

Reaction of 1-((Pentamethylcyclopentadienyl)(dicarbonyl)ferrio)-2-(2,4,6-*tert*-butylphenyl)diphosphene with 1,2,4-Triazoline-3,5-diones: Formations and Structures of the First 1,2-Diaza-3,4-diphosphetidines and *E,E*-1,7-Dioxa-4,5,10,11-tetraaza-3,4,8,9-tetraphosphacyclododeca-5,11-diene

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Reaction of $[(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{Fe-P-P-Mes}^*]$ **1** (Mes* = 2,4,6-Bu₃C₆H₂) with 1,2,4-triazoline-3,5-diones

$[\text{N}=\text{N}-\text{C}(\text{O})\text{N}(\text{R})\text{C}(\text{O})]$ **2** (**a**: R = Ph; **b**: R = 4-EtOC₆H₄) in benzene at ambient temperature affords the first 1,2-diaza-3,4-diphosphetidines as part of the bicyclic compounds **4**, whereas in diethyl ether solution the twelve-membered macrocycle **5** is obtained.

In the series of the four-membered phosphorus–nitrogen ring systems **A–F** derivatives with the 1,3-diaza-2,4-diphosphetidine-**D**,¹ the azatriphosphetidine-**E**,² and the cyclotetraphosphane-**F** skeleton³ were described in the literature. Moreover radicals derived from ring **B** were detected by EPR evidence.⁴ Here we perform a synthetic approach to the novel 1,2-diaza-3,4-diphosphetidines **C**.

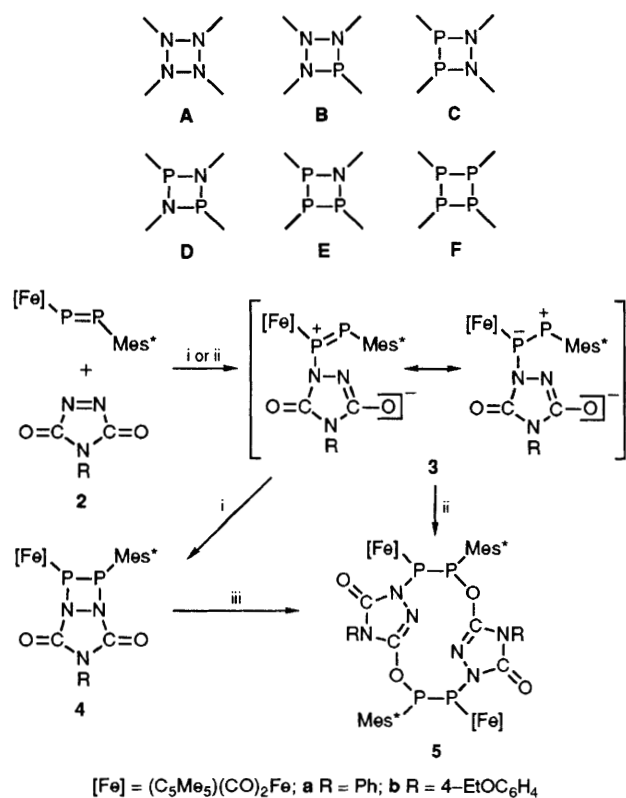
Reaction of $[(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{Fe-P-P-Mes}^*]$ **1**⁵ with the 4-aryl-1,2,4-triazoline-3,5-diones **2** (**a**: aryl = C₆H₅; **b**: aryl = 4-EtOC₆H₄) in benzene at 20 °C lead to the orange–yellow complexes **4**, as the result of a [2 + 2]-cycloaddition. The formation of **4** is accompanied by a strong highfield shift in the ³¹P NMR spectrum ($\Delta\delta$ PFe = 383.0 and 381.6; $\Delta\delta$ PMes* = 443.2 and 443.1 ppm) with respect to the resonances of **1** (715.2 d, 553.5 d, ¹J_{PP} 594.2 Hz) while the coupling constant of **1** is decreased considerably (¹J_{PP} 107.6 Hz in **4a**; 106.3 Hz in **4b**).

The reaction of **1** and **2** takes a different course, when performed in diethyl ether in the temperature range from –60 to +20 °C. Here red crystalline **5a** and **b** are isolated by fractional crystallization. At –40 °C doublets in the ³¹P NMR

spectrum at δ 143 and 345 with the large coupling ¹J_{PP} 635 Hz are in agreement with the formation of the zwitterionic adduct **3**. When warmed up these signals disappear in favour of the doublet resonances of **5a** at δ 166.6 and 144.5 (¹J_{PP} 220.9 Hz) or **5b** at δ 164.6 and 142.7 (¹J_{PP} 220.4 Hz). With prolonged stirring of the diethyl ether solution of **4**, ring opening and a [6 + 6] head-to-tail cyclodimerization of **3** to the macrocycle **5** occurs.

The molecular structures of the novel ring systems **4** and **5** could not unambiguously be derived from spectroscopic data† and thus were elucidated by single crystal X-ray diffraction analysis‡ of **4a** and **5b**.

The most interesting feature of the structure of **4a** is the bicyclic organophosphorus ligand on iron. It consists of a 1,2-diaza-3,4-diphosphetidine which is fused to a 1,2,4-triazolidine-3,5-dione *via* the atoms N(1) and N(2). The four-membered ring is puckered [dihedral angle between the planes P(2)–P(1)–N(1) and P(2)–N(2)–N(1) = 164.1°] and shows significantly elongated PN- [P(1)–N(1) = 1.825(5), P(2)–N(2) = 1.777(5) Å] and P–P-bonds [2.275(2) Å] (calculated values are 1.766° and 2.227° Å, respectively). For the



Scheme 1. Reagents and conditions: i, **1** benzene, 20 °C, 1 h, **2** (1 mol equiv.); ii, **1**, **2**, diethyl ether, –30 to +20 °C, 1 h; iii, **4**, diethyl ether, 24 h, 20 °C

† Selected NMR data for **4a**: ³¹P NMR (C₆D₆ 40.534 MHz): 110.4 (d, ¹J_{PP} 106.3 Hz, P–Mes*), 333.6 (d, ¹J_{PP} 106.3 Hz, P–Fe); ¹³C {¹H} NMR (C₆D₆): 157.5 (m, N₂C=O), 157.8 (m, N₂C=O), 214.9 (m, FeCO), 216.4 (m, FeCO); IR (Nujol) ν/cm^{-1} : [$\nu(\text{FeCO})$] 1955, 1990.

4b: ³¹P NMR (C₆D₆): 110.3 (d, ¹J_{PP} 107.6 Hz, P–Mes*), 332.2 (d, ¹J_{PP} 107.6 Hz, P–Fe); IR (Nujol) ν/cm^{-1} [$\nu(\text{FeCO})$] 1959, 1996.

5a: ³¹P NMR (C₆D₆): 144.5 (d, ¹J_{PP} 220.9 Hz), 166.6 (d, ¹J_{PP} 220.9 Hz); ¹H NMR (C₆D₆): 1.33 (s, 9H, *p*-Bu^t), 1.51 (s, 15H, C₅Me₅), 1.75 (s, 9H, *o*-Bu^t), 2.03 (s, 9H, *o*-Bu^t), 6.89–6.95 (m, 2H, NPh), 7.41–7.59 (m, 3H, N–Ph), 7.74 (d, *J* 7.6 Hz, 2H, *m*-aryl-H); ¹³C {¹H} NMR (C₆D₆): 161.7 (s, OC=N), 163.2 (s, N₂C=O), 213.2 (m, FeCO), 215.1 (m, FeCO); IR (Nujol) ν/cm^{-1} [$\nu(\text{FeCO})$] 1957, 2012.

5b: ³¹P NMR (C₆D₆): 142.7 (d, ¹J_{PP} 220.4 Hz), 164.6 (d, ¹J_{PP} 220.4 Hz); ¹H NMR (C₆D₆): 1.00 (m, 3H, OCH₂Me), 1.32 (s, 9H, *p*-Bu^t), 1.53 (s, C₅Me₅), 1.80 (s, 9H, *o*-Bu^t), 2.05 (s, *o*-Bu^t), 3.48 (m, 2H, OCH₂CH₃), 7.10 (m, 4H, C₆H₄), 7.53 (d, *J* 13 Hz, *m*-aryl-H); ¹³C {¹H} NMR (C₆D₆): 159.1 (s, OC=N), 163.1 (s, N₂C=O), 213.9 (d, *J* 10.9 Hz, FeCO), 215.2 (d, *J* 9.7 Hz, FeCO); IR (Nujol) ν/cm^{-1} [$\nu(\text{FeCO})$] 1962, 2010.

‡ Crystal data: C₃₈H₄₉FeN₃O₄P₂ **4a**, *M* = 729.6, triclinic, space group *P* $\bar{1}$, *a* = 10.561(2), *b* = 13.391(4), *c* = 14.745(4) Å, α = 87.96(2), β = 69.76(2), γ = 82.36(2)°, *V* = 1938.8(9) Å³, *Z* = 2, $\lambda(\text{Mo-K}\alpha)$ = 0.71073 Å, $\mu(\text{Mo-K}\alpha)$ = 0.508 mm^{–1}; *D*_c = 1.250 g cm^{–3}; $2\theta_{\text{max}}$ = 55°. The structure was solved by direct methods and refined by full-matrix least-squares refinement to a current *R*_w = 0.044, based on 4285 reflections with *F*_o ≥ 4.0σ(*F*_o).

C₈₀H₁₀₆Fe₂N₆O₁₀P₄ **5b**, *M* = 1547.4, orthorhombic, space group *Pbca*, *a* = 16.291(5), *b* = 25.581(7), *c* = 41.297(11) Å, α = β = γ = 90°, *V* = 17 209(7) Å³, *Z* = 8, $\lambda(\text{Mo-K}\alpha)$ = 0.71069 Å, $\mu(\text{Mo-K}\alpha)$ = 0.47 mm^{–1}; *D*_c = 1.250 g cm^{–3}; $2\theta_{\text{max}}$ = 45°. The structure was solved by direct methods and refined by full-matrix least-squares refinement to a current *R*_w = 0.081, based on 6104 reflections [*F*_o ≥ 4σ(*F*_o)].

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

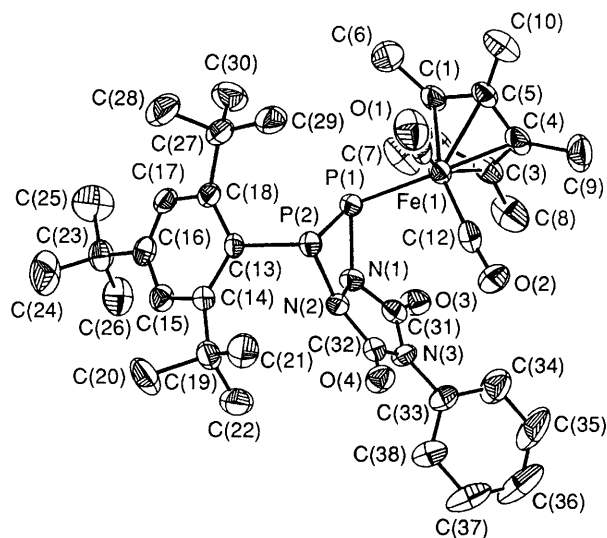


Fig. 1 ORTEP view of the structure of **4a** in the crystal. Important bond lengths (Å) and angles (°) are: Fe–P(1) 2.296(2), P(1)–P(2) 2.275(2), P(2)–C(13) 1.881(5), P(1)–N(1) 1.825(5), P(2)–N(2) 1.777(5), N(1)–N(2) 1.429(6); Fe(1)–P(1)–P(2) 108.4(1), P(1)–P(2)–C(13) 97.9(2), P(1)–P(2)–N(2) 76.5(2), N(1)–N(2)–P(2) 103.9(3), P(1)–N(1)–N(2) 101.9(3), P(1)–N(1)–C(31) 128.7(4), N(2)–N(1)–C(31) 107.9(4), P(2)–N(2)–C(32) 133.7(3), N(1)–N(2)–C(32) 109.8(4).

parent molecule $P_2N_2H_4$ a much longer PP bond (2.320 Å) and normal PN single bond distances (1.756 and 1.757 Å) were calculated. The dihedral angle in the heterocycle was found to be 173.7°. ⁸

Compound **5** represents the first example of *E,E*-1,7-dioxa-4,5,10,11-tetraaza-3,4,8,9-tetraphosphadodeca-5,11-diene. The macrocycle is present in a crown conformation, in which two boat-like halves defined by the atoms N(2), C(14), O(4), P(3), P(4), N(5) and N(2), N(1), P(1), P(2), O(9), C(53) and N(5) are connected *via* N(2) and N(5).

The two five-membered rings, fused to the macrocycle, adopt a parallel orientation (dihedral angle 17.5°). Within the latter the P–P (2.250(4), 2.235(4) Å), the P–N [1.772(9), 1.771(8) Å], and the P–O contacts [1.733(7), 1.737(7) Å] indicate the bond order of unity (calc. P–O = 1.72 Å⁶).

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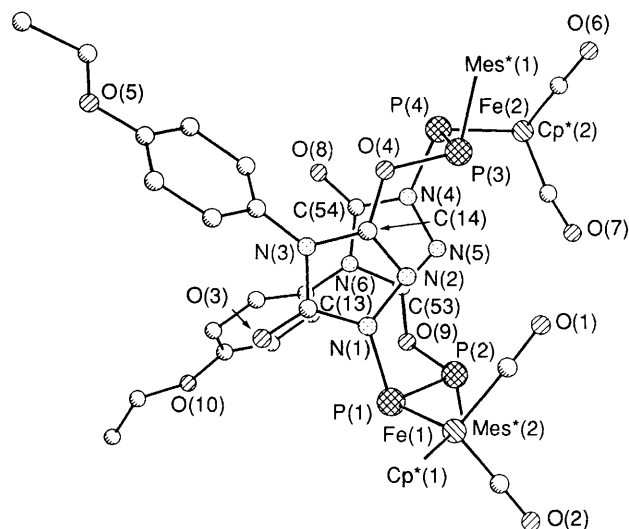


Fig. 2 View of the structure of **5b** in the crystal. The supermesityl rings Mes*(1) and Mes*(2) as well as the η^5 -C₅Me₅ ligand Cp*(1) and Cp*(2) are omitted for clarity. Important bond lengths (Å) and angles (°) are: Fe(1)–P(1) 2.277(3), Fe(2)–P(2) 2.250(4), P(1)–P(2) 2.235(4), P(3)–P(4) 2.250(4), N(1)–N(2) 1.417(11), N(4)–N(5) 1.422(11), P(1)–N(1) 1.772(9), P(4)–N(4) 1.771(8), P(2)–O(9) 1.737(7), P(3)–O(4) 1.733(7); N(1)–P(1)–P(2) 93.5(3), P(1)–P(2)–O(9) 101.0(3), N(4)–P(4)–P(3) 92.6(3), P(4)–P(3)–O(4) 99.6(3), Fe(1)–P(1)–P(2) 105.0(1), Fe(2)–P(4)–P(3) 105.6(1).

References

- O. J. Scherer and W. Gläsel, *Chem. Ber.*, 1977, **110**, 3874; E. Niecke and O. J. Scherer, *Nachr. Chem. Techn.*, 1975, **23**, 395; E. Niecke and D. Gudat, *Angew. Chem.*, 1991, **103**, 251 and references cited therein.
- E. Niecke, R. Rüger, B. Krebs and M. Dartmann, *Angew. Chem.*, 1983, **95**, 570; *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 552.
- L. Weber, D. Bungardt, K. Reizig, R. Boese and R. Benn, *Chem. Ber.*, 1987, **120**, 451 and references cited therein.
- J. C. Brand and B. P. Roberts, *J. Chem. Soc., Chem. Commun.*, 1981, 1107.
- L. Weber, K. Reizig, D. Bungardt and R. Boese, *Organometallics*, 1987, **6**, 110.
- Lehrbuch der Anorganischen Chemie*, ed. de Gruyter, Holleman-Wiberg, Berlin, New York 1976, vol. 81–90, p. 129.
- K. F. Tebbe, *Z. Anorg. Allg. Chem.*, 1980, **468**, 202.
- W. W. Schoeller, T. Busch, J. Niemann, T. Dabisch and W.-D. Stohrer, *Heteroatom Chem.*, 1991, **2**, 213.