Synthesis of the First Example of a 1,3,4,6-Tetraphospha-hexatriene Complex

Agustin Galindo del Pozo,[a] Anne-Marie Caminade,[a] Françoise Dahan,[b] Jean-Pierre Majoral,*[a] and René Mathieu*[b]

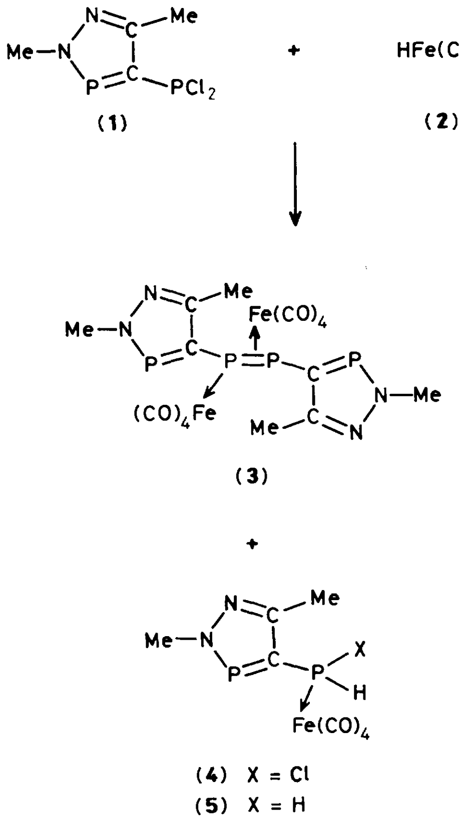
[a] *UA 454, Université Paul Sabatier, 118, route de Narbonne, 31062 Toulouse Cedex, France*

[b] *Laboratoire de Chimie de Coordination du CNRS, Unité nº 8241 liée par convention à l'Université Paul Sabatier, 205, route de Narbonne, 31077 Toulouse Cedex, France*

A convenient access to the first example of a 1,3,4,6-tetraphospha-hexatriene complex, a diphosphene bearing two cyclic dico-ordinated phosphorus substituents and σ,η²-bonded to Fe(CO)₄ units, and characterized by *X*-ray structure analysis, is described.

Although a great deal has been published in the last decade about the chemistry of compounds containing λ^3-phosphorus with co-ordination number 2, only a few investigations were concerned with the preparation of conjugated polyenes in which one or more carbon atoms are replaced by di-co-ordinated phosphorus atoms.[1] We now report the synthesis of a diazaphosphole substituted diphosphene σ,η^2 complex, *i.e.* a compound in which a P=P and two P=C double bonds are conjugated.

Reaction of compound (**1**)[2] with the anionic iron hydrido carbonyl metallate $[HFe(CO)_4]^-$ (**2**),[3] in dichloromethane, leads to the formation of complex (**3**) in 31% yield.† Depending on the experimental conditions, low yields of the new monohalogeno and primary phosphine complexes (**4**) and (**5**) are also obtained.‡ The red tetraphospha-hexatriene (**3**),‡ isolated in crystalline form, was characterized by mass spectrometry and elemental analyses. The ^{31}P n.m.r. spectrum showed the pattern expected for an ABXY system with the AB part shifted up field[3a] [$\delta(^{31}P)$ -52.4 and $+8.2$ p.p.m.] and the XY part (no coupling between X and Y) in the PC



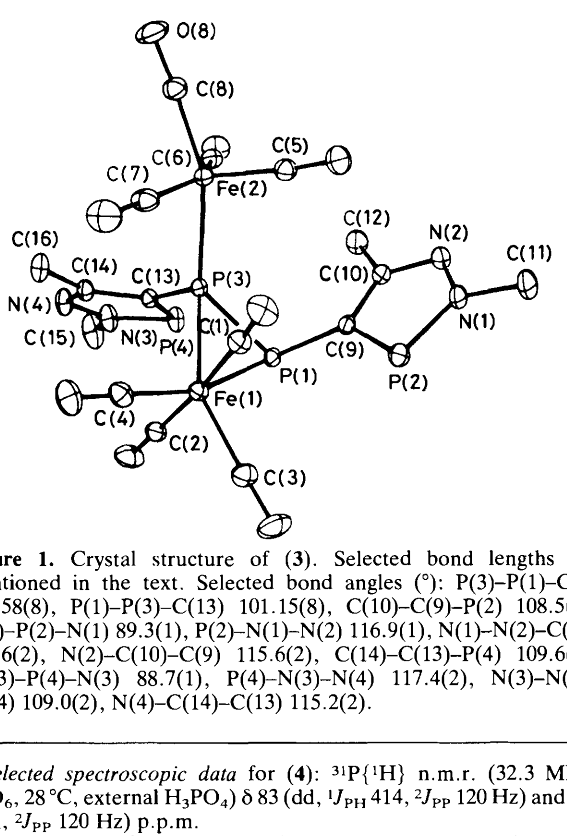


Figure 1. Crystal structure of (**3**). Selected bond lengths are mentioned in the text. Selected bond angles (°): P(3)–P(1)–C(9) 105.58(8), P(1)–P(3)–C(13) 101.15(8), C(10)–C(9)–P(2) 108.5(2), C(9)–P(2)–N(1) 89.3(1), P(2)–N(1)–N(2) 116.9(1), N(1)–N(2)–C(10) 109.6(2), N(2)–C(10)–C(9) 115.6(2), C(14)–C(13)–P(4) 109.6(2), C(13)–P(4)–N(3) 88.7(1), P(4)–N(3)–N(4) 117.4(2), N(3)–N(4)–C(14) 109.0(2), N(4)–C(14)–C(13) 115.2(2).

---

† To (**1**) (1 mmol) in dichloromethane (15 ml) was added dropwise $[PPh_4][HFe(CO)_4]$ (1 mmol) in dichloromethane (12 ml) at room temperature. The solution then was stirred for 30 min. Evaporation to dryness and extraction of the residue with hexane (3 × 15 ml) gave, after concentration of the extracts and cooling to −40 °C, (**3**) as red crystals; mass spectrum *m/z* 624 (M^+), with successive loss of 8 CO. Satisfactory elemental analyses were obtained.

‡ *Selected spectroscopic data* for (**4**): $^{31}P\{^1H\}$ n.m.r. (32.3 MHz, C_6D_6, 28 °C, external H_3PO_4) δ 83 (dd, $^1J_{PH}$ 414, $^2J_{PP}$ 120 Hz) and 261 (dm, $^2J_{PP}$ 120 Hz) p.p.m.

For (**5**): $^{31}P\{^1H\}$ n.m.r. δ -57 (dt, $^1J_{PH}$ 374, $^2J_{PP}$ 101 Hz) and 252 (dm, $^2J_{PP}$ 101 Hz) p.p.m.

For (**3**): $^{31}P\{^1H\}$ n.m.r. (32.3 MHz, CD_2Cl_2, 28 °C, external H_3PO_4) δ -52.38 (P-1, dd, $^1J_{P1P3}$ 384, $^2J_{P1P2}$ 166 Hz), $+8.22$ (P-3, ddd, $^1J_{P3P1}$ 384, $^3J_{P2P3}$ 19, $^2J_{P3P4}$ 36 Hz), 224.76 (P-2, dd, $^2J_{P2P1}$ 166, $^3J_{P2P3}$ 19 Hz), 244.3 (P-4, d, $^2J_{P4P3}$ 36 Hz) p.p.m.; ^1H n.m.r. (90 MHz, C_6D_6, internal $SiMe_4$, 28 °C) δ 2.68 (d, $^4J_{HP}$ 1.4 Hz, 3H, Me), 2.73 (d, $^4J_{HP}$ 1.4 Hz, 3H, Me) 3.24 (d, $^3J_{HP}$ 7.7 Hz, 3H, NMe), 3.38 (d, $^3J_{HP}$ 7.8 Hz, 3H, NMe); $^{13}C\{^{31}P$ and $^1H\}$ n.m.r. (62.89 MHz, $CDCl_3$, 28 °C, internal $SiMe_4$) δ C-16 15.39 (s), C-12 15.51 (s), C-15 41.39 (d, J_{C15P4} 18 Hz), C-11 41.12 (d, J_{C11P2} 18 Hz), C-13 141.20 (dd, J_{C13P1} 16.25, J_{C13P4} 59 Hz), C-9 152.71 (dd, J_{C9P1} 26, J_{C9P2} 59 Hz), C-14 157.38 (br. s), C-10 159.69 (br. dd, J_{C10P1} 16.25, J_{C10P2} 7 Hz), C-5—8 216.46 (d, J_{CP3} 11 Hz), C-3,4 205.64 and 201.24 (br. s), C-1,2 204.77 (dd, J_{CP3} 11, J_{CP} 6 Hz), and 201.90 (dd, J_{CP3} 11, J_{CP1} 6 Hz). (Assignments are based on selective decoupling of phosphorus nuclei); i.r. (hexane) ν(CO) 2101, 2054, 2045, 2026, 2020, 1982, 1970, 1962, and 1940 cm⁻¹.

double bond region [δ (^{31}P) +224.8 and +244.3 p.p.m.]. $^{13}C\{^{31}P\}$ and ^{1}H n.m.r. spectra further support this assumption.‡ Moreover, characteristic CO vibration frequencies for a σ, η^2 diphosphene complex were found in the i.r. spectrum.[3a]

The structure of (**3**) was clearly established by a single crystal *X*-ray diffraction study (Figure 1).§ The diphosphene is in a *trans*-configuration. The phosphorus–phosphorus bond [2.1504(8) Å] is considerably longer than normal free PP double bonds, and is typical for a diphosphene acting as a side-on and end-on bonding ligand.¶ Endocyclic and exocyclic bond distances suggest that the unsaturation is delocalized: C=N 1.320(3) and 1.322(3) Å; P=C 1.713(2) and 1.714(3) Å; N–N 1.337(3) and 1.351(4) Å; C–C (endo) 1.423(4) and 1.410(3) Å; P–C 1.801(2) and 1.802(2) Å (normal bond lengths: C–N 1.26; P=C 1.67—1.69; N–N 1.46; C–C 1.51; P–C 1.85 Å).

We have previously shown that the reactivity of dichlorophosphines $RPCl_2$ towards (**2**) strongly depends on the nature of the substituent R.[3] Indeed, a σ, η^2 diphosphene complex is obtained only when R = Ph, while various halogenophosphine or diphosphane complexes are formed from alkyl or aminodichlorophosphines. It seems therefore that the conjugation also plays a key role in the formation of compound (**3**). Taking into account this observation, the synthesis of multi-conjugated dico-ordinated phosphorus polyenes is underway.

We thank the C.N.R.S. for a grant to A. G. P.

Received, 24th November 1987; Com. 1708

References

1 R. Appel, V. Barth, and F. Knoch, *Chem. Ber.*, 1983, **116**, 939; R. Appel, P. Fölling, W. Schuhn, and F. Knoch, *Tetrahedron Lett.*, 1986, **27**, 1661; R. Appel and R. Moors, *Angew. Chem.*, 1986, **98**, 570; *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 567; R. Appel, V. Winklaus, and F. Knoch, *Chem. Ber.*, 1987, **120**, 243; A. Schmidpeter, C. Leyh, and K. Karaghiosoff, *Angew. Chem.*, 1985, **97**, 127; *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 124; O. J. Scherer, H. Sitzmann, and G. Wolmershäuser, *Angew. Chem.*, 1985, **97**, 358; *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 351; G. Märkl, W. Weber, and W. Weiss, *Chem. Ber.*, 1985, **118**, 2365; V. D. Romanenko, L. S. Kachkovskaya, and L. N. Markovskii, *Z. Obsch. Khim.*, 1985, **55**, 2140; P. B. Hitchcock, M. J. Maah, and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1986, 733.

2 J. Luber and A. Schmidpeter, *J. Chem. Soc., Chem. Commun.*, 1976, 887; J. H. Weinmaier, J. Luber, A. Schmidpeter, and S. Pohl, *Angew. Chem.*, 1979, **91**, 442; *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 441; J. H. Weinmaier, G. Brunnhuber, and A. Schmidpeter, *Chem. Ber.*, 1980, **113**, 2278.

3 (a) R. Mathieu, A.-M. Caminade, J.-P. Majoral, S. Attali, and M. Sanchez, *Organometallics*, 1986, **5**, 1914; (b) R. Mathieu, A.-M. Caminade, J.-P. Majoral, and J.-C. Daran, *J. Am. Chem. Soc.*, 1986, 8007; (c) J.-P. Majoral, R. Mathieu, A.-M. Caminade, S. Attali, and M. Sanchez, *Phosphorus Sulfur*, 1987, **30**, 443; (d) A.-M. Caminade, J.-P. Majoral, A. Igau, and R. Mathieu, *Nouv. J. Chem.*, 1987, **6**, 457; (e) A.-M. Caminade, J.-P. Majoral, R. Mathieu, and Y. Y. C. Yeung Lam Ko, *J. Chem. Soc., Chem. Commun.*, 1987, 639; (f) A.-M. Caminade, J.-P. Majoral, M. Sanchez, R. Mathieu, S. Attali, and A. Grand, *Organometallics*, 1987, **6**, 1459.

4 K. M. Flynn, H. Hope, B. D. Murray, M. M. Olmstead, and P. Power, *J. Am. Chem. Soc.*, 1983, **105**, 7750.

---

§ *Crystal data*: $C_{16}H_{12}Fe_2N_4O_8P_4$, monoclinic, space group $P2_1/c$, a = 14.334(2), b = 10.714(1), c = 17.474(2) Å, β = 112.36(1)°, U = 2481.8(9) Å^3, Z = 4, D_c = 1.67 g cm^{-3}. Measurement: CAD4; solution: SHELX programs. 5416 unique reflections, 4438 observed [$I > 3\sigma(I)$], empirical absorption corrections, number of variables: 307, R = 0.023, R_w = 0.026. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

¶ P=P distances: 2.139 Å for $Fe(CO)_4\{\mu\text{-}Fe(CO)_4\}(PPh)_2$,[3a] 2.184 Å for $Fe(CO)_4\{\mu\text{-}Fe(CO)_4\}(P\text{-}2,4,6\text{-}Bu^t{}_3C_6H_2O)_2$.[4]