# Insertion of the P=C-Functionality of (Pentamethylcyclopentadienyl)(dicarbonyl)[1,3,3-tris(trimethylsilyl)–$\eta^1$-1,2-diphosphaallyl]iron into a $C_5Me_5$ C–H Bond: Formation of a Chelating ($\eta^1$-P, $\eta^5$-$C_5$)-3-Tetramethylcyclopentadienyl-1,2-diphosphapropanido Ligand

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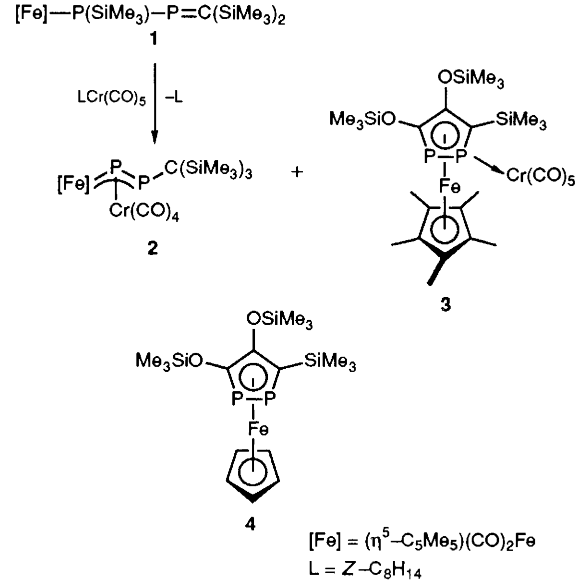
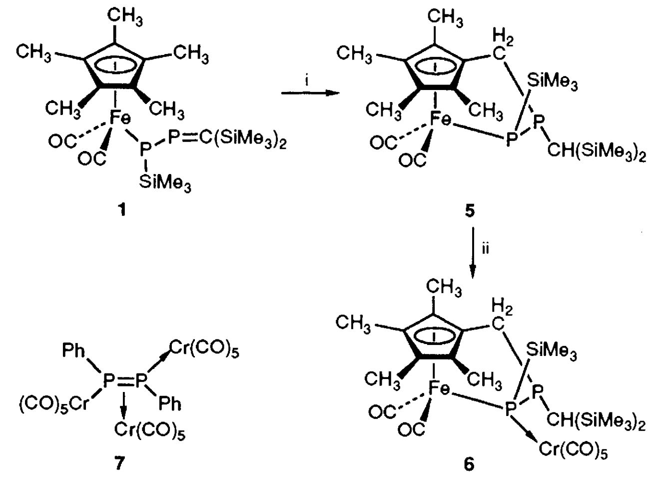
Heating a methylcyclohexane solution of [($\eta^5$-$C_5Me_5$)$(CO)_2$Fe–P($SiMe_3$)–P=C$(SiMe_3)_2$] **1** gives rise to the insertion of the P=C-moiety into the CH-bond of a ring methyl group forming the chelate complex {$\eta^5$-$C_5Me_4CH_2$P[CH$(SiMe_3)_2$]P($SiMe_3$)Fe$(CO)_2$} **5** which is trapped by (*Z*-cyclooctene)Cr$(CO)_5$ and fully characterized as its Cr$(CO)_5$ adduct **6**.

Transition metal complexes of low-coordinated organophosphorus compounds are attractive molecules, which display an interesting and versatile chemistry.[1] Recently, we have demonstrated that $\eta^3$-phosphaallyl iron complexes rearrange to metallophosphaalkenes by treatment with (*Z*-cyclooctene)-Cr$(CO)_5$ or $Fe_2(CO)_9$.[2] The $\eta^1$-diphosphaallyl complex ($\eta^5$-$C_5Me_5$)$(CO)_2$Fe–P($SiMe_3$)–P=C$(SiMe_3)_2$ **1** was converted by the chromium reagent into the first $\eta^3$-ferradiphosphaallyl complex **2** and small amounts of the first $\eta^5$-1,2-diphosphaferrocene **3**.[3]

The related sandwich complex **4** was obtained by Niecke and Schmidt from the thermal reaction of the $\eta^1$-diphosphaallyl complex ($\eta^5$-$C_5H_5$)$(CO)_2$Fe–P($SiMe_3$)–P=C$(SiMe_3)_2$.[4] Complex **1**, however, behaved differently upon heating, and here we report the novel insertion of a P=C-function into an aliphatic CH-bond of the $C_5Me_5$ ligand.

In a typical experiment a methylcyclohexane solution of ($\eta^5$-$C_5Me_5$)$(CO)_2$Fe–P($SiMe_3$)–P=C$(SiMe_3)_2$ **1** was heated at 85 °C for 5 h. Crude **5** remained after filtration and evaporation to dryness as a brown tar. All attempts to obtain an





**Scheme 1** *Reagents and conditions*: i, methylcyclohexane, 85 °C, 5 h; ii, methylcyclohexane, (*Z*-cyclooctene)$Cr(CO)_5$, 20 °C, 15 min

analytically pure material failed. In order to obtain a crystalline derivative of **5** which would allow full characterization, a slight excess of (*Z*-cyclooctene)$Cr(CO)_5$[5] was added to the reaction mixture at room temperature and stirring continued for 15 min. After filtration the solution was evaporated to dryness and the solid residue was washed with n-pentane and diethyl ether. The orange–yellow powder was recrystallized from toluene at −30 °C to give crystalline **6** in 59% yield. In benzene solution at 20 °C slow dissociation of the $Cr(CO)_5$ unit with the occurrence of **5** was observed.

The composition and constitution of **6** are deduced from satisfactory elemental analyses, spectroscopic data,† and an X-ray structure analysis.‡ The doublets in the $^{31}P$ NMR spectrum of **5** at δ 23.3 and −83.4 ($^1J_{PP}$ 171 Hz) are shifted to low field by complexation and imply diphosphane structures for **5** and **6**.

Only four signals for the ring methyl protons and a multiplet at δ 3.25 representing two protons indicated that one Me group of the $C_5Me_5$ ring took part in the reaction. From IR evidence of **6** we concluded the presence of a $Cr(CO)_5$ group attached to a powerful donor ligand. This was confirmed by X-ray analysis which displays a dicarbonyl iron complex with the chelating ($\eta^5$-C,$\eta^1$-P)-3-tetramethylcyclopentadienyl-1,2-diphosphapropan-1-ido ligand. The five-membered metallaheterocycle defined by the atoms Fe P(2) P(1) C(2) C(1) adopts an envelope conformation with the $CH(SiMe_3)_2$ and $SiMe_3$ substituents in equatorial positions and *trans*-orientated. The Fe–P bond of 2.377(2) Å is close to the upper end of the range of 2.12 to 2.39 Å, which is reported for Fe–P distances in low-valent iron carbonyls.[6] The pentacarbonylchromium fragment is coordinated to metallated phosphorus atom P(2) in an axial orientation. The Cr–P distance of 2.545(2) Å is close to the sum of the covalence radii of $Cr^0$ (1.48 Å)[7] and P (1.10 Å)[8] and well comparable with the Cr–P distances of the side-on ligated $Cr(CO)_5$ group in **7**, whereas the end-on coordinated $Cr(CO)_5$ moieties give rise to Cr–P bonds ranging from 2.387–2.411 Å.[9] The remarkably long Fe–P and Cr–P contacts in **6** are due to the steric encumberance in the molecule.

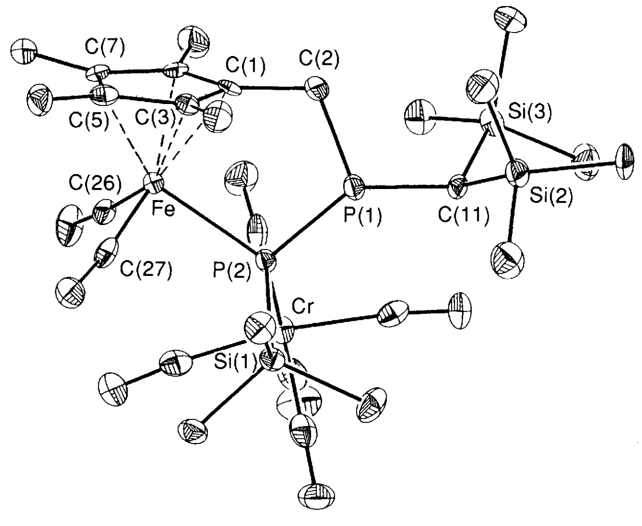


**Fig. 1.** ORTEP view of the structure of **6** in the crystal, important bond lengths (Å) and angles (°) are: Cr–P(2) 2.545(2), P(2)–P(1) 2.252(2), P(2)–Si(1) 2.278(2), P(1)–C(2) 1.870(6), P(1)–C(11) 1.869(5), C(2)–C(1) 1.495(8), Fe–C(1) 2.116(5), Fe–C(3) 2.111(5), Fe–C(5) 2.110(6), Fe–C(7) 2.124(5), Fe–C(26) 1.779(6), Fe–C(27) 1.777(6): Fe–P(2)–P(1) 97.2(1), Fe–P(2)–Si(1) 108.6(1), Fe–P(2)–Cr 121.9(1), Cr–P(2)–Si(1) 103.4(1), Cr–P(2)–P(1) 128.3(1), P(2)–P(1)–C(2) 99.5(2), P(2)–P(1)–C(11) 103.9(2), C(2)–P(1)–C(11) 103.9(2), P(1)–C(2)–C(1) 109.1(4), C(2)–C(1)–Fe 125.9(4), C(1)–Fe–P(2) 88.6(1)

The formation of **6** can formally be viewed as the insertion of the P=C group into the CH bond of one methyl substituent at the $C_5Me_5$ ring. Such an insertion is novel in phosphaalkene chemistry, but has precedent in the chemistry of phosphenium ions,[10] $\lambda^3$-dioxophosphoranes[11] and $\lambda^3$-dithiophosphoranes.[12]

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† *Selected spectroscopic data* for **5**: $^{31}P\{^1H\}$NMR (methylcyclohexane) (ref. 85% $H_3PO_4$): δ −83.4 (d, $^1J_{PP}$ 171 Hz, PFe), 23.3 [d, $^1J_{PP}$ 171 H, $PCH(SiMe_3)_2$].

**6**: $^{31}P\{^1H\}$ NMR ($C_6D_6$): δ −62.6 (d, $^1J_{PP}$ 234 Hz, PFe), 49.0 [d, $^1J_{PP}$ 234 Hz, P–$CH(SiMe_3)_2$]; $^{31}P$ NMR ($C_6D_6$): δ −62.6 (dm, $^1J_{PP}$ 234 Hz, PFe), 49.0 (dd, $^1J_{PP}$ 234; $^2J_{PH}$ 25 Hz, $PCH(SiMe_3)_2$; $^1H$ NMR ($C_6D_6$): δ 0.19 [d, $^4J_{PH}$ 1.2 Hz, 9H, $C(SiMe_3)$], 0.38 [s, 9H, $C(SiMe_3)$], 0.72 (d, $^3J_{PH}$ 3.7 Hz, 9H, $PSiMe_3$), 1.07 (s, 3H, $C_5CH_3$), 1.10 (s, 3H, $C_5CH_3$), 1.82 (s, 3H, $C_5CH_3$), 1.84 (d, $^4J_{PH}$ 1.0 Hz, 3H, $C_5CH_3$); 2.08 (m, 1H, $CHSi_2$), 3.25 (m, 2H, $PCH_2$); IR $\nu_{max}$/cm$^{-1}$ (KBr): 2045, 2007, 1957, 1911, 1891 (CO).

‡ *Crystal data*: $C_{27}H_{42}CrFeO_7P_2Si_3$ **6**, *M* = 732.7, monoclinic space group $P2_1/n$, $a$ = 9.673(3), $b$ = 21.662(7), $c$ = 16.824(5) Å, $\beta$ = 92.74(2)°, $V$ = 3521.1(1.7) Å$^3$, $Z$ = 4, $\lambda$(Mo-K$\alpha$) = 0.71069 Å, $\mu$(Mo-K$\alpha$) = 0.95 mm$^{-1}$. The structure was solved by direct methods and refined by full-matrix least-squares refinement to a current $R$ = 0.056, based on 3250 reflections with $F_o \geqslant 4.0\sigma(F)$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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