

Reaction of (Pentamethylcyclopentadienyl)(dicarbonyl)[1,3,3-tris(trimethylsilyl)- η^1 -1,2-diphosphaallyl] Iron with Pentacarbonylchromium: Formation of the First η^3 -Ferradiphosphaallyl and η^5 -1,2-Diphosphacyclopentadienyl Complexes

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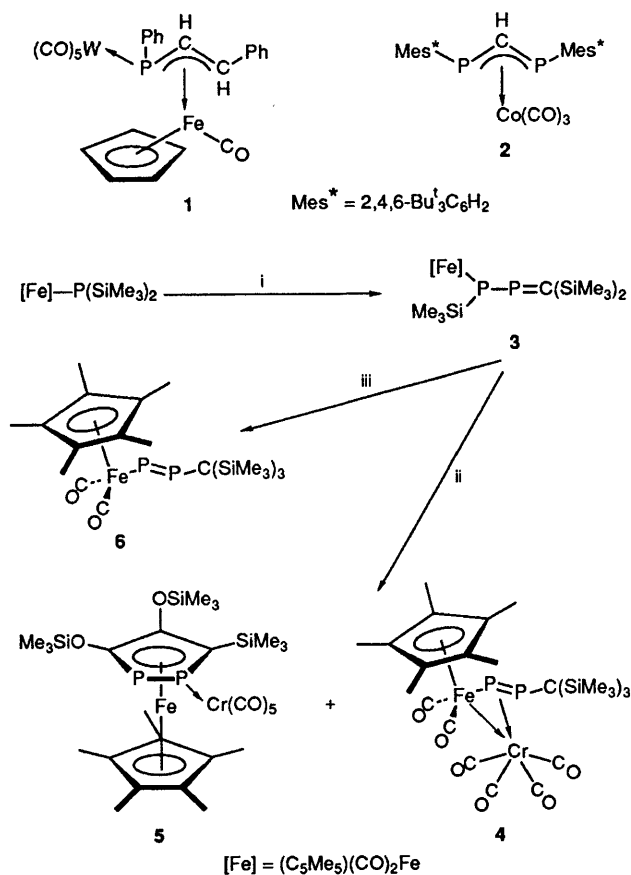
Reaction of $[(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{Fe-P}(\text{SiMe}_3)\text{-P}=\text{C}(\text{SiMe}_3)_2]$ **3** with $(Z\text{-cyclooctene})\text{Cr}(\text{CO})_5$ affords the η^3 -1-ferra-2,3-diphosphaallyl complex $\{[(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{Fe-P}=\text{P}-\text{C}(\text{SiMe}_3)_3]\text{Cr}(\text{CO})_4\}$ **4** and the first 1,2-diphosphaferrocene $\{(\eta^5\text{-C}_5\text{Me}_5)[\eta^5\text{-1,2-P}_2\text{C}_3(\text{OSiMe}_3)_2(\text{SiMe}_3)\text{Cr}(\text{CO})_5]\text{Fe}\}$ **5**, the molecular structures of which have been determined by X-ray analysis.

There is still considerable interest in the ligand properties of low coordinated phosphorus compounds and their higher congeners.¹ The concept of isoelectronic compounds and the diagonal relationship in the periodic table have proven especially fruitful in the design and understanding of novel classes of coordination compounds. Thus, complexes with

η^3 -1-phosphaallyl ligands such as **1**² or η^3 -1,3-diphosphaallyl complexes such as **2**³ have been described in the literature.

This communication reports a convenient access to the first η^3 -1-ferra-2,3-diphosphaallyl complex **4** and the first 1,2-diphosphaferrocene **5**.

Reaction of $(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{Fe-P}(\text{SiMe}_3)_2$ ⁴ with chloro-



Scheme 1 Reagents and conditions: i, **3**, pentane, 20 °C, $\text{Cl-P}=\text{C}(\text{SiMe}_3)_2$ (1 mol equiv.); ii, **4,5**, pentane, 20 °C, $(\text{Z-C}_8\text{H}_{14})\text{Cr}(\text{CO})_5$ (3.4 mol equiv.); iii, **6**, pentane, 20 °C, $(\text{Z-C}_8\text{H}_{14})\text{Cr}(\text{CO})_5$ (0.1 mol equiv.)

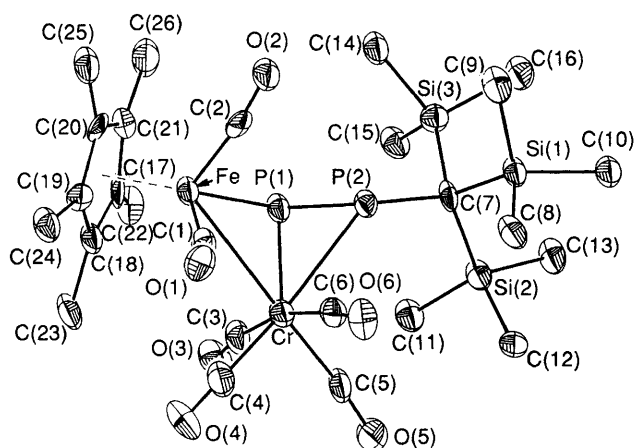


Fig. 1 ORTEP view of the structure of **4** in the crystal. Important bond lengths (Å) and angles (°) are: Cr–Fe 2.945(3), Cr–P(1) 2.395(4), Cr–P(2) 2.635(4), Fe–P(1) 2.313(3), P(1)–P(2) 2.090(4), Fe–C(1) 1.813(12), Fe–C(2) 1.752(10), Cr–C(3) 1.894(12), Cr–C(4) 1.878(12), Cr–C(5) 1.838(11), Cr–C(6) 1.906(12); Fe–P(1)–P(2) 101.5(1), P(1)–P(2)–C(7) 110.1(3).

bis(trimethylsilyl)methylenephosphane⁵ in pentane at 20 °C lead to the black crystalline η^1 -1,2-diphosphaallyl complex **3** (35% yield). Treatment of **3** with an excess of $(\text{Z-C}_8\text{H}_{14})\text{Cr}(\text{CO})_5$ ⁶ afforded the tetracarbonylchromium complex **4** in 62% yield, and a few crystals of compound **5**.

Both compounds **4** and **5** were isolated by column chromatography on Florisil with pentane as eluent. Crystallisation of the complexes was achieved by storing a concentrated pentane solution at –35 °C. If **3** is allowed to react with 5 mol% of

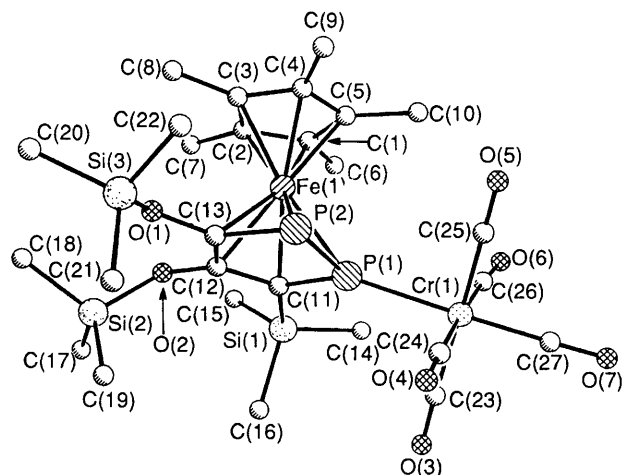


Fig. 2 View of the structure of **5** in the crystal. Important bond lengths (Å) and angles (°) are: Fe(1)–P(1) 2.286(2), Fe(1)–P(2) 2.344(2), Fe(1)–C(11) 2.113(6), Fe(1)–C(12) 2.110(6), Fe(1)–C(13) 2.100(6), P(1)–P(2) 2.119(3), P(1)–C(11) 1.771(6), P(2)–C(13) 1.783(6), C(11)–C(12) 1.427(9), C(12)–C(13) 1.409(9), O(1)–C(13) 1.377(8), O(2)–C(11) 1.364(8), P(1)–Cr(1) 2.391(2), P(1)–P(2)–C(13) 91.6(2), P(1)–C(11)–C(12) 112.7(5), P(2)–P(1)–C(11) 98.6, P(2)–C(13)–C(12) 118.8(5), C(11)–C(12)–C(13) 118.1(6).

$(\text{Z-C}_8\text{H}_{14})\text{Cr}(\text{CO})_5$ over a period of three days the diphosphene complex **6** was obtained as the main product in 30% yield by chromatography. Composition and constitution of **3–6** are proved by satisfactory elemental analyses, spectroscopic data,† and X-ray structure analyses‡ in the case of **4** and **5**. The formation of **5** involves a metal-induced 1,3- Me_3Si shift from phosphorus to carbon.

Doublets in the ^{31}P NMR spectrum of **4** at δ 431.5 and 134.9 ($^1J_{\text{PP}}$ 524 Hz) and IR evidence in the $\nu(\text{CO})$ region [$\nu(\text{CO}) = 2013, 1989, 1946, 1916, 1894 \text{ cm}^{-1}$] indicate the presence of a π -bonded diphosphene ligand in a tetracarbonylchromium complex. This was confirmed by X-ray analysis which displays an η^3 -ligand, unsymmetrically ligated to the chromium atom

† Selected spectroscopic data: for **3**: ^{31}P NMR (pentane): δ –30.3 (d, $^1J_{\text{PP}}$ 295 Hz, FeP), 502.9 (d, $^1J_{\text{PP}}$ 295 Hz, PC); ^1H NMR (C_6D_6): δ 0.45 (d, $^4J_{\text{PH}}$ 2.1 Hz, 9H, CSiMe_3), 0.51 (d, $^3J_{\text{PH}}$ 3.5 Hz, 9H, PSiMe_3), 0.63 (d, $^4J_{\text{PH}}$ 0.9 Hz, 9H, CSiMe_3), 1.42 (d, $^4J_{\text{PH}}$ 0.6 Hz, C_3Me_5); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 215.8 (dd, J_{PC} 105.8, 3.1 Hz, P=C) 218.0 (d, J_{PC} 7.4 Hz, CO); IR (KBr): 1946, 1988 cm^{-1} [$\nu(\text{CO})$].

4: ^{31}P NMR (pentane): δ 431.5 (d, $^1J_{\text{PP}}$ 524 Hz, FeP) 134.9 (d, $^1J_{\text{PP}}$ 524 Hz, PC); ^1H NMR (C_6D_6): δ 0.53 (s, 27H, SiMe_3), 1.32 (s, 15H, C_5Me_5); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 211.5 (s, FeCO), 225.5 (s, FeCO), 226.4 m, 227.6 m, 232.7 m (CrCO); IR (KBr): 2013, 1989, 1946, 1916, 1894 cm^{-1} [$\nu(\text{CO})$].

5: ^{31}P NMR (pentane): δ 11.1 (d, $^1J_{\text{PP}}$ 389.7 Hz, CrP), –87.0 (d, $^1J_{\text{PP}}$ 389.7 Hz, PC).

6: ^{31}P NMR (pentane): δ 602.3 (d, $^1J_{\text{PP}}$ 654.8 Hz, PC), 788.2 (d, $^1J_{\text{PP}}$ 654.8 Hz, Fe–P); ^1H NMR (C_6D_6): δ 0.52 (s, 27H, SiMe_3), 1.39 (s, 15H, C_5Me_5); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): 216.2 (dd, J_{PC} 12.6, 1.4 Hz, FeCO); IR (KBr): 1998, 1948 cm^{-1} [$\nu(\text{CO})$].

‡ Crystal data: $\text{C}_{26}\text{H}_{42}\text{CrFeO}_6\text{P}_2\text{Si}_3$ **4**, $M = 704.7$, monoclinic space group $P2_1/n$, $a = 9.338(5)$, $b = 15.498(13)$, $c = 23.375(14)$ Å, $\beta = 92.85(5)^\circ$, $V = 3378(4)$ Å³, $Z = 4$, $\lambda(\text{Mo-K}\alpha) = 0.71069$ Å, $\mu(\text{Mo-K}\alpha) = 0.98 \text{ mm}^{-1}$, $D_c = 1.385 \text{ g cm}^{-3}$. The structure was solved by direct methods and refined by full-matrix least-squares refinement to a current $R_w = 0.065$, based on 2908 reflections with $F_o \geq 4.0\sigma(F_o)$.

$\text{C}_{27}\text{H}_{42}\text{CrFeO}_7\text{P}_2\text{Si}_3$ **5**, $M = 732.7$, monoclinic space group $P2_1/c$, $a = 11.889(2)$, $b = 18.692(3)$, $c = 16.688(3)$ Å, $\beta = 103.89(1)^\circ$, $V = 3600(11)$ Å³, $Z = 4$, $\lambda(\text{Mo-K}\alpha) = 0.71073$ Å, $\mu(\text{Mo-K}\alpha) = 0.92 \text{ mm}^{-1}$. The structure was solved by direct methods and refined by full-matrix least-squares refinement a current $R_w = 0.045$, based on 3765 reflections with $F_o \geq 4.0\sigma(F_o)$.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Date Centre. See Notice to Authors, Issue No. 1.

of a $\text{Cr}(\text{CO})_4$ moiety *via* the two phosphorus atoms [$d\{\text{Cr}-\text{P}(1)\} = 2.395(4)$; $d\{\text{Cr}-\text{P}(2)\} = 2.635(4)$ Å] and the iron centre [$d(\text{Cr}-\text{Fe}) = 2.945(3)$ Å]. This situation represents a novel mode of coordination in organophosphorus chemistry and is best understood as an η^3 -1-ferra-2,3-diphosphaallyl system.

Compound **5** represents the first example of a 1,2-diphosphaferrocene, whereas 1,1'-⁷ and 1,3-diphosphaferrocenes^{8,9} are already known. The 1,2 diphospholyl ring is planar and eclipsed oriented to the C_5Me_5 ligand with a dihedral angle of 5.7° . The P-P and the P-C bond distances are determined as 2.119(3), 1.771(6) and 1.783(6) Å, respectively. A pentacarbonyl chromium unit is ligated to the phosphorus atom P(1) [$d\{\text{P}(1)-\text{Cr}\} = 2.391(2)$ Å]. The bond length P(1)-Fe of 2.286(2) Å is markedly shortened as compared to the distance Fe-P(2) [2.344(2) Å]. Obviously, the CO building blocks of the heterocyclic ligand are derived from the terminal carbonyl ligands in **3**. Me_3Si group migration from phosphorus and carbon in **3** to the oxygen atoms might have resulted in the formation of the two Me_3SiO -substituents of the ring.

A similar shift has been observed in the reaction of $\text{Cl}-\text{P}=\text{C}(\text{SiMe}_3)_2$ with $\text{LiP}(\text{SiMe}_3)\text{Mes}^*$.¹⁰ A metal induced 1,3- Me_3Si -shift has only recently been described.¹¹ Because of the vicinity of two bulky groups [$(\text{Me}_3\text{Si})\text{C}$ and $\text{Cr}(\text{CO})_5$] at the P=P bond decomplexation occurs with formation of the free diphosphenyl complex **6** in the catalytic reaction, whereas with an excess of (*Z*- C_8H_{14}) $\text{Cr}(\text{CO})_5$ rearrangement to **4** and **5** is observed.

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