Dicarbonyl(η^5-pentamethylcyclopentadienyl)ferrio(t-butyl)chlorophosphine: a Metallo-phosphine exhibiting Multifaceted Reactivity

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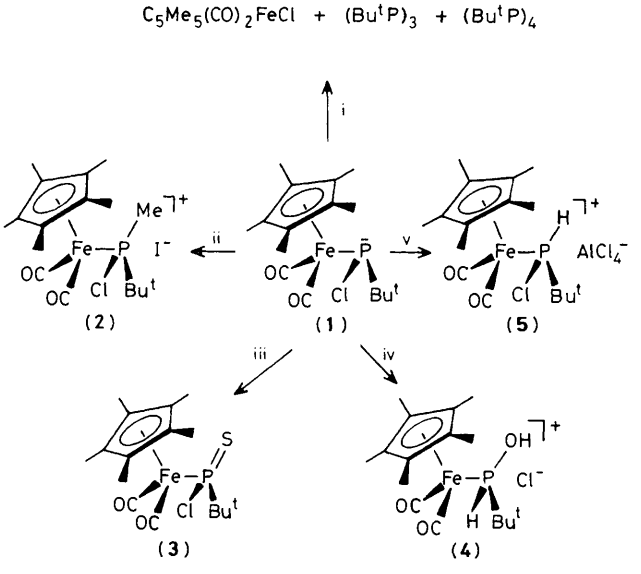
Dicarbonyl(η^5-pentamethylcyclopentadienyl)ferrio(t-butyl)chlorophosphine (**1**) has been found to display a wide range of reactivity; the *X*-ray structure of (**1**) is also reported.

Metallo-diorganophosphines, L_nM–PR_2, have been shown to exhibit high reactivity at the phosphorus and metal centres.[1] We now report a significant extension of the reactivity of this class of compound by the introduction of a P–halogen substituent.

Dicarbonyl(η^5-pentamethylcyclopentadienyl)ferrio(t-butyl)chlorophosphine (**1**) (Scheme 1) is readily accessible from the heterogeneous reaction of equimolar quantities of Bu^tPCl_2 and $Na[Fe(CO)_2C_5Me_5]$ in methylcyclohexane at −78 °C.†‡ The *X*-ray structure of yellow, crystalline (**1**) (Figure 1)§ reveals that the phosphorus geometry is close to tetrahedral [sum of angles 317.2(2)°]. This relative flattening of the phosphorus pyramid compared with ordinary phosphines[2] presumably results from a combination of the steric demand and the electropositive character of the organoiron fragment. The conformation of (**1**) (viewed down the P–Fe, *z*-axis) (Figure 2) is the one which minimises repulsions between the phosphorus lone pair and the filled a″ and 2a′-orbital of the metal fragment and avoids $C_5Me_5\cdots Bu^t$ steric interactions.[3] Photolysis (or, less cleanly, thermolysis) of (**1**) results in the facile transfer of Cl from P to Fe, and the concomitant extrusion of a t-butylphosphinidene unit which oligomerises to a 5 : 1 molar mixture of $(Bu^tP)_3$ and $(Bu^tP)_4$.[4] Photolysis of (**1**) in the presence of an equimolar quantity of Me_3P accelerates the rate of phosphinidene extrusion and results in the formation of η^5-$C_5Me_5(CO)(Me_3P)FeCl$ and in the exclusive formation of $(Bu^tP)_3$.

Despite the presence of an electronegative ligand, the reactivity at phosphorus remains high as evidenced by the ready methylation and thiation of (**1**) to afford (**2**) and (**3**), respectively.† The reactivity of the P–Cl bond is also high since (**1**) reacts readily with H_2O to produce the phosphonium salt, (**4**),† which presumably results from protonation of the initial hydrolysis product, η^5-$C_5Me_5(CO)_2FeP(Bu^t)OH$.



Scheme 1. i, 7 h, *hν*, 254 nm, C_6H_6; ii, MeI, C_6H_6; iii, S_8, C_6H_6; iv, H_2O, C_6H_6; v, Al_2Cl_6, CH_2Cl_2, −78 °C.

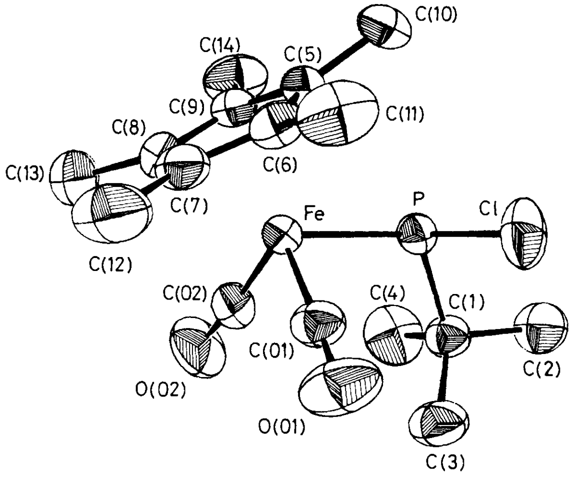


Figure 1. ORTEP view of $C_5Me_5(CO)_2FeP(Bu^t)Cl$ (**1**). Important parameters include: bond lengths, Fe–P = 2.285(1), P–Cl = 2.131(2), P–C(1) = 1.871(5) Å; bond angles, Fe–P–Cl = 103.20(7), Fe–P–C(1) 116.2(2), Cl–P–C(1) = 97.8(2)°.

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† M.p. and $^{31}P\{^1H\}$ n.m.r. (δ, p.p.m.) data: (**1**) (m.p. 94 °C), 323.3 (C_6D_6); (**2**) (m.p. 140 °C), 180.6 ($CDCl_3$); (**3**) (m.p. 123 °C), 223.8 (C_6D_6); (**4**) (m.p. 148 °C), 157.4 (CD_3CN); η^5-$C_5Me_5(CO)_2Fe$-$P(O)(H)(Bu^t)$ (m.p. 137 °C), 131.0 ($CDCl_3$); (**5**) (m.p. 194 °C), 166.3 ($CDCl_3$).

‡ Analogous compounds with Ph [m.p. 172 °C, $\delta^{31}P$ 121.3 p.p.m. ($CDCl_3$)], Me [$\delta^{31}P$ 148.4 p.p.m. (C_6D_6)], NMe_2 [m.p. 90 °C, $\delta^{31}P$ 379.1 p.p.m. (C_6D_6), and Cl [m.p. 137 °C, $\delta^{31}P$ 478.7 p.p.m. (C_6D_6)] instead of Bu^t can also be prepared by this route.

§ *Crystal data:* $C_{16}H_{24}ClFeO_2P$, $M = 370.64$, monoclinic, $P2_1/c$ (No. 14), $a = 14.092(2)$, $b = 14.043(5)$, $c = 9.531(2)$ Å, $\beta = 102.66(2)°$, $U = 1840(1)$ Å^3, $Z = 4$, $D_c = 1.332$ g cm^{-3}, $\lambda = 0.71069$ Å, μ(Mo-K_α) = 10.5 cm^{-1}.

Of 3249 measured intensities (Enraf–Nonius CAD4), 2029 were considered observed [$I > 3.0\sigma(I)$]. After correction for Lorentz, polarisation, and decay (but not for absorption), the structure was solved by using a Patterson map which revealed the Fe and P positions. Subsequent refinement (full matrix, least squares) afforded R and R_w values of 0.0407 and 0.0727, respectively.

The atomic co-ordinates for this structure are available from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

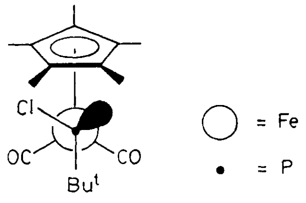

Figure 2. Newman-projection of (**1**).

However, attempts to prepare this compound by deprotonation of (**4**) with $Me_3P{=}CH_2$ resulted in the isomeric phosphine oxide, η^5-$C_5Me_5(CO)_2FeP(O)(H)(Bu^t)$.† The reaction of (**1**) with Al_2Cl_6 in CH_2Cl_2 solution[5] results in the formation of the phosphonium cation (**5**) rather than the anticipated cation, $[\eta^5$-$C_5Me_5(CO)_2FeP(Bu^t)]^+$.[6] Possibly (**5**) arises from a redox reaction involving Al_2Cl_6/CH_2Cl_2 followed by hydrogen abstraction from the solvent.[5]

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References

1 W. Malisch, R. Maisch, I. J. Colquhoun, and W. McFarlane, *J. Organomet. Chem.*, 1981, **220**, C1; W. Angerer, W. Malisch, and W. S. Sheldrick, *Chem. Ber.*, 1985, **118**, 1261.
2 B. Linde and T. Mann, *J. Chem. Phys.*, 1960, **32**, 512; J. J. Daly, *J. Chem. Soc.*, 1964, 3799.
3 B. E. R. Schilling, R. Hoffmann, and D. L. Lichtenberger, *J. Am. Chem. Soc.*, 1979, **101**, 585.
4 For a review of polyphosphines, see M. Baudler, *Angew. Chem., Int. Ed. Engl.*, 1982, **118**, 1261.
5 For the use of Al_2Cl_6/CH_2Cl_2 as an oxidising agent, see *e.g.* H. Bock and W. Kaim, *Acc. Chem. Res.*, 1982, **15**, 9.
6 G. R. Clark, W. R. Roper, and A. H. Wright, *J. Organomet. Chem.*, 1984, **273**, C17; H. Nakazawa, W. E. Buhro, G. Bertrand, and J. A. Gladysz, *Inorg. Chem.*, 1984, **23**, 3431.