

Synthesis of a Di-iron-spirocyclotriphosphazene and a Tri-iron-cluster-cyclotriphosphazene

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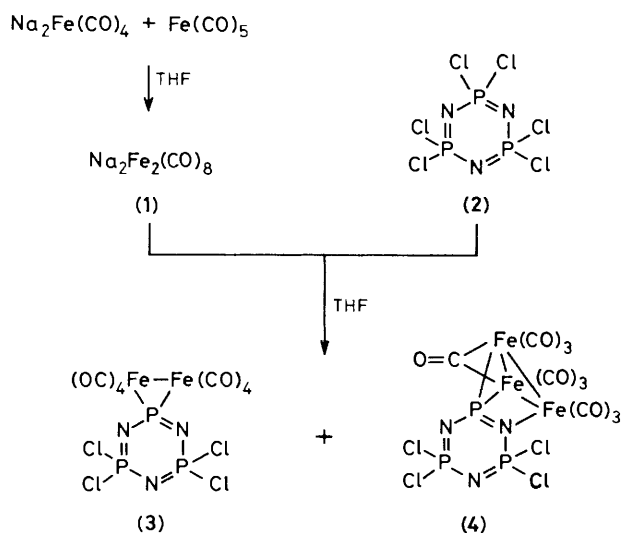
Di-iron and tri-iron-cyclophosphazene complexes have been obtained *via* the reactions of hexachlorocyclotriphosphazene with disodium octacarbonyldiferrate(−I), and their structures determined by spectroscopic and crystallographic techniques.

As part of our interest in phosphazene compounds that contain direct phosphorus–metal linkages,^{1,2} we report here the preparation and proof of the structure of two novel iron–carbonyl-containing cyclotriphosphazenes (3) and (4). The spiro-di-ironphosphazene (3) was obtained *via* the reaction of hexachlorocyclotriphosphazene (2) with disodium octacarbonyldiferrate(−I) (1). Compound (3) is the first example of a cyclic chlorophosphazene which contains direct phosphorus-to-metal bonds, with the organometallic unit arranged in a P–Fe–Fe three-membered ring. So far it has proved impossible to prepare such derivatives *via* the reaction of (NPCl₂)₃ with monofunctional organometallic reagents.^{1,2} Further reaction of (3) yielded the tri-iron-cluster-substituted phosphazene (4). Compound (4) illustrates the potential of the phosphazene ring system to participate in both covalent phosphorus–metal bonding and in nitrogen–metal coordination *via* donation of the lone pair electrons on the

nitrogen atoms. Compounds (3) and (4) represent prototypes for a potentially large group of phosphazene-bound transition metal carbonyl complexes, both cyclic and polymeric.

Specifically, (1) was prepared from equimolar amounts of disodium tetracarbonylferrate(−II)† and pentacarbonyliron in tetrahydrofuran (THF).³ Treatment of (1) with (2) at −78 °C, followed by warming to 25 °C yielded a dark red mixture. After removal of the solvent, extraction with methylene dichloride–hexane, and chromatography on silica gel, (3) and (4) were isolated as orange (11% yield, m.p. 142 °C, decomp.) and dark purple (1%, decomp. 160 °C) crystalline solids, respectively. Compound (4) was also obtained by treatment of (1) with pure (3), following a similar procedure.

† Obtained commercially from the Alfa-Ventron Corporation as the dioxan adduct.



Scheme 1

The structures of (3) and (4) were established by a combination of ^{31}P n.m.r.,[‡] i.r., and mass spectrometric[§] techniques. The ^{31}P n.m.r. spectrum of (3) showed an A_2X spin pattern with the PCl_2 chemical shifts at 13.1 and PFe_2 at 222.5 p.p.m., whereas (4) showed an AMX pattern with the PCl_2 resonances at 14.5 and 27.1, and PFe_2 at 217.9 p.p.m. The i.r. spectra, measured in hexane, showed terminal carbonyl stretching bands for (3) at 2120m, 2076s, 2051s, 2039s, 2027s, and 2013w cm^{-1} . Compound (4) showed terminal carbonyl bands at 2093m, 2057s, 2044s, 2030s, 2018m, 2006m, and 1972br, and a band assigned to a bridging carbonyl group at 1870br cm^{-1} .

In addition to the data indicated above, preliminary results from single-crystal X-ray analyses have confirmed the pro-

[‡] N.m.r. spectra were obtained for solutions of (3) and (4) in CDCl_3 and were referenced to H_3PO_4 .

[§] Chemical ionization mass spectrometric analyses of (3) and (4) showed the expected parent ions at $m/z = 611$ and 723, respectively.

posed structures. Data sets[¶] were collected for both products and each was refined to convergence. *Crystal data:* (3), $\text{C}_8\text{Cl}_4\text{Fe}_2\text{N}_3\text{O}_8\text{P}_3$, $M = 612.53$, monoclinic, space group $P2_1$, $a = 8.150(3)$, $b = 16.723(3)$, $c = 15.556(4)$ Å, $\beta = 97.22(3)^\circ$, $U = 2103(2)$ Å³, $Z = 4$, with an R factor of 0.071 (2776 reflections, $I > 2\sigma$); (4) $\text{C}_{10}\text{Cl}_4\text{Fe}_3\text{N}_3\text{O}_{10}\text{P}_3$, $M = 724.40$, tetragonal, space group $P4_2/n$, $a = 24.153(2)$, $c = 8.468(1)$ Å, $U = 4940(1)$ Å³, $Z = 8$, and an R factor of 0.085 (2018 reflections, $I > 2\sigma$). Both structures were solved by direct methods (using a MULTAN 78 program) and standard Fourier techniques. In the final cycles of least squares for each complex, all heavy atoms were refined anisotropically except for the C and O atoms of the carbonyl groups in compound (3), which were refined isotropically.** Average bond distances and angles of particular interest in (3) are as follows. The Fe-Fe distance is 2.746(3), the P-Fe distances are 2.23(1), the P-N skeletal bonds that flank the spiro unit are 1.61–1.64 Å, and the Fe-P-Fe angle is 76.1(1)°. For compound (4) the P-Fe distances are 2.187(3), the Fe(P)-Fe(P) distance is 2.618(1), the Fe(P)-Fe(N) distances are 2.647(3) Å, and the Fe-P-Fe angle is 73.5(1)°. The presence of the Fe-N bond [2.04(1) Å] in (4) results in a lengthening of the P-N bond [1.67(1) Å] associated with the cluster (relative to the other P-N distances, 1.53–1.61 Å). In addition, the three-membered spiro-subunit defines a plane that does not include the distal nitrogen atom of the phosphazene ring.

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[¶] Data ($\text{Mo-K}\alpha$) were collected on an Enraf-Nonius CAD-4 diffractometer at room temperature.

** The atomic co-ordinates for this work are available on request from Prof. Dr G. Bergerhoff, Institut für Anorganische Chemie, Universität, Gerhard-Domagk-Str. 1, D-5300 Bonn 1, W. Germany. Any request should be accompanied by the full literature citation for this communication.