# Stepwise Formation of Chiral Clusters *via* $\sigma^3$, $\lambda^4$-Phosphanediyl Compounds of Type $(R)(\eta^1\text{-}C_5Me_5)P{=}ML_n$

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The chiral cluster $(2,4,6\text{-}Bu^t_3C_6H_2O)P\text{-}Fe(CO)(\eta^5\text{-}C_5Me_5)\text{-}(\mu_2\text{-}CO)\text{-}Fe(CO)_3Mn(CO)_4$ **6** has been synthesized stepwise from $(R)(\eta^1\text{-}C_5Me_5)P{=}Mn(CO)_4$ **1** ($R = 2,4,6\text{-}Bu^t_3C_6H_2O$) and $Fe_2(CO)_9$ **2**; the rearrangement of $\eta^2\text{-}\{(R)(\eta^1\text{-}C_5Me_5)\text{-}P{=}Mn(CO)_4\}Fe(CO)_4$ **3** to $(R)[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]P{=}Mn(CO)_4$ **4** proves to be the decisive step in this synthesis; the X-ray structure analysis of **4** and **6** are reported.

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There is wide interest in chiral heterometallic clusters.[1] The synthesis of these type of compounds can be achieved most commonly by exchange of organometallic building blocks in non-chiral clusters[2] or addition of new organometallic fragments to unsaturated organometallic compounds.[3]

We recently described the synthesis of the bifunctional complex $(R)(\eta^1\text{-}C_5Me_5)(P{=}Mn(CO)_4$ **1** ($R = 2,4,6\text{-}Bu^t_3\text{-}C_6H_2O$).[4] This compound contains two potential coordination sites (the P=Mn double bond unit and the $\eta^1\text{-}C_5Me_5$ fragment) for coordinatively unsaturated organometallic building blocks. Addition of various organometallic fragments to **1** is expected to result in the formation of chiral clusters.

Here we describe the stepwise synthesis of the chiral cluster $(R)P\text{-}Fe(CO)(\eta^5\text{-}C_5Me_5)\text{-}(\mu_2\text{-}CO)\text{-}Fe(CO)_3\text{-}Mn(CO)_4$ **6** by the reaction of $(R)(\eta^1\text{-}C_5Me_5)P{=}Mn(CO)_4$ **1**[4] with $Fe_2(CO)_9$ **2**.

An overview of all reactions described is given in Scheme 1.

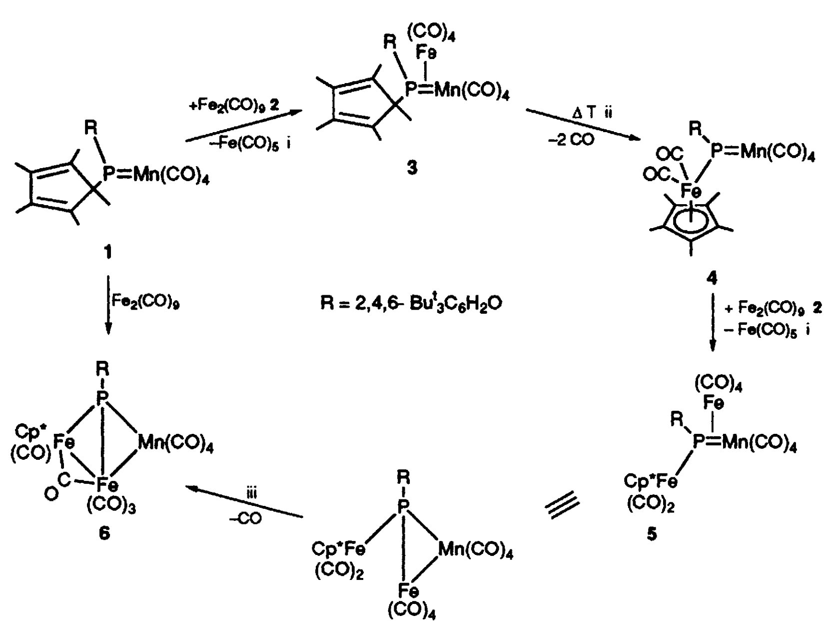
The reaction between $(R)(\eta^1\text{-}C_5Me_5)P{=}Mn(CO)_4$ **1** ($R = 2,4,6\text{-}Bu^t_3C_6H_2O$)[4] and 2.5 equiv. of $Fe_2(CO)_9$ **2** at 25 °C affords in high yield $\eta^2\text{-}[(R)(\eta^1\text{-}C_5Me_5)P{=}Mn(CO)_4]Fe(CO)_4$ **3**, in which the phosphorus–manganese double bond is side-on coordinated to the organometallic building block $Fe(CO)_4$ (Scheme 1). In refluxing toluene, **3** can be converted in almost quantitative yield to the dinuclear phosphinidene complex $(R)[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]P{=}Mn(CO)_4$ **4**, in which the pentamethylcyclopentadiene phosphine substituent has been transferred to the iron atom and is now an $\eta^5$-pentamethylcyclopentadienyl ligand. The phosphorus atom is again trigonal planar as in **1** and the phosphorus–manganese double bond has been regenerated.

Complex **4** reacts with further $Fe_2(CO)_9$ **2** at 25 °C to afford **5**: The phosphorus–manganese double bond is now π-bonded to a $Fe(CO)_4$ building block generated *in situ* from $Fe_2(CO)_9$. **5** has the constituents for the formation of **6**, and at 35 °C can be smoothly converted to **6** after decarbonylation and subsequent formation of an iron–iron bond. In **6**, the RP cap is bridging three different organometallic building blocks: $Mn(CO)_4$, $Fe(CO)_3$ and $(\eta^5\text{-}C_5Me_5)Fe(CO)$, thus giving a chiral cluster (Scheme 1; Fig. 1).

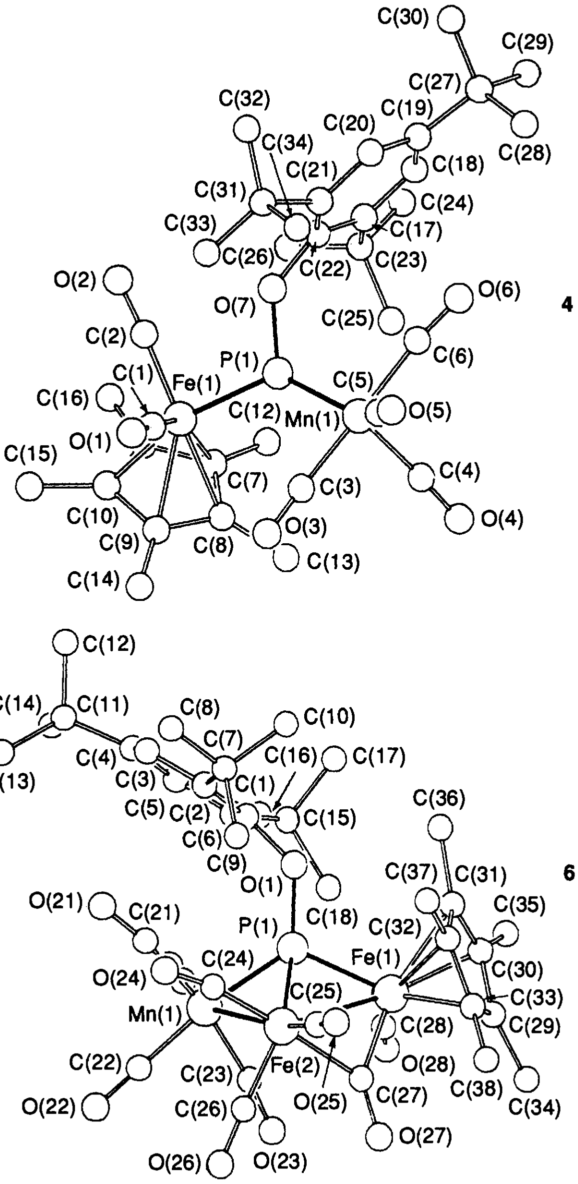
All synthesised compounds have been fully characterized by analytical as well as spectroscopic data. **4** and **6** were further characterized by X-ray structure analysis (Fig. 1).†

The structure of **4** is similar to that of other $\sigma^3,\lambda^4$-phosphanediyl complexes of type $(R)(R')P{=}ML_n$ ($ML_n$ = $Mn(CO)_4$,[4] $Co(CO)_3$,[5] $Mo(\eta^5\text{-}C_5H_5)(CO)_2$,[6–8] $W(\eta^5\text{-}C_5H_5)(CO)_2$;[6,9] R, R′ = singly bonded organic ligand). **4** contains a phosphorus–manganese double bond, which is significantly shorter (2.126 Å) than the distances usually found in organomanganese phosphine compounds (2.15–2.25 Å) (Fig. 1)[1,10] and only slightly longer than the phosphorus manganese double bond in **1** of 2.084 Å.[4] The Mn(1), Fe(1), P(1) and O(7) atoms lie in a plane (max. deviation: 0.0294 Å). The phosphorus–iron bond length (2.258 Å, Fig. 1) is typical for a phosphorus–iron single bond.[10,11]

The structure of cluster **6** is best described as an edge-opened tetrahedron with the constituent atoms P(1), Mn(1), Fe(1) and Fe(2). The Fe(1)···Mn(1) distance (3.934 Å) shows clearly that these atoms are not bonded. The phosphorus–manganese bond length (2.239 Å) corresponds to a phosphorus–manganese single bond,[10] being longer than the P=Mn bond in **4** (2.126 Å) and in **1** (2.084 Å).[4]



**Scheme 1** Synthesis of **6** by reaction of $(R)(\eta^1\text{-}C_5Me_5)P{=}Mn(CO)_4$ **1** ($R = 2,4,6\text{-}Bu^t_3C_6H_2O$) with $Fe_2(CO)_9$ **2**. *Reagents and conditions*: i, 25 °C, *toluene, 12 h; ii, refluxing toluene, 4 h; iii, 35 °C, toluene, 3 h.*



**4**

**6**

**Fig. 1** Molecular geometry and atom labeling scheme for **4** and **6**. Important intraatomic bond distances (Å) and angles (°): **4**: P(1)–Mn(1) 2.126(2), P(1)–Fe(1) 2.258(2), P(1)–O(7) 1.662(4), Mn(1)–P(1)–Fe(1) 133.1(1), Mn(1)–P(1)–O(7) 124.2(2), Fe(1)–P(1)–O(7) 102.6(2). **6**: Mn(1)–P(1) 2.239(4), Fe(1)–P(1) 2.211(4), Fe(2)–P(1) 2.258(5), Mn(1)–Fe(2) 2.811(4), Fe(1)–Fe(2) 2.700(3), P(1)–O(1) 1.640(1), Mn(1)–P(1)–Fe(1) 124.2(2), Mn(1)–P(1)–Fe(2) 77.4(1), Mn(1)–Fe(2)–Fe(1) 91.1(1), Mn(1)–P(1)–O(1) 122.9(3), Fe(1)–P(1)–Fe(2) 74.3 (1), Fe(1)–P(1)–O(1) 111.8(3), Fe(2)–Mn(1)–P(1) 51.6(1), Fe(2)–Fe(1)–P(1) 53.6(1), Fe(2)–P(1)–O(1) 131.8(3).

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## Footnote

† *Crystal data* for **4**: $C_{34}H_{44}FeMnO_7P$, $M = 706.48$. Monoclinic, space group $P2_1/c$; $a = 17.370(3)$, $b = 13.002(2)$, $c = 17.690(3)$ Å; $\beta = 106.51(2)°$, $V = 3830(1)$ Å$^3$, $Z = 4$; $D_c = 1.369$ g cm$^{-3}$. R3m/V Siemens diffractometer, using the θ-2θ technique [2θ limits: 2–42°, scan range: 0.75°, scan speed: $2.4 \leq \omega \leq 29.3°$ min$^{-1}$ (in 2θ)] and Mo-Kα radiation (λ = 0.71069 Å), graphite monochromator. Crystal dimensions: 0.20 × 0.18 × 0.15 mm, 3547 observed data [$I \geq 2\sigma(I)$] from 3967 data measured were refined to $R = 0.06$, $R_w = 0.055$ (statistical weights); **4** contains in the crystallographic independent unit one dissordered $CH_2Cl_2$ as solvent molecule.

For **6**: $C_{37}H_{44}Fe_2MnO_{10}P$, $M = 846.36$. Monoclinic, space group $P2_1/c$; $a = 21.64(2)$, $b = 9.904(4)$, $c = 22.36(2)$ Å; $\beta = 108.90(5)°$, $V = 4533(4)$ Å$^3$, $Z = 4$; $D_c = 1.302$ g cm$^{-3}$. R3m/V Siemens diffractometer, using the θ-2θ technique [2θ limits: 2–40°, scan range: 0.75°, scan speed: $2.3 \leq \omega \leq 29.3°$ min$^{-1}$ (in 2θ)] and Mo-Kα radiation (λ = 0.71069 Å), graphite monochromator. Crystal dimensions: 0.30 × 0.22 × 0.17 mm, 3278 observed data [$I \geq 2\sigma(I)$] from 4240 data measured were refined to $R = 0.076$, $R_w = 0.073$ (statistical weights); **6** contains in the crystallographic independent unit 1/2 dissordered toluene as solvent molecule.

Both structures were solved by direct methods (SHELXTL PLUS).[12] Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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