Reaction of 1-(Pentamethylcyclopentadienyl)(dicarbonyl)ferriodicarbonylbutylnylphenyl)diophosphine with 1,2,4-Triazoline-3,5-diones: Formations and Structures of the First 1,2-Diaza-3,4-diphenophosphine and E,E,1,7-Dioxacyclopentadec-5-11-diene

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Reaction of [(Mes&CO)(CO)]_2Fe=P=P-Mes* with 1,2,4-triazoline-3,5-diones [N=N-C(O)(R)=O](CO)_(2) 2 (a: R = Ph; b: R = 4-4EtOC_6H_4) in benzene at ambient temperature affords the first 1,2-diaza-3,4-diphenophosphine 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 azatriphosphidene-E, 2 and the cyclotetraphosphophane-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 as part of the bicyclic compounds 4, whereas in diethyl ether solution the twelve-membered macrocycle 5 is obtained.

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 (δ 143 and 345 with the large coupling 1Jpp 635 Hz) 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 (1Jpp 220.9 Hz) or 5b at δ 164.6 and 142.7 (1Jpp 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 6 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-diphenophosphine which is fused to a 1,4-triazolidine-3,5-diene via the atoms N1 and N(2). The four-membered ring is puckered [dihedral angle between the planes P2-P1(11)-N(1) and P2-P1(12)-N(1) = 164.1°] and shows significantly elongated PN- [P(1)-N(1) = 1.766 and 2.227 Å], respectively. For the

Structure 5C was solved by direct methods and refined by full-matrix least-squares refinement to a current R = 0.044, based on 6104 reflections with Fc = 2400(F0). 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.

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Fig. 1 ORTEP view of the structure of 4a in the crystal. Important bond lengths (Å) and angles (°) are: Fe-P(l) 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) 1.420(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) 128.7(4), P(1)-N(1)-Fe(1) 109.8(4).parent molecule P$_2$N$_2$H$_4$ 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-di-oxa-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).

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