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The First Azatriphosphapentadiene, Stabilized on an Iron Center: Formation and X-ray Structural Characterization

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Summary: Reaction of [ClP=N(2,4,6-(t-Bu)$_3$C$_6$H$_2$)] (**1**) with Na[(η^3-(2,4,6-(t-Bu)$_3$C$_6$H$_2$)PC(H)P(2,4,6-(t-Bu)$_3$C$_6$H$_2$))Fe(CO)$_3$] (**2**) affords the novel 1-aza-2,3,5-triphosphapenta-1,4-diene complex [(η^1,η^1-Ar*P=C(H)P-(Ar*)P=NAr*)Fe(CO)$_3$] (**3**; Ar* = 2,4,6-(t-Bu)$_3$C$_6$H$_2$), the structural features of which are discussed in relation to those of a carbon analogue.

Compounds containing phosphorus engaged in multiple bonds to main-group elements and especially transition-metal complexes thereof are still under intensive investigation. This interest is mainly based on the versatility of such ligands being able to coordinate to metal centers in many different ways, including chelation. The substitution of carbon atoms in polyenes by phosphorus atoms is well-known by now[1]; however, the number of azaphosphapolyenes is still rather limited.

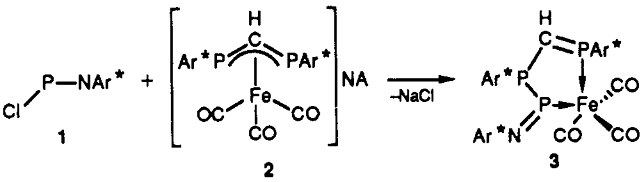
We report here on the first 1-aza-2,3,5-triphosphapenta-1,4-diene complexed by a tricarbonyliron fragment, which was prepared by treating the (1,3-diphosphaallyl)-ferrate(1–) complex **2**[2] (2.18 g, 3 mmol) with the chloroiminophosphane **1**[3] (0.98 g, 3 mmol) in diethyl ether at ambient temperature (Scheme I).

Complex **3**[4] is obtained in 76% yield and can be recrystallized from pentane, thus affording deep red single crystals.

The formation of **3** can formally be viewed as a combination of a 1,3-diphosphaallyl anion with an iminophosphenium cation in the coordination sphere of an iron atom.

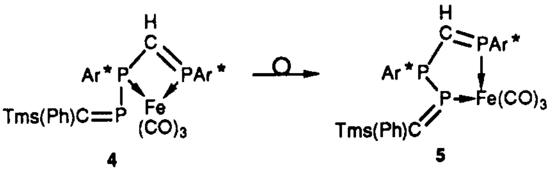
Valuable information concerning the elucidation of the structure of **3** was gained from the ^{31}P{^{1}H} and ^{31}P NMR spectra showing characteristic AMX patterns. The resonances of this AMX system were attributed to the iminophosphane moiety (P$_A$), the phosphaalkene phosphorus atom (P$_M$), and the phosphane nucleus (P$_X$), respectively. However, the exact coordination geometry only became apparent after a single-crystal X-ray diffraction study had been carried out.[5] Some interesting details also revealed by this study account for the observed stability of compound **3**.

Scheme I



Ar* = 2,4,6-t-Bu$_3$C$_6$H$_2$

Scheme II



Tms = Si(CH$_3$)$_3$

The presence of a [Fe(CO)$_3$] fragment and the η^1,η^1 coordination involving two phosphorus atoms of the pentadiene ligand, anticipated from the spectroscopic data, have been confirmed. The geometry around the iron center is essentially trigonal bipyramidal with P1, C2(O2), and C4(O4) occupying equatorial positions and P3 and C3(O3) in axial positions; thus, the pentadiene ligand is in the *s* form. The resulting five-membered chelate core contributes substantially to the stability of complex **3**. Assuming that P2 acts as an equatorial ligand, this would lead to considerable steric strain due to the formation of a four-membered ring.

Here, mention should be made of the 1,3,4-triphosphapentadiene complex **4** obtained by Appel et al.,[2] which is structurally akin to **3** and which was reported to rearrange to the as yet unidentified product **5**. Bearing in mind the results of the structure determination of **3**, we propose an analogous structure for **5** (Scheme II) The obvious strain relief in going from a four-membered ring in **4** to a five-membered ring in **5** strongly supports this interpretation.

Due to its steric demand and its π-acceptor strength the iminophosphane part of the molecule is found in an equatorial position.[6] Furthermore, the remarkably short Fe1–P1 distance of 213.5 (2) pm can be attributed to the P=N moiety being an effective π-acceptor, which also entails some deviations of the equatorial interligand angles from the ideal value of 120°. Similar σ-donor/π-acceptor

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(1) (a) Appel, R.; Niemann, B.; Schuhn, W.; Knoch, F. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 932 and references cited therein. (b) Appel, R., Lecture 2-5, presented at the 11th International Conference on Phosphorus Chemistry, Tallinn, USSR, 1989.

(2) Appel, R.; Schuhn, W. *J. Organomet. Chem.* 1987, *329*, 179.

(3) Niecke, E.; Nieger, M.; Reichert, F. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1715.

(4) Data for compound **3** are as follows. ^{31}P{^{1}H}NMR (δ, C$_6$D$_6$, H$_3$PO$_4$ external) 380.9 (dd; 334.7, 39.8 Hz); 230.1 (dd; 152.6, 39.8 Hz); 20.1 (dd; 334.7, 152.6 Hz). ^{31}P NMR: 380.9 (ddd; 334.7, 39.8, 51.3 Hz); 230.1 (ddd; 152.6, 39.8, 31.5 Hz); 20.1 (ddd; 334.7, 152.6, 19.1 Hz). ^{1}H NMR (δ, C$_6$D$_6$): 7.6 (d, 3 Hz, Ar*); 7.5 (d; 3 Hz; Ar*); 7.2 (s (br), Ar*); 1.3 (s, s, s; 9 H, 9 H, 9 H; *p*-CMe$_3$); 1.4, 1.5, 1.6 (s, 18 H, *o*-CMe$_3$); CH could not be identified. ^{13}C{^{1}H}NMR (δ, C$_6$D$_6$): 211.5 (ddd (br); 5.9 Hz; CO); 160.2 (dd; 11.9, 3.4 Hz; C1/PAr*); 160.0 (d; 13.0 Hz; C1/Ar*PC); 155.6 (dd; 5.5, 3.7 Hz; C2/PAr*); 153.2 (d; 5.6 Hz; C2/PNAr*); 153.0 (d; 5.1 Hz; C2/Ar*PC); 143.2 (d; 4.7 Hz; C4/PAr*); 140.2 (ddd; 40.2, 37.6, 4.7 Hz; P=C); 137.8 (d; 4.9 Hz; C4/Ar*PC); 137.2 (d; 5.1, C4/PNAr*); 132.9 (dd; 7.5 Hz, 3.6 Hz, Cl/PNAr*); 124.3 (d; 8.6 Hz, C3/PAr*); 123.1 (d; 9.5 Hz; C3/Ar*PC); 122.0 (d; 4.3 Hz; C3/PNAr*); 40.2 (d; 1.3 Hz), 39.4 (d; 4.5 Hz), 35.4 (d; 3.6 Hz), *o*-*C*Me$_3$; 36.9 (s), 36.8 (s), 34.7 (s), *p*-*C*Me$_3$; 35.1 (s, br), 34.4 (d; 4.4 Hz), 32.7 (s, br), *o*-C*Me*$_3$; 31.7 (s), 31.3 (s), 30.5 (s), *p*-C*Me*$_3$. IR (cm^{-1}, pentane): 2042 (vs), 1990 (m, br), 1970 (m, br). Anal. Calcd for C$_{58}$H$_{88}$FeNO$_3$P$_3$: C, 69.94; H, 8.91; N, 1.41. Found: C, 70.12; H, 8.86; N, 1.39.

(5) Some crystal data for **3** are as follows: C$_{58}$H$_{88}$FeNO$_3$P$_3$·C$_5$H$_{12}$·0.5CH$_3$CN, M$_r$ = 996.1 (without solvent), monoclinic, space group $P2_1/n$ (No. 14), red crystals, dimensions 0.3 × 0.5 × 0.6 mm, a = 1440.8 (4) pm, b = 2694.9 (6) pm, c = 1883.1 (4) pm, β = 109.46 (2)°, V = 6.894 nm^3, Z = 4, D_c = 1.05 g cm^{-3}, μ(MoKα) = 0.32 mm^{-1}. A total of 11 969 symmetry-independent reflections were recorded with $2\theta_{max}$ = 45°. Of these, 5485 reflections ($|F| > 4\sigma(F)$) were used to solve (direct methods) and refine (624 parameters) the structure of **3**. Non-hydrogen atoms were refined anisotropically; R = 0.083 (R_w = 0.097, $w^{-1} = \sigma^2(F) + 0.0001F^2$).

(6) Haas, H.; Sheline, R. K. *J. Chem. Phys.* **1967**, *47*, 2996.

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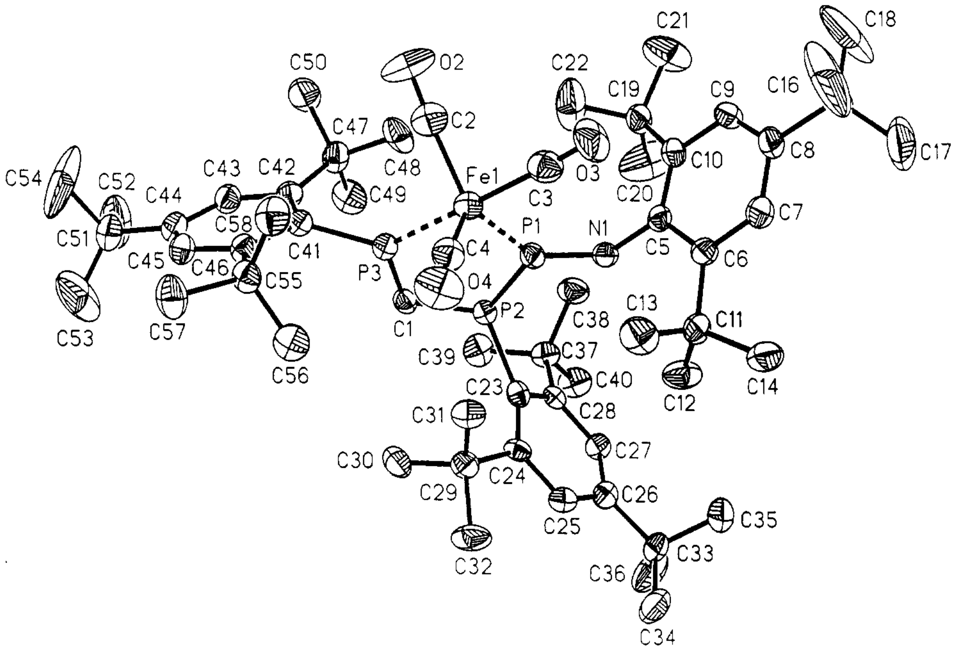

Figure 1. Thermal ellipsoid plot (30%) of **3** with important bond lengths (pm) and angles (deg): Fe(1)-P(1) = 213.5 (2), Fe(1)-P(3) = 225.3 (3), P(1)-P(2) = 220.1 (3), P(1)-N(1) = 155.7 (7), P(2)-C(1) = 174.8 (8), P(2)-C(23) = 185.0 (7), P(3)-C(1) = 168.7 (7), P(3)-C(41) = 185.1 (9), N(1)-C(5) = 142.5 (11); P(1)-Fe(1)-P(3) = 85.4 (1), Fe(1)-P(1)-P(2) = 117.2 (1), Fe(1)-P(1)-N(1) = 137.8 (2), P(2)-P(1)-N(1) = 104.3 (3), P(1)-P(2)-C(1) = 97.1 (3), P(1)-P(2)-C(23) = 113.5 (3), C(1)-P(2)-C(23) = 120.6 (3), Fe(1)-P(3)-C(1) = 118.6 (3), Fe(1)-P(3)-C(41) = 136.3 (2), C(1)-P(3)-C(41) = 104.0 (4), P(1)-N(1)-C(5) = 128.5 (5), P(2)-C(1)-P(3) = 120.3 (5).

properties are exhibited by a complexed diphosphabutadiene ligand, which was obtained by Weber et al.[7] in the reaction of $[(\eta^5\text{-}C_5Me_5)(CO)_2Fe{-}P{=}PAr^*]$ with $[MeC{\equiv}CC(O)OMe]$. The iron–phosphorus distance in the product structurally related to **3** was also found to be very short (211.7 (2) pm).

The extremely strong back-bonding exerted by the metal center can be evaluated by comparison of the Fe1–P1 bond distance with the iron–phosphorus distance in $[(\eta^1\text{-}Ar^*P{=}PAr^*)Fe(CO)_4]$ (221.5 pm).[8] With the Fe1–P3 bond length amounting to 225.3 (3) pm, this exemplifies once more the considerable difference between a P=C and a P=N fragment with regard to their respective π-acceptor properties. However, as a whole the heteropentadiene system appears to be a weaker π-acceptor than two carbonyl ligands, which can be inferred from the positions of the IR signals shifted to lower wavenumbers compared to the values found for iron pentacarbonyl.

The pyramidalization of the phosphane P2 (sum of angles 343.6°) leads to a slight distortion of the P3–Fe1–C3 axis, meaning that these three atoms making an angle of 170.3° do not lie in a plane. The P2–C1 and P3–C1 bond lengths (174.8 (8) and 168.7 (7) pm, respectively) imply a certain delocalization of π-electron density involving P2, to which can be attributed some sp^2 character. The P–N bond distance (155.7 (7) pm) and the valence angle at the nitrogen atom (128.5 (5)°) lie within the range of values so far observed for this class of compounds.[9]

In summary, compound **3** represents an intrinsically stabilized molecule, which is why it is not surprising that reactions aiming at the liberation of the heteropentadiene ligand did fail.

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for a scholarship (to J.H.).

Supplementary Material Available: Tables of positional parameters, bond distances and angles, and anisotropic thermal parameters for non-hydrogen atoms and atomic coordinates and isotropic thermal parameters for hydrogen atoms (8 pages); a listing of observed and calculated structure factors (43 pages). Ordering information is given on any current masthead page.

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[9] Niecke, E. Iminophosphanes. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Thieme Verlag: in press. Niecke, E.; Gudat, D. *Angew. Chem., Int. Ed. Engl.*, in press.