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

Lothar Weber,* Ralf Kirchhoff, Roland Boese and Hans-Georg Stammler
Fakultät für Chemie der Universität Bielefeld, Universitätsstrasse 25, D-4800 Bielefeld 1, Germany
Institut für Anorganische Chemie der Universität Essen, Universitätsstrasse 5-7, D-4300 Essen 1, Germany

Reaction of [(η^5-C_5Me_5)(CO)_2Fe-P(SiMe_3)~P~P=C(SiMe_3)~I with (Z-cycl~octene)Cr(CO)~ affords the
η^3-1-ferra-2,3-diphosphaallyl complex {[(η^5-C_5Me_5)(CO)_2Fe-P-P-C(SiMe_3)~I]Cr(CO)~} and the first
1,2-diphosphaferrocene {[(η^5-C_5Me_5)(η^5-1,2-P_2C_3OSiMe_3~P~P=Cr(CO)~I]Fe}~}, 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
congenors. 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 (η^5-C_5Me_5)(CO)_2Fe-P(SiMe_3)~ with chloro-
bis(trimethylsilyl)methylenephosphane$^5$ in pentane at 20 °C lead to the black crystalline 1,2-diphosphaallyl complex 6 afforded the tetracarbonylchromium complex. This was confirmed by X-ray analysis which displays the π-bonded diphosphene ligand in a tetracarbonylchromium complex. This was proved by satisfactory elemental analyses, spectroscopic data,$^6$ and X-ray structure analyses$^7$ in the case of 4 and 5. The formation of 5 involves a metal-induced 1,3-Me$_3$Si shift from phosphorus to carbon.

Doublets in the 31P NMR spectrum of 4 at $\delta$ 431.5 and 134.9 (J$_{pp}$ 524 Hz) and IR evidence in the ν(CO) region [ν(CO) = 2013, 1989, 1946, 1894 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 π-ligand, unsymmetrically ligated to the chromium atom.

$^5$ Selected spectroscopic data: for 3: 31P NMR (pentane): δ = −30.3 (d, $^{1}J_{pp}$ 295 Hz, FeP), 50.2 (d, $^{1}J_{pp}$ 295 Hz, PC); 1'H NMR (CD$_5$D$_5$): δ 6.8 (m, 20H, C$_5$Me$_5$), δ 2.18 (d, J$_{pp}$ 389.7 Hz, CrP), δ −87.0 (d, J$_{pp}$ 389.7 Hz, PC). 4: 31P NMR (pentane): δ 431.5 (d, $^{1}J_{pp}$ 524 Hz, FeP), 134.9 (d, $^{1}J_{pp}$ 524 Hz, PC), 1'H NMR (CD$_5$D$_5$): δ 6.53 (20H, C$_5$Me$_5$), δ 1.32 (s, 15H, C$_{15}$Me$_{15}$); 13C{1H} NMR (CD$_5$D$_5$): δ 215.8 (dd, J$_{pp}$ 12.6, 1.4 Hz, C$_{26}$H$_{42}$CrFeO$_6$P$_2$Si$_3$). 5: 31P NMR (pentane): δ 11.1 (d, $^{1}J_{pp}$ 389.7 Hz, CrP), δ −87.0 (d, $^{1}J_{pp}$ 389.7 Hz, PC). 6: 31P NMR (pentane): δ 602.3 (d, $^{1}J_{pp}$ 654.8 Hz, FeP), 0.52 (s, 73H, SiMe$_3$), 1.39 (s, 15H, C$_{15}$Me$_{15}$); 13C{1H} NMR (CD$_5$D$_5$): δ 216.2 (dd, J$_{pp}$ 12.6, 1.4 Hz, FeCO); IR (KBr): 1894 cm$^{-1}$ ν(CO)].

$^6$ Crystal data: C$_{26}$H$_{42}$CrFeO$_6$P$_2$Si$_3$, M = 704.7, monoclinic space group P2$_1$/m, a = 9.388(5), b = 15.498(13), c = 23.375(14) Å, β = 92.85(5), V = 3378(4) Å$^3$, Z = 4, λ(Mo-Kα) = 0.71069 Å, μ(Mo-Kα) = 0.98 mm$^{-1}$, D$_m$ = 1.385 g cm$^{-3}$. The structure was solved by direct methods and refined by full-matrix least-squares refinement to a current R$_e$ = 0.065, based on 2998 reflections with F$_o$ = 4.00.F$_o$.

C$_{26}$H$_{42}$CrFeO$_6$P$_2$Si$_3$, M = 732.7, monoclinic space group P2$_1$/c, a = 11.899(2), b = 18.692(3), c = 16.689(3) Å, β = 103.89(1), V = 3600(11) Å$^3$, Z = 4, λ(Mo-Kα) = 0.71073 Å, μ(Mo-Kα) = 0.92 mm$^{-1}$. The structure was solved by direct methods and refined by full-matrix least-squares refinement to a current R$_e$ = 0.045, based on 3765 reflections with F$_o$ = 4.00.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 Cr(CO)₄ moiety via the two phosphorus atoms \[d(\text{Cr-P(1)}) = 2.395(4); d(\text{Cr-P(2)}) = 2.635(4) \text{ Å}\] and the iron centre \[d(\text{Cr-Fe}) = 2.945(3) \text{ Å}\]. This situation represents a novel mode of coordination in organophosphorus chemistry and is best understood as an \(\eta^2\)-ferro-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 \(\text{C}_5\text{Me}_5\) 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) \[d(\text{P(1)-Cr}) = 2.391(2) \text{ Å}\]. 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. \(\text{Me_3Si}\) group migration from phosphorus and carbon in 3 to the oxygen atoms might have resulted in the formation of the two \(\text{Me_3SiO}\)-substituents of the ring.

A similar shift has been observed in the reaction of \(\text{Cl-P=C(SiMe}_3)\_2\) with \(\text{LiP(SiMe}_3)\_2\) as \(\text{LiP(SiMe}_3)\_2\). A metal induced 1,3-\(\text{Me_3Si}\)-shift has only recently been described.\(^1\) Because of the vicinity of two bulky groups [(\(\text{Me_3Si}\)C) and Cr(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 (\(\text{Z-C}_8\text{H}_{14}\))Cr(CO)₅ rearrangement to \(\text{C}_5\text{Me}_5\) is observed.

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References