The First 3-Methanediyl-1,3,5,6-tetraphosphabicyclo[3.1.0]hex-2-ene. Evidence for a [3 + 2] Cycloaddition of a 2,4,5,6-Tetraphosphahepta-1,3,6-triene

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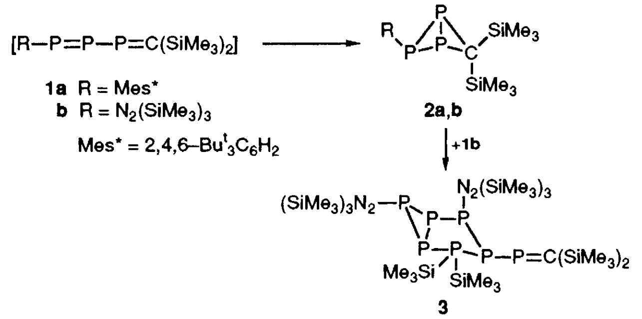
Reaction of $(\eta^5\text{-}C_5Me_5)(CO)_2FeP(SiMe_3)_2$ with three equivalents of $Cl{-}P{=}C(SiMe_3)_2$ affords the first 3-methanediyl-1,3,5,6-tetraphosphabicyclo[3.1.0.]hex-2-ene **7**, the molecular structure of which has been determined by X-ray analysis.

Conjugated and non-conjugated phosphacarbaoligoenes with P=C– and P=P– functionalities are only stable in the presence of very bulky substituents.[1] Otherwise they tend to undergo intramolecular cyclization processes to produce interesting bicyclic organophosphorus systems such as **2** or **3**.[2]

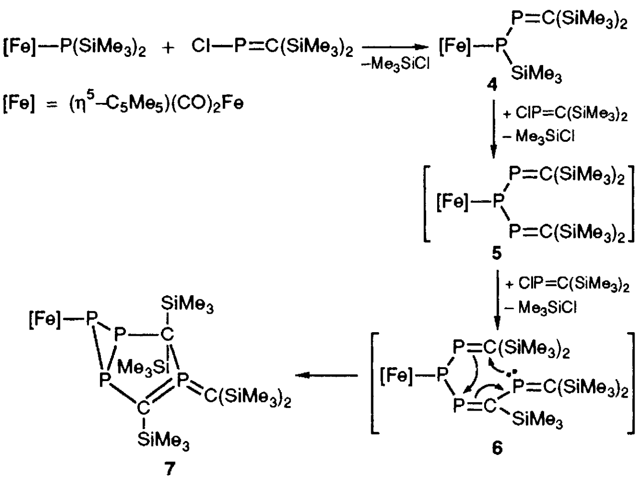
Metallated phosphacarbaoligoenes of the type **4** display an interesting coordination chemistry with the generation of novel ligand systems,[3] which motivated us to synthesize the metallated 2,3,4-triphosphapenta-1,4-diene **5**. To our surprise we obtained the bicyclic bismethylenephosphorane **7** instead of **5**.

Reaction of $(\eta^5\text{-}C_5Me_5)(CO)_2FeP(SiMe_3)_2$[4] with two equivalents of chlorobis(trimethylsilyl)methylenephosphane[5] in tetrahydrofuran (THF) at 20 °C lead to the formation of the diphosphaallyl complex $(\eta^5\text{-}C_5Me_5)(CO)_2FeP(SiMe_3)P{=}C(SiMe_3)_2$ **4** and minor amounts of the red crystalline **7**. In the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture there was no evidence for the 2,3,4-triphosphapenta-1,4-diene **5**. Previously Appel described the synthesis of an analogue of **5** the compound $Bu^tP[P{=}C(Ph)(SiMe_3)]_2$, which, however, decomposed during the attempted isolation.[6]

The yield of **7** could be optimized to 27% when $(\eta^5$-



Scheme 1



Scheme 2

$C_5Me_5)(CO)_2FeP(SiMe_3)_2$ was treated with a threefold excess of the chloromethylenephosphane. Separation of **7** was achieved by removing the solvent and crystallization of the residue from diethyl ether at −30 °C. The constitution of **7** as a representative of the unknown 3-methanediyl-1,3,5,6-tetraphosphabicyclo[3.1.0]hex-2-ene system was shown by electron impact mass spectrometry (70 eV, M^+ m/z 772) as well as by ^{31}P NMR.†

The bicyclic structure of **7** (Fig. 1) is further confirmed by X-ray crystal determination.‡

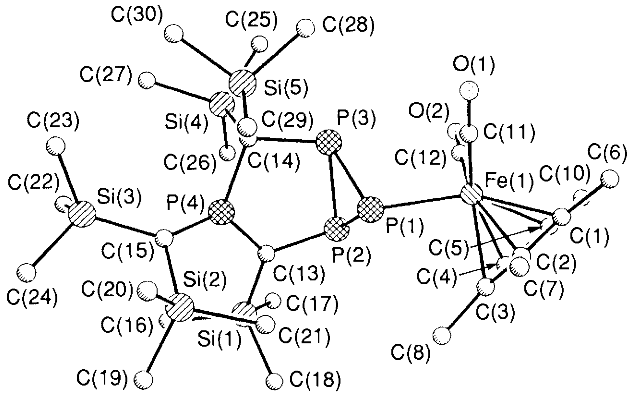


Fig. 1 View of **7** with selected bond lengths (Å) and angles (°): P(1)–P(2) 2.202(4), P(1)–P(3) 2.195(3), P(2)–P(3) 2.210(3), P(1)–Fe(1) 2.321(3), P(2)–C(13) 1.799(9), P(4)–C(13) 1.680(8), P(4)–C(14) 1.853(8), P(4)–C(15) 1.673(10), P(3)–C(14) 1.893(8), Si(1)–C(13) 1.876(8), Si(2)–C(15) 1.864(8), Si(3)–C(15) 1.853(8), Si(4)–C(14) 1.927(8), Si(5)–C(14) 1.920(8); P(1)–P(2)–P(3) 59.7(1), P(1)–P(3)–P(2) 60.0(1), P(2)–P(1)–P(3) 60.4(1), P(2)–P(3)–C(14) 102.1(3), P(3)–C(14)–P(4) 106.5(3), C(14)–P(4)–C(15) 127.7(4), C(13)–P(4)–C(14) 108.7(4), C(13)–P(4)–C(15) 123.4(4), P(2)–C(13)–P(4) 118.2(5), P(3)–P(2)–C(13) 98.1(3), P(2)–C(13)–Si(1) 114.5(5), P(4)–C(13)–Si(1) 126.5(5), P(4)–C(15)–Si(3) 127.3(5), P(4)–C(15)–Si(2) 116.9(4), Si(2)–C(15)–Si(3) 115.7(5)

The molecule exhibits the sterically favoured envelope conformation with an endocyclic P=C bond distance of 1.680(8) Å, which compares well with the exocyclic PC double bond [1.673(10) Å]. The phosphorus P(4) and both carbon atoms C(13) and C(15) are planar [$\Sigma_{\text{bond angles}}$ 359.8(4), 359.2(5) and 359.9(5)°], respectively. The planes defined by P(2)–C(13)–Si(1) and Si(2)–C(15)–Si(3) are twisted by 34.6 and 48.8° with respect to plane P(4)–C(13)–C(15). We propose that **7** is formed by an intramolecular electrocyclic reaction of transient 2,4,5,6-tetraphosphahepta-1,3,6-triene **6**. The latter results from the condensation of the hypothetical **5** and $Cl{-}P{=}C(SiMe_3)_2$.

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† *Selected spectroscopic data* for **7**: $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = -174.0$ (ddd, $^1J_{31}$ 218, $^1J_{32}$ 179, $^2J_{34}$ 15 Hz, P3), −144.7 (ddd, $^1J_{21}$ 193, $^1J_{23}$ 179, $^2J_{24}$ 32 Hz, P2), −49.7 (ddd, $^1J_{13}$ 218, $^1J_{12}$ 193, $^3J_{14}$ 15 Hz, P1), 171.9 (dt, $^2J_{42}$ 32, $^2J_{43}$ $^3J_{41}$ 15 Hz, P4); ^1H NMR (C_6D_6): $\delta = 0.42$ (d, J_{PH} 2.6 Hz, 9H, $SiMe_3$), 0.46 (s, 9H, $SiMe_3$), 0.52 (s, 9H, $SiMe_3$), 0.68 (d, J_{PH} 1.4 Hz, 9H, $SiMe_3$), 0.72 (m, 9H, $SiMe_3$), 1.45 (d, J_{PH} 0.7 Hz, 15 H, C_5Me_5); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 3.19$ (m, $SiMe_3$), 5.02 (m, $SiMe_3$), 6.95 (m, $SiMe_3$), 9.42 [dd, J_{PC} 6.0, 1.0 Hz, $C_5(CH_3)_5$], 39.65 [ddd, J_{PC} 98.3, 35.1, 8.5 Hz, $P_2C(SiMe_3)$], 56.22 [dt, J_{PC} 20.9, 4.5 Hz, $P{=}C(SiMe_3)_2$], 96.34 [d, J_{PC} 1.1 Hz, $C_5(CH_3)_5$], 215.37 (m, CO); IR (KBr): ν/cm^{-1} = 1990, 1947 [ν(CO)].

‡ *Crystal data*: $C_{30}H_{60}FeO_2P_4Si_5$ **7**: M = 773.0, triclinic space group $P\bar{1}$, $a = 9.174(2)$, $b = 12.136(4)$, $c = 20.041(6)$ Å, $\alpha = 80.81(3)$, $\beta = 84.89(2)$, $\gamma = 74.95(2)°$, $V = 2124.4(11)$ Å^3, $Z = 2$, λ (Mo-$K\alpha$) = 0.71073 Å, μ (Mo-Kα) = 0.665 mm^{-1}, $D_c = 1.208$ g cm^{-3}. The structure was solved by direct methods and refined by full-matrix least-squares refinement to a current $R_w = 0.060$, based on 3570 reflections with $F_o > 4.0\sigma(F_o)$. Atomic coordinates, bond lengths, angles and displacement parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

References

1 R. Appel in *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, ed. M. Regitz and O. J. Scherer, Georg Thieme Verlag, Stuttgart, New York, 1990, p. 157 and references cited therein.
2 R. Appel, B. Niemann and M. Nieger, *Angew. Chem.*, 1988, **100**, 957; *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 957; R. Appel, *Phosphorus, Sulfur, Silicon*, 1990, **49/50**, 297 and references cited therein; E. Niecke, O. Altmeyer and M. Nieger, *J. Chem. Soc., Chem. Commun.*, 1988, 945.
3 L. Weber, R. Kirchhoff, R. Boese and H. G. Stammler, *J. Chem. Soc., Chem. Commun.*, 1991, 1293; E. Niecke and D. Schmidt, *J. Chem. Soc., Chem. Commun.*, 1991, 1659.
4 L. Weber, K. Reizig and R. Boese, *Chem. Ber.*, 1985, **118**, 1193.
5 R. Appel and A. Westerhaus, *Tetrahedron Lett.*, 1981, **22**, 2159.
6 R. Appel, V. Kündgen and F. Knoch, *Chem. Ber.*, 1985, **118**, 1353.