

Synthesis and Structure of a Bridging Phospha-alkenyl Complex

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The first bridging phospha-alkenyl complex, $[\mu_2\text{-PC}(\text{SiMe}_3)_2]_2(\text{CO})_6$ (**1**), has been prepared and the structure of (**1**) has been determined by X-ray crystallography.

Interest in the co-ordination chemistry of phospha-alkenes ($\text{RP}=\text{CR}'_2$) stems from the fact that they can function as σ (P donor)¹ or η^2 (P=C π -donor)² ligands. We report here a new mode of ligation for a phospha-alkenyl ligand and the first complex containing more than one phospha-alkenyl ligand.

In a typical preparation, 6.10 mmol of

$\text{Na}_2[\text{Fe}(\text{CO})_4] \cdot \text{dioxane}$ was treated with 3.34 mmol of $(\text{Me}_3\text{Si})_2\text{C}=\text{PCl}^3$ and 1.87 mmol of 1,5-diazabicyclo[5.4.0]undec-5-ene in 100 ml of tetrahydrofuran at 25 °C. After stirring the reaction mixture for 24 h at 25 °C, the solvent was evacuated and the crude product separated by column chromatography (silica gel-n-hexane). Yellow-

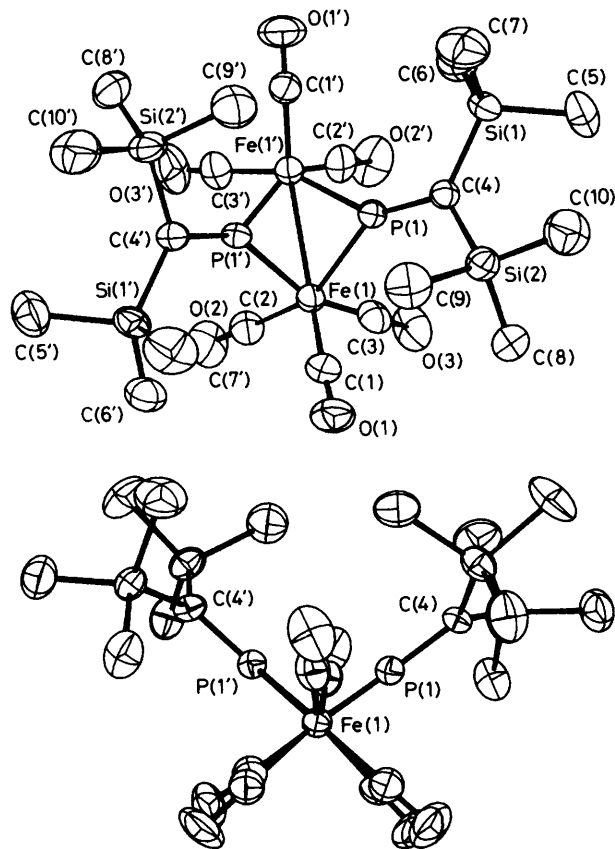
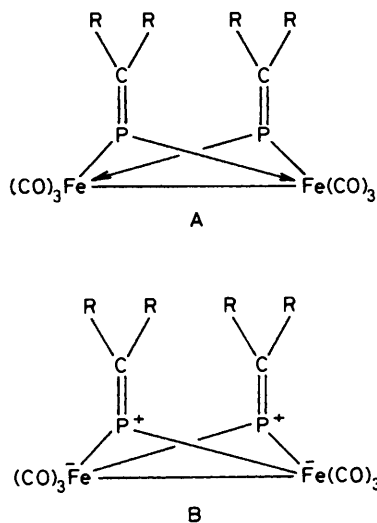


Figure 1. Molecular structure of (1) showing the atom numbering scheme. Principal bond lengths, Å, and angles, ° are: Fe(1)–Fe(1') 2.666(1), Fe(1)–P(1) 2.184(1), P(1)–C(4) 1.650(4), Fe(1)–P(1)–Fe(1') 75.0(1), Fe(1)–P(1)–C(4) 142.5(1), P(1)–C(4)–Si(1) 121.6(2), P(1)–C(4)–Si(2) 116.0(2), Si(1)–C(4)–Si(2) 122.0(2).



orange crystals of (1) (m.p. 182–188 °C) were formed from n-hexane solutions maintained at –20 °C. The composition [(Me₃Si)₂CP]₂Fe₂(CO)₆ for (1) was established by the detection of an electron impact mass spectral peak at *m/z* 658, followed by the sequential loss of six CO molecules. The low field position of the only ³¹P-{¹H} n.m.r. (32.384 MHz) resonance for (1) at +452.6 p.p.m. (relative to 85% H₃PO₄) implied the presence of equivalent ligands with phosphorus-

carbon double bonds.† The foregoing data suggested a symmetrical bis(μ₂-phospha-alkenyl)Fe₂(CO)₆ structure for (1). This structure has been confirmed by X-ray crystallography (Figure 1).‡ Each molecule of (1) possesses crystallographically imposed C₂ symmetry and the P₂Fe₂ core is of the 'butterfly' type found in, for example, bis(phosphido)Fe₂(CO)₆ complexes.⁴ The phosphorus-carbon bond length for (1) [1.650(4) Å] corresponds to a bond order of 2.0 and falls in the range observed for σ-co-ordinated and free phospha-alkenes.^{1,5} Moreover, within experimental error, the phosphorus and carbon atoms both adopt trigonal planar geometries. Finally, we note that the electronic structure of (1) can be discussed in terms of canonical forms A and B. Canonical form B emphasizes the parallel between (1) and bridging vinylidene complexes.⁶

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References

- H. E. Hosseini, H. W. Kroto, J. F. Nixon, M. J. Maah, and M. J. Taylor, *J. Chem. Soc., Chem. Commun.*, 1981, 199; H. W. Kroto, J. F. Nixon, M. J. Taylor, A. A. Frew, and K. W. Muir, *Polyhedron*, 1982, **1**, 89; T. C. Klebach, R. Lourens, F. Bickelhaupt, C. H. Stam, and A. Van Herk, *J. Organomet. Chem.*, 1982, **210**, 211; Th. A. Van der Knaap, F. Bickelhaupt, H. Van der Poel, G. van Koten, and C. H. Stam, *J. Am. Chem. Soc.*, 1982, **104**, 1756.
- A. H. Cowley, R. A. Jones, C. A. Stewart, A. L. Stuart, J. L. Atwood, W. E. Hunter, and H.-M. Zhang, *J. Am. Chem. Soc.*, 1983, **105**, 3737; S. I. Al-Resayes, S. I. Klein, H. W. Kroto, M. F. Meidine, and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1983, 930; Th. A. Van der Knaap, L. W. Jenneskens, J. H. Meeuwissen, F. Bickelhaupt, D. Walther, E. Dinjus, E. Uhlig, and A. L. Spek, *J. Organomet. Chem.*, 1983, **254**, C33.
- R. Appel and A. Westerhaus, *Tetrahedron Lett.*, 1981, **22**, 2159.
- B. K. Teo, M. B. Hall, R. F. Fenske, and L. F. Dahl, *Inorg. Chem.*, 1975, **14**, 3103; J. K. Burdett, *J. Chem. Soc., Dalton Trans.*, 1977, 423; R. E. Ginsburg, R. K. Rothrock, R. G. Finke, J. P. Collman, and L. F. Dahl, *J. Am. Chem. Soc.*, 1979, **101**, 6550.
- R. Appel, F. Knoll, and I. Ruppert, *Angew. Chem., Intl. Ed. Engl.*, 1981, **20**, 731; H. W. Kroto, *Chem. Soc. Rev.*, 1982, **11**, 435; A. H. Cowley, R. A. Jones, J. G. Lasch, N. C. Norman, C. A. Stewart, A. L. Stuart, J. L. Atwood, W. E. Hunter, and H.-M. Zhang, *J. Am. Chem. Soc.*, 1984, **106**, 7015.
- M. I. Bruce and G. Swinger, *Adv. Organomet. Chem.*, 1983, **22**, 60.

† For unligated phospha-alkenes without π-donor substituents the range of ³¹P n.m.r. chemical shifts is ca. 230–430 p.p.m. R. Appel, F. Knoll, and I. Ruppert, *Angew. Chem., Intl. Ed. Engl.*, 1981, **20**, 731; A. H. Cowley and N. C. Norman, in *³¹P NMR Spectroscopy. Structural and Stereochemical Investigations of Organic and Metal Complex Compounds.* Ch. 12, eds. J. G. Verkade and L. D. Quin, Verlag Chemie, in the press.

‡ *Crystal data:* (1), C₂₀H₃₆Fe₂O₆P₂Si₄, *a* = 16.156(3), *b* = 9.490(1), *c* = 21.410(10) Å, β = 96.02(3)°, *U* = 3264.6 Å³, monoclinic, space group C2/c (No. 15), *Z* = 4, *D_c* = 1.34 g cm⁻³, μ(Mo-Kα) = 11.56 cm⁻¹; data were collected on an Enraf-Nonius CAD-4 diffractometer over the range 2.0 ≤ 2θ ≤ 50.0° at 298 K. Corrections for Lorentz, polarisation effects, and absorption were applied but not for decay (<1.0%). From a total of 3 144 unique measured reflections, 2 245 were considered observed and used to solve (Patterson) and refine (difference Fourier, full-matrix, least-squares) the structure of (1). All non-hydrogen atoms were refined anisotropically. Final least-squares converged smoothly to give residual *R* = 0.0342 and *R_w* = 0.0379. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.