Reaction of 1-{(Pentamethylcyclopentadienyl)(dicarbonyl)ferrio}-2-(2,4,6-tri-*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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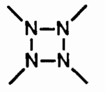
Reaction of $[(\eta^5\text{-}C_5Me_5)(CO)_2Fe{-}P{=}P{-}Mes^*]$ **1** (Mes* = 2,4,6-$Bu^t_3C_6H_2$) with 1,2,4-triazoline-3,5-diones $[\overline{N{=}N{-}C(O)N(R)C}(O)]$ **2** (**a**: R = Ph; **b**: R = 4-$EtOC_6H_4$) in benzene at ambient temperature affords the first 1,2-diaza-3,4-diphosphetidines as 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** skeleton[3] 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 $[(\eta^5\text{-}C_5Me_5)(CO)_2Fe{-}P{=}P{-}Mes^*]$ **1**[5] with the 4-aryl-1,2,4-triazoline-3,5-diones **2** (**a**: aryl = C_6H_5; **b**: aryl = 4-$EtOC_6H_4$) 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 ^{31}P NMR spectrum (Δδ PFe = 383.0 and 381.6; Δδ 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 ^{31}P 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.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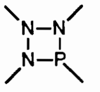
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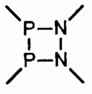
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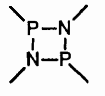
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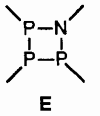
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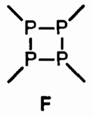
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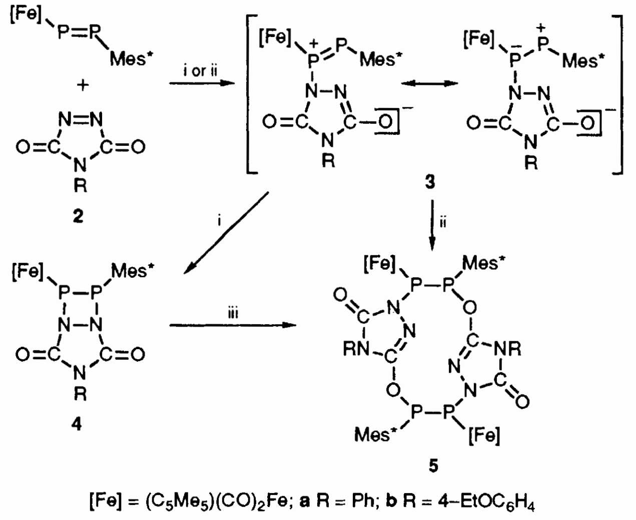

[Fe] = $(C_5Me_5)(CO)_2Fe$; **a** R = Ph; **b** R = 4-$EtOC_6H_4$

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

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 at 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 1.76[6] and 2.22[7] Å, respectively). For the

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† *Selected NMR data* for **4a**: ^{31}P NMR (C_6D_6 40.534 MHz): 110.4 (d, $^1J_{PP}$ 106.3 Hz, P–Mes*), 333.6 (d, $^1J_{PP}$ 106.3 Hz, P–Fe); $^{13}C\{^1H\}$ NMR (C_6D_6): 157.5 (m, $N_2C{=}O$), 157.8 (m, $N_2C{=}O$), 214.9 (m, FeCO), 216.4 (m, FeCO); IR (Nujol) ν/cm^{-1}: [ν(FeCO)] 1955, 1990.

4b: ^{31}P NMR (C_6D_6): 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} [ν(FeCO)] 1959, 1996.

5a: ^{31}P NMR (C_6D_6): 144.5 (d, $^1J_{PP}$ 220.9 Hz), 166.6 (d, $^1J_{PP}$ 220.9 Hz); ^1H NMR (C_6D_6): 1.33 (s, 9H, *p*-Bu^t, 1.51 (s, 15H, C_5Me_5), 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); $^{13}C\{^1H\}$ NMR (C_6D_6): 161.7 (s, OC=N), 163.2 (s, $N_2C{=}O$), 213.2 (m, FeCO), 215.1 (m, FeCO); IR (Nujol) ν/cm^{-1} [ν(FeCO)] 1957, 2012.

5b: ^{31}P NMR (C_6D_6): 142.7 (d, $^1J_{PP}$ 220.4 Hz), 164.6 (d, $^1J_{PP}$ 220.4 Hz), ^1H NMR (C_6D_6): 1.00 (m, 3H, OCH_2*Me*), 1.32 (s, 9H, *p*-Bu^t) 1.53 (s, C_5Me_5), 1.80 (s, 9H, *o*-Bu^t), 2.05 (s, *o*-Bu^t), 3.48 (m, 2H, O*C*H_2CH_3), 7.10 (m, 4H, C_6H_4), 7.53 (d, *J* 13 Hz, *m*-aryl-H); $^{13}C\{^1H\}$ NMR (C_6D_6): 159.1 (s, OC=N), 163.1 (s, $N_2C{=}O$), 213.9 (d, *J* 10.9 Hz, FeCO), 215.2 (d, *J* 9.7 Hz, FeCO); IR (Nujol) ν/cm^{-1} [ν(FeCO)] 1962, 2010.

‡ *Crystal data*: $C_{38}H_{49}FeN_3O_4P_2$ **4a**, $M = 729.6$, triclinic, space group $P\bar{1}$, $a = 10.561(2)$, $b = 13.391(4)$, $c = 14.745(4)$ Å, $\alpha = 87.96(2)$, $\beta = 69.76(2)$, $\gamma = 82.36(2)°$, $V = 1938.8(9)$ Å^3, $Z = 2$, λ(Mo-Kα) = 0.71073 Å, μ(Mo-Kα) = 0.508 mm^{-1}; $D_c = 1.250$ g cm^{-3}; $2\theta_{max} = 55°$. 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 $F_o \geq 4.0\sigma(F)$.

$C_{80}H_{106}Fe_2N_6O_{10}P_4$ **5b**, $M = 1547.4$, orthorhombic, space group *Pbca*, $a = 16.291(5)$, $b = 25.581(7)$, $c = 41.297(11)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 17\,209(7)$ Å^3, $Z = 8$, λ(Mo-Kα) = 0.71069 Å, μ(Mo-Kα) = 0.47 mm^{-1}; $D_c = 1.250$ g cm^{-3}; $2\theta_{max} = 45°$. 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 $[F_o \geq 4\sigma(F_o)]$.

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.

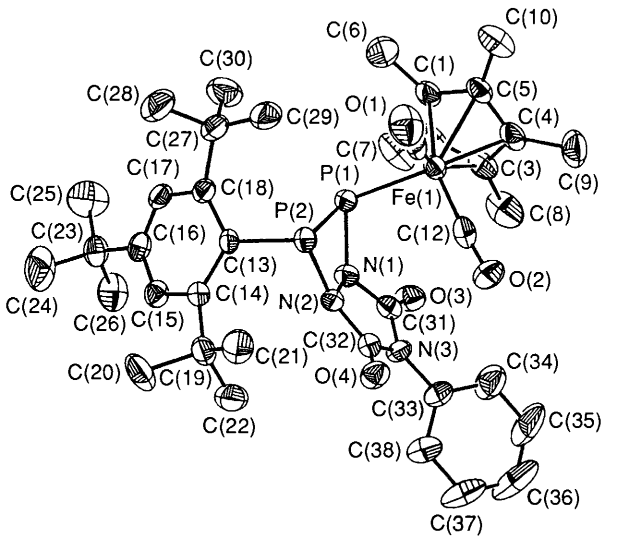

Fig. 1 ORTEP view of the structure of **4a** in the crystal. Important bond lengths (Å) and angles (°) are: Fe–P(1) 2.296(2), P(1)–P(2) 2.275(2), P(2)–C(13) 1.881(5), P(1)–N(1) 1.825(5), P(2)–N(2) 1.777(5), N(1)–N(2) 1.429(6); Fe(1)–P(1)–P(2) 108.4(1), P(1)–P(2)–C(13) 97.9(2), P(1)–P(2)–N(2) 76.5(2),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

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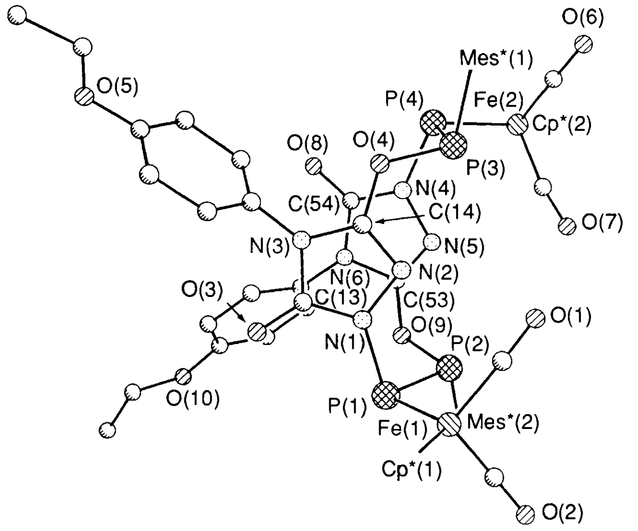

Fig. 2 View of the structure of **5b** in the crystal. The supermesityl rings Mes*(1) and Mes*(2) as well as the η^5-C_5Me_5 ligand Cp*(1) and Cp*(2) are omitted for clarity. Important bond lengths (Å) and angles (°) are: Fe(1)–P(1) 2.277(3), Fe(2)–P(2) 2.250(4), P(1)–P(2) 2.235(4), P(3)–P(4) 2.250(4), 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).

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