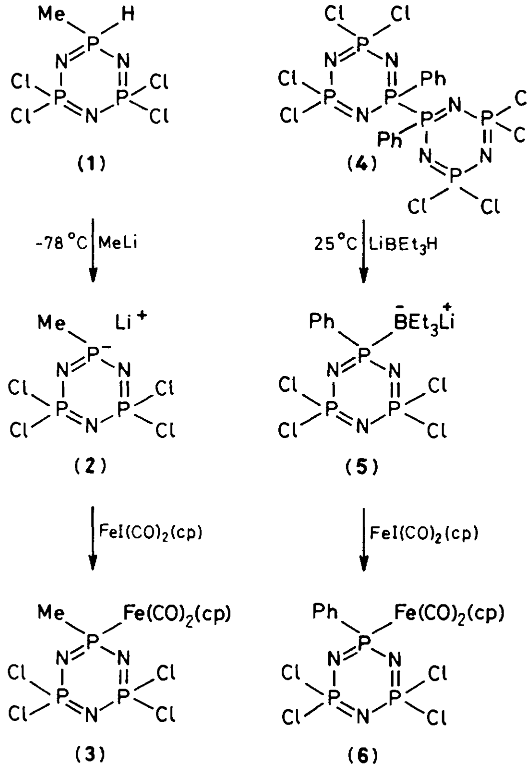
Iron-Bound Cyclotriphosphazenes Derived from Phosphazene Anions. *X*-Ray Crystal Structure of $N_3P_3Cl_4(CH_3)[Fe(CO)_2(C_5H_5)]$

Robin A. Nissan, Mark S. Connolly, Mario G. L. Mirabelli, Robert R. Whittle, and Harry R. Allcock*
Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802 U.S.A.

Iron-bound cylotriphosphazene complexes have been prepared *via* the reactions of lithium 1-methyl-3,3,5,5-tetrachlorocyclotriphosphazenide and lithium 1-phenyl-1-triethylborata-3,3,5,5-tetrachlorocyclotriphosphazene with dicarbonylcyclopentadienyliodoiron, and their structures determined by spectroscopic and crystallographic techniques.

We report here the first synthesis from phosphazene anions of cyclotriphosphazenes that bear iron complexes as side groups. Previous work has shown that similar compounds can be prepared by the interaction of halogenophosphazenes with transition metal anions; however, these reactions are complex and halogen abstraction and skeletal cleavage side reactions occur



cp = η^5-cyclopentadienyl.

concurrently.[1–4] The nucleophilic species in the new route are the cyclotriphosphazenes and not the metal; therefore, undesirable side reactions are virtually eliminated. This is especially important if these techniques are to be applied to linear, high-polymeric phosphazene systems.

The iron-bound phosphazene (**3**) was prepared by the reaction of the phosphazene[5] (**1**) with methyl-lithium (0.98 equiv.) in tetrahydrofuran (THF) solvent at −78 °C, followed by treatment of the phosphazene anion (**2**) with dicarbonylcyclopentadienyliodoiron (Alfa-Ventron Corp.; 1.08 equiv. in THF). The reaction solution was allowed to warm to room temperature, the solvent was removed under reduced pressure, and the residue was extracted with hexane–methylene dichloride (80:20 v/v). Chromatography on silica gel gave (**3**) (52%, m.p. 165 °C) as a yellow crystalline solid.

Phosphazene anions (**2**) are known to be unstable at temperatures above −60 °C.[6] Thus, this reaction sequence requires that the metal complex must react completely with (**2**) at low temperatures. For many transition metal complexes this is a serious limitation. However, this problem can be avoided by the preparation of novel phosphazene anions (**5**), that are stable at ambient or elevated (66 °C) temperatures.[7]

Specifically, the iron-bound phosphazene (**6**) was prepared by the reaction of the bi(cyclotriphosphazene) (**4**) with lithium triethylborohydride (Aldrich; 1.0 M solution in THF; 2.25 equiv.) in THF solvent at 25 °C, followed by treatment with dicarbonylcyclopentadienyliodoiron (1.3 equiv.; 120 h reaction time). After removal of the solvent under reduced pressure, extraction with hexane–methylene dichloride (80:20 v/v), and chromatography on silica gel, compound (**6**) (48%, m.p. 163 °C) was isolated as a pale yellow crystalline solid.

An analysis of the ^{31}P n.m.r. spectrum of the reaction mixtures indicated that (**3**) and (**6**) were formed with 100 and 90% conversion, respectively, and that no side reactions were evident. The modest yields of these compounds actually isolated appear to be a consequence of degradation of the products during chromatographic isolation.

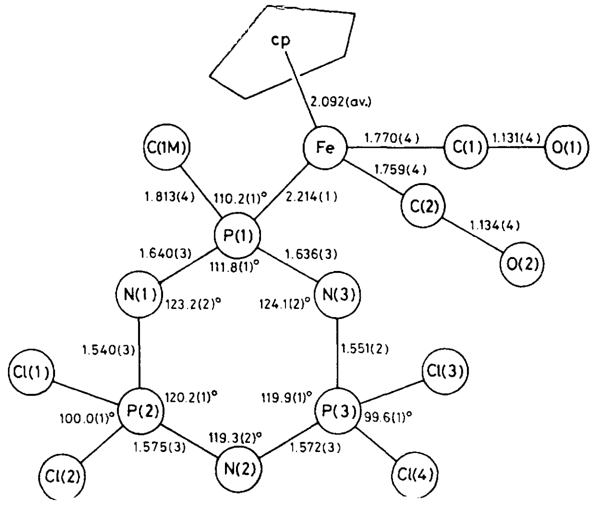


Figure 1. *X*-Ray structure of complex (**3**), with bond lengths in Å and angles in degrees.

The structures of (**3**) and (**6**) were determined by a combination of ^{31}P and ^{1}H n.m.r.,† and i.r. spectroscopy;† they gave satisfactory elemental analyses. Additional characterization of (**3**) was obtained by *X*-ray analysis of a single crystal grown at −4 °C from a methylene dichloride solution layered with hexane.

Crystal Data: $C_8H_8Cl_4FeN_3O_2P_3$, $M = 468.75$, monoclinic, space group $P2_1/n$, $a = 9.492(14)$, $b = 12.643(4)$, $c = 14.824(4)$ Å, $\beta = 106.54(6)°$, $U = 1705(4)$ Å^3, $Z = 4$, $D_c = 1.826$ g/cm^3, Mo-K_α radiation. 1849 Reflections with $I > 2\sigma(I)$, collected on an Enraf–Nonius diffractometer, were used and the structure was refined by heavy metal Patterson techniques to a final R value of 0.045.‡ The structure, including bond lengths and angles, is shown in Figure 1. Of particular interest is a lengthening of the P(1)–N(1) and P(1)–N(3) bonds with respect to $(NPCl_2)_3$ [1.581(3) Å],[8,9] as a result of the presence of a methyl and a dicarbonylcyclopentadienyliron moiety bound to P(1). In addition, the N(1)–P(1)–N(3) angle is considerably narrowed and the C(1M)–P(1)–Fe angle is widened relative to $(NPCl_2)_3$ [118.4(3) and 101.4(2)°, respectively].[8,9]

We are now examining the reactivity of these phosphazene anions with other transition metal complexes. Such synthetic routes form the starting point for a broad range of organometallic phosphazene preparations.

---

† N.m.r. spectra were recorded on a Bruker WP-200 spectrometer operating at 81.0 (^{31}P) and 200.0 MHz (^{1}H) for solutions of (**3**) and (**6**) in $CDCl_3$ and were referenced to H_3PO_4 and $CDCl_3$, respectively: (**3**), ^{31}P{^{1}H} AX_2, 108.4 {t, P(Me)[Fe(CO)$_2$(C$_5$H$_5$)]} and 10.1 p.p.m. (d, PCl$_2$), *J*(PNP) 35.2 Hz; ^{1}H, δ 2.0 [dt, Me, *J*(PCH) 10.1, *J*(PNPCH) 2.0 Hz] and 5.1 [d, C_5H_5, *J*(PFeCH) 1.2 Hz]; (**6**) ,^{31}P{^{1}H} AX_2, 102.5 {t, P(Ph)[Fe(CO)$_2$(C$_5$H$_5$)]} and 9.3 p.p.m. (d, PCl$_2$), *J*(PNP) 39.7 Hz; ^{1}H, δ 4.9 [d, C_5H_5, *J*(PFeCH) 1.2 Hz], 7.8 [m, C_6H_5(*o*)], and 7.5 [m, C_6H_5 (*m*,*p*)]; i.r., 3110(m) and 3060(w) (νCH); 2030(vs), 1985(vs), and 1950(m) (νCO); 1220(sh), 1200(vs), 1180(vs), 1160(vs), 1155(vs), and 1100(s) (νPN); 575(vs), 555(vs), 525(vs), 505(vs), 465(s), and 435 (s) cm^{-1} (νPCl).

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

We thank the U.S. Army Research Office and the U.S. Office of Naval Research for the support of this work.

Received, 6th April 1983; Com. 431

References

1 H. R. Allcock, P. P. Greigger, L. J. Wagner, and M. Y. Bernheim, *Inorg. Chem.*, 1981, **20**, 716.
2 H. R. Allcock, L. J. Wagner, and M. L. Levin, *J. Am. Chem. Soc.*, 1983, **105**, 1321.
3 P. R. Suszko, R. R. Whittle, and H. R. Allcock, *J. Chem. Soc., Chem. Commun.*, 1982, 649.
4 H. R. Allcock, G. H. Riding, and R. R. Whittle, to be published.
5 H. R. Allcock and P. J. Harris, *J. Am. Chem. Soc.*, 1979, **101**, 6221.
6 H. R. Allcock, P. J. Harris, and R. A. Nissan, *J. Am. Chem. Soc.*, 1981, **103**, 2256.
7 H. R. Allcock, M. S. Connolly, and R. R. Whittle, *Organometallics*, in the press.
8 H. R. Allcock, 'Phosphorus–Nitrogen Compounds,' Academic Press, New York, 1972, chap. 3, Appendix I.
9 G. J. Bullen, *J. Chem. Soc. A*, 1971, 1450.