

New ferrocenylmethylphosphines – Preparation, characterisation and coordination chemistry of $\text{PH}(\text{CH}_2\text{Fc})_2$, $\text{P}(\text{CH}_2\text{Fc})_3$ [$\text{Fc} = \text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4)$] and their derivatives

René Kalio, Peter Lönnecke¹, Evamarie Hey-Hawkins*

Institut für Anorganische Chemie der Universität Leipzig, Johannisallee 29, D-04103 Leipzig, Germany

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Abstract

The new ferrocenylmethylphosphines $\text{PH}(\text{CH}_2\text{Fc})_2$ (**1**) [$\text{Fc} = \text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4)$] and $\text{P}(\text{CH}_2\text{Fc})_3$ (**2**) and the phosphonium salt $[\text{P}(\text{CH}_2\text{Fc})_3(\text{CH}_2\text{OH})]\text{I}$ (**3**) were synthesised from $\text{P}(\text{CH}_2\text{OH})_3$ and $[\text{FcCH}_2\text{NMe}_3]\text{I}$. $[\text{P}(\text{CH}_2\text{Fc})(\text{CH}_2\text{OH})_3]\text{Cl}$ (**4**) was obtained from $\text{P}(\text{CH}_2\text{Fc})(\text{CH}_2\text{OH})_2$, CH_2O and HCl . The new phosphines and phosphonium salts were fully characterised by NMR and IR spectroscopy and MS. $[\text{Mo}(\text{CO})_6]$ reacts with **1** to give $[\text{Mo}(\text{CO})_5\{\text{PH}(\text{CH}_2\text{Fc})_2\}]$ (**5**) in high yield, but attempts to employ **2** as a ligand failed. The reaction of $[\text{P}(\text{CH}_2\text{Fc})_3(\text{CH}_2\text{OH})]\text{I}$ (**3**) and $[\text{PH}(\text{CH}_2\text{Fc})_3]\text{I}$ (obtained *in situ* from **3** and $\text{Na}_2\text{S}_2\text{O}_5$) with $[\text{Wl}_2(\text{CO})_3(\text{NCMe})_2]$ gave the complex salts $[\text{P}(\text{CH}_2\text{Fc})_3(\text{CH}_2\text{OH})][\text{Wl}_3(\text{CO})_4]$ (**6**) and $[\text{PH}(\text{CH}_2\text{Fc})_3][\text{Wl}_3(\text{CO})_4]$ (**7**), respectively. $[\text{P}(\text{CH}_2\text{Fc})_4]\text{I}$ (**8**) was synthesised from $\text{PH}_2\text{CH}_2\text{Fc}$ and $[\text{FcCH}_2\text{NMe}_3]\text{I}$. Crystal structures were obtained for **1**, **3–8**.

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1. Introduction

With respect to organometallic complexes incorporating phosphines, the majority of studies have involved tertiary phosphines [1]. Not surprisingly, complexes of primary and secondary phosphines have received much less attention, due to the toxicity and high reactivity of the free phosphines (some are even pyrophoric). This lack of attention has prompted the development of primary and secondary phosphines that are more air-stable and hence easier to use [2–8]. Interest in these phosphines has arisen from the possibility of post-coordination modification of the PH bond, allowing for chemical flexibility in the synthesis of new and intriguing transition metal phosphine complexes [9]. Developments in this area include the use of bulky aryl

groups [5,6] or aminoalkyl substituents [7]. Recently, Henderson et al. [2–4] used the ferrocenylmethyl fragment to stabilize primary phosphines. Due to the redox properties of the ferrocenyl unit and the possibility to readily obtain chiral compounds, ferrocenylphosphines are an important class of ligands in transition metal chemistry [10,11]. Henderson et al. found the phosphine $\text{PH}_2\text{CH}_2\text{Fc}$ [$\text{Fc} = \text{Fe}(\eta^5\text{-C}_5\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)$] to be indefinitely air-stable [4], probably due to electronic rather than steric effects, as well as having the ability to coordinate to molybdenum carbonyls or $[(p\text{-cymene})\text{RuCl}_2]$ ($p\text{-cymene} = 1\text{-Me-4-Pr}^i\text{C}_6\text{H}_4$), without alteration of the PH_2 group, whereas P–H activation occurred in the reaction with $[\text{Ru}_3(\text{CO})_{12}]$ to give two products with capping phosphinidene ligands [3].

We have now extended this chemistry to the sterically demanding air-stable secondary and tertiary ferrocenylphosphines $\text{PH}(\text{CH}_2\text{Fc})_2$ (**1**) and $\text{P}(\text{CH}_2\text{Fc})_3$ (**2**) and the phosphonium salts $[\text{P}(\text{CH}_2\text{Fc})_3(\text{CH}_2\text{OH})]\text{I}$ (**3**) and $[\text{P}(\text{CH}_2\text{Fc})(\text{CH}_2\text{OH})_3]\text{Cl}$ (**4**). Whereas $[\text{Mo}(\text{CO})_6]$ reacts with **1** to give $[\text{Mo}(\text{CO})_5\{\text{PH}(\text{CH}_2\text{Fc})_2\}]$ (**5**), no reaction

* Corresponding author. Tel.: +49 (0)341 9736151; fax: +49 (0)341 9739319.

E-mail address: hey@rz.uni-leipzig.de (E. Hey-Hawkins).

¹ Crystal structure determination.

occurred with the bulky phosphine **2**. The phosphonium salts $[P(CH_2Fc)_3(CH_2OH)]I$ (**3**) and $[PH(CH_2Fc)_3]I$ (obtained *in situ* from **3** and $Na_2S_2O_5$) react with $[Wl_2(CO)_3(NCMe)_2]$ to give the complex salts $[P(CH_2Fc)_3(CH_2OH)][Wl_3(CO)_4]$ (**6**) and $[PH(CH_2Fc)_3][Wl_3(CO)_4]$ (**7**). A mechanism for the formation of these anions is proposed. Furthermore, a convenient pathway for the synthesis of the bulky phosphonium salt $[P(CH_2Fc)_4]I$ (**8**) was found.

We have already shown that the phosphines PH_2Fc , PH_2CH_2Fc , and $PH(CH_2Fc)_2$ ($=L$) react with transition metal complexes with reactive $M-X$ bonds ($X = \text{halide}$) without loss of HX but with clean formation of the corresponding phosphine complexes, such as $[Cp^R TaCl_4(L)]$ ($Cp^R = C_5H_4Me, C_5Me_5$) [12], $[(p\text{-cymene})RuCl_2(L)]$ [3,13], $[(p\text{-cymene})Ru(Cl)(L)_2](PF_6)$ [14], *trans*- $[Ru(Cl)_2(L)_4]$ [14], $[Ml_2(CO)_3(L)_2]$ and $[Ml_2(CO)_2(L)_3]$ ($M = Mo, W$) [15–17]. The unexpected formation of the unique complex salt $[Wl(CO)_2(PH_2CH_2Fc)_4]I$ is another example of the unusual coordinating properties of these phosphines [18].

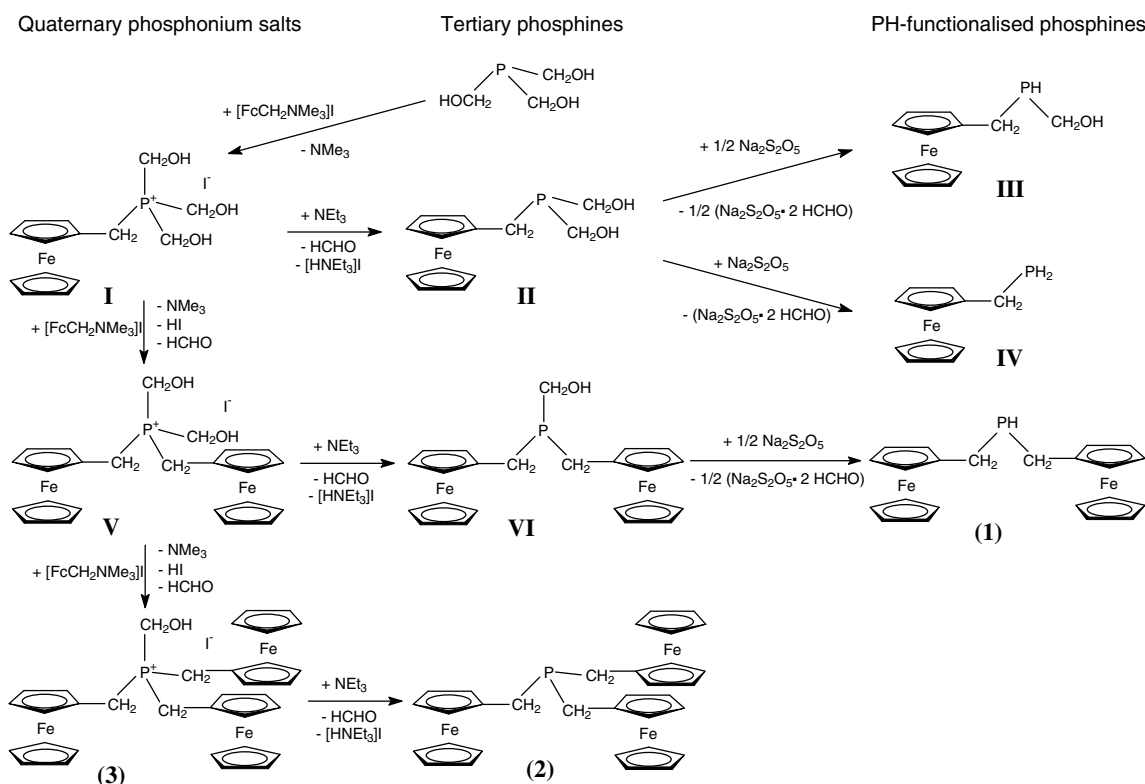
2. Results and discussion

2.1. Synthesis of $PH(CH_2Fc)_2$ (**1**), $P(CH_2Fc)_3$ (**2**), $[P(CH_2Fc)_3(CH_2OH)]I$ (**3**), $[P(CH_2Fc)(CH_2OH)_3]Cl$ (**4**) and $[P(CH_2Fc)_4]I$ (**8**)

Marr and White [19] showed that tertiary ferrocenylmethylphosphines are available from secondary or primary

phosphines and $[FcCH_2NMe_3]I$, the products of which are tertiary bis(ferrocenylmethyl)phosphines and quaternary bis(ferrocenylmethyl)phosphonium salts. Accordingly, bis(hydroxymethyl)phosphinomethylferrocene $P(CH_2Fc)(CH_2OH)_2$ (**II**) [31,32] and racemic $P(CHMeFc)(CH_2OH)_2$ [20] are available via ferrocenylmethylation of $P(CH_2OH)_3$ with $[FcCH_2NMe_3]I$ and $[FcCHMeNEt_2Me]I$, which gives the phosphonium salt $[P(CH_2Fc)(CH_2OH)_3]I$ (**I**) and $[P(CHMeFc)(CH_2OH)_3]I$, respectively, from which the free phosphine $P(CH_2Fc)(CH_2OH)_2$ (**II**) or $P(CHMeFc)(CH_2OH)_2$, respectively, is then obtained by addition of NEt_3 . Henderson et al. reported the formation of side products in the reaction with $[FcCH_2NMe_3]I$ [31] one of which was $PH(CH_2Fc)(CH_2OH)$ (**III**) ($\delta = -51.4$ ppm), while the others were not further characterised, which makes purification of $P(CH_2Fc)(CH_2OH)_2$ (**II**) by recrystallisation necessary. $PH(CH_2Fc)(CH_2OH)$ (**III**) is apparently formed from the phosphonium salts under alkaline conditions (elimination of HI and $HCHO$).

When we carried out the synthesis of **II**, we also observed the formation of $PH(CH_2Fc)_2$ (**1**) ($\delta = -53.4$ ppm) besides $PH(CH_2Fc)(CH_2OH)$ (**III**) as side product (by ^{31}P NMR). Compound **1** was formed when an excess [21] of $[FcCH_2NMe_3]I$ was employed and the reaction time was prolonged (Scheme 1 [22]). The phosphonium salt $[P(CH_2Fc)_2(CH_2OH)_2]I$ (**V**) eliminates HI under alkaline conditions to give $P(CH_2Fc)_2(CH_2OH)$ (**VI**), which eliminates $HCHO$ giving $PH(CH_2Fc)_2$ (**1**). At the same time $P(CH_2Fc)_2(CH_2OH)$ (**VI**) can also react with



Scheme 1. Formation of ferrocenylmethyl-substituted phosphines from $[FcCH_2NMe_3]I$ and $P(CH_2OH)_3$, including work-up to give PH functionalised phosphines.

Table 1
Crystal data and structure refinement for compounds **1**, **3–8**

	1	3	4	5	6	7	8
Formula	C ₂₂ H ₂₃ Fe ₂ P	C ₃₄ H ₃₆ Fe ₃ IOP	C ₁₄ H ₂₀ ClFeO ₃ P	C ₂₇ H ₂₃ Fe ₂ MoO ₅ P	C ₃₈ H ₃₆ Fe ₃ I ₃ O ₅ PW	C ₃₇ H ₃₄ Fe ₃ I ₃ O ₄ PW	C ₄₅ H ₄₅ Cl ₃ Fe ₄ IP
Formula weight	430.07	786.05	358.57	666.06	1335.74	1305.71	1073.43
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	P2 ₁ 2 ₁ 2 ₁	Pmma	P $\bar{1}$	P2 ₁ /n	Cc	P2 ₁ /c
Unit cell dimensions							
<i>a</i> (pm)	1917.3(3)	995.14(11)	1465.06(14)	776.16(16)	1123.85(15)	1550.0(2)	1876.3(3)
<i>b</i> (pm)	763.16(11)	1244.22(14)	949.08(9)	1120.6(2)	1454.73(19)	1341.8(2)	1335.1(2)
<i>c</i> (pm)	1268.69(19)	2495.0(3)	1083.11(10)	1530.4(3)	2510.5(3)	1924.7(3)	1727.7(3)
α (°)	90	90	90	84.487(4)	90	90	90
β (°)	103.815(5)	90	90	78.739(4)	95.231(2)	91.557(4)	91.124(3)
γ (°)	90	90	90	86.247(4)	90	90	90
Volume (nm ³)	1.8026(5)	3.0893(6)	1.5060(2)	1.2980(5)	4.0873(9)	4.0015(10)	4.2734(13)
<i>Z</i>	4	4	4	2	4	4	4
Temperature (K)	208(2)	223(2)	223(2)	208(2)	223(2)	208(2)	210(2)
Density (calculated) (Mg/m ⁻³)	1.585	1.690	1.581	1.704	2.171	2.167	1.668
Absorption coefficient (mm ⁻¹)	1.699	2.467	1.288	1.676	6.194	6.322	2.310
Crystal size (mm ³)	0.30 × 0.20 × 0.04	0.30 × 0.20 × 0.20	0.30 × 0.30 × 0.15	0.20 × 0.05 × 0.02	0.25 × 0.25 × 0.10	0.20 × 0.20 × 0.20	0.40 × 0.40 × 0.05
θ Range for data collection (°)	2.19–28.82	1.63–28.83	2.34–28.80	1.36–29.04	1.62–29.07	2.01–31.65	1.88–29.19
<i>F</i> (000)	888	1576	744	668	2520	2456	2152
Index ranges	−20 ≤ <i>h</i> ≤ 25, −8 ≤ <i>k</i> ≤ 10, −17 ≤ <i>l</i> ≤ 13	−13 ≤ <i>h</i> ≤ 13, −11 ≤ <i>k</i> ≤ 16, −33 ≤ <i>l</i> ≤ 29	−19 ≤ <i>h</i> ≤ 16, −12 ≤ <i>k</i> ≤ 10, −14 ≤ <i>l</i> ≤ 14	−10 ≤ <i>h</i> ≤ 7, −14 ≤ <i>k</i> ≤ 14, −20 ≤ <i>l</i> ≤ 14	−14 ≤ <i>h</i> ≤ 14, −10 ≤ <i>k</i> ≤ 19, −32 ≤ <i>l</i> ≤ 33	−22 ≤ <i>h</i> ≤ 21, −19 ≤ <i>k</i> ≤ 10, −28 ≤ <i>l</i> ≤ 28	−25 ≤ <i>h</i> ≤ 20, −18 ≤ <i>k</i> ≤ 17, −17 ≤ <i>l</i> ≤ 23
Reflections collected	5765	20408	9555	8344	26872	16845	26199
Independent reflections	2179	7463	1992	5884	9940	11208	10467
Data/restraints/parameters	[<i>R</i> _{int}] = 0.0384 2179/0/162	[<i>R</i> _{int}] = 0.0392 7463/0/397	[<i>R</i> _{int}] = 0.0377 1992/0/143	[<i>R</i> _{int}] = 0.0413 5884/0/345	[<i>R</i> _{int}] = 0.0590 9940/0/460	[<i>R</i> _{int}] = 0.0224 11208/3/446	[<i>R</i> _{int}] = 0.0518 10467/6/515
Goodness-of-fit on <i>F</i> ²	1.040	0.861	1.059	1.188	0.937	1.059	1.145
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0335, <i>wR</i> ₂ = 0.0800	<i>R</i> ₁ = 0.0267, <i>wR</i> ₂ = 0.0416	<i>R</i> ₁ = 0.0309, <i>wR</i> ₂ = 0.0785	<i>R</i> ₁ = 0.0862, <i>wR</i> ₂ = 0.1361	<i>R</i> ₁ = 0.0387, <i>wR</i> ₂ = 0.0755	<i>R</i> ₁ = 0.0434, <i>wR</i> ₂ = 0.0953	<i>R</i> ₁ = 0.0641, <i>wR</i> ₂ = 0.1079
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0456, <i>wR</i> ₂ = 0.0855	<i>R</i> ₁ = 0.0443, <i>wR</i> ₂ = 0.0436	<i>R</i> ₁ = 0.0405, <i>wR</i> ₂ = 0.0824	<i>R</i> ₁ = 0.1513, <i>wR</i> ₂ = 0.1643	<i>R</i> ₁ = 0.0794, <i>wR</i> ₂ = 0.0846	<i>R</i> ₁ = 0.0546, <i>wR</i> ₂ = 0.0997	<i>R</i> ₁ = 0.1036, <i>wR</i> ₂ = 0.1205
Absolute structure parameter		−0.001(10)				0.014(6)	
Largest difference peak and hole (e Å ⁻³)	0.533/−0.435	0.479/−0.456	0.696/−0.298	0.765/−1.089	0.706/−1.522	3.219/−0.789	0.744/−0.722
CCDC numbers	260049	260046	260048	260050	260047	260051	644750

[FcCH₂NMe₃]I to afford [P(CH₂Fc)₃(CH₂OH)]I (**3**). Elimination of HI and HCHO from **3** (either already in the reaction mixture or during alkaline work-up) results in formation of the tertiary phosphine P(CH₂Fc)₃ (**2**) (Scheme 1). We have not observed formation of the quaternary phosphonium salt [P(CH₂Fc)₄]I (**8**) under the conditions in this reaction mixture. The fully ferrocenylmethylated phosphonium iodide **8** was obtained on refluxing a 3:1 mixture of [FcCH₂NMe₃]I and PH₂CH₂Fc for 72 h in ethanol.

By comparison of the ³¹P NMR data with those of the phosphonium chloride [P(CH₂Fc)(CH₂OH)₃]Cl (**4**), which

was independently obtained from P(CH₂Fc)(CH₂OH)₂, HCHO and HCl, the corresponding iodide, [P(CH₂Fc)(CH₂OH)₃]I (**1**), was identified in the reaction mixture (Scheme 1).

As the selective formation of either phosphine is virtually impossible (even starting from P(CH₂Fc)(CH₂OH)₂ (**II**) instead of P(CH₂OH)₃) the reaction sequence shown in Scheme 1 was carried out by using Na₂S₂O₅ for the elimination of formaldehyde [31], and the products [PH₂CH₂Fc (**IV**), PH(CH₂Fc)₂ (**1**), P(CH₂Fc)₃ (**2**), ratio 13:11:1; and [P(CH₂Fc)₃(CH₂OH)]I (**3**)] were separated as described in

Section 4. The yield of $[P(CH_2Fc)_3(CH_2OH)]I$ (**3**) could be increased if the reaction solution was extracted with CH_2Cl_2 prior to addition of NEt_3 . Pure **3** could then be obtained as orange rhombohedral crystals by column chromatography.

2.2. NMR spectroscopy

The ^{31}P NMR data of all ferrocenylmethylphosphine derivatives observed in the reaction between $P(CH_2OH)_3$ with $[FcCH_2NMe_3]I$ (Scheme 1) are summarised in Table 2. Apparently, the hydroxymethyl group and the ferrocenylmethyl group have a similar effect on the chemical shift, as secondary phosphines are generally observed at ca. -52 ppm, tertiary at -17 to -24 ppm and quaternary phosphonium salts at $+17$ to $+25$ ppm.

2.3. Molecular structures of $PH(CH_2Fc)_2$ (**1**),

$[P(CH_2Fc)_3(CH_2OH)]I$ (**3**), $[P(CH_2Fc)(CH_2OH)_3]Cl$ (**4**) and $[P(CH_2Fc)_4]I$ (**8**)

$PH(CH_2Fc)_2$ (**1**) crystallises in the monoclinic space group $C2/c$. The molecule is located on a crystallographic C_2 -axis which passes through the phosphorus atom and causes a disorder of the P–H proton and the lone pair of electrons at P(1) (Fig. 1, Table 3). The C_5 –Fe– C_5 axes of the two ferrocenyl groups have a dihedral angle of 83.2° and thus an almost orthogonal orientation. Whereas in PH_2CH_2Fc the P atom is at the largest distance possible from the ferrocenyl unit [4], in **1** the phosphorus atom lies between the two Fc substituents. The $P \cdots Fe$ distances of 386 pm are too long for $P \cdots Fe$ interaction, so the unusual orientation is probably due to packing effects.

The molecular structures of **3** and **4** are shown in Figs. 2 and 3, and selected bond lengths and angles are listed in Tables 4 and 5. The phosphorus atom in **3** is coordinated almost ideally tetrahedrally by the three ferrocenylmethyl groups and one hydroxymethyl substituent, even though the molecule seems rather sterically crowded. The molecule of **4** is located on a crystallographic mirror plane, which

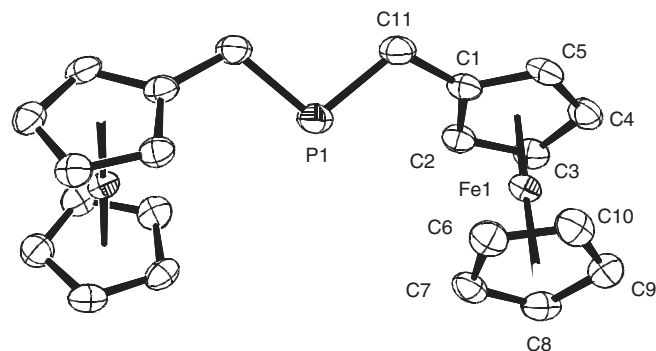


Fig. 1. Molecular structure of **1**. The PH proton is disordered over two positions (not shown).

Table 3
Selected bond lengths (pm) and angles ($^\circ$) for $PH(CH_2Fc)_2$ (**1**)

P(1)–C(11)	185.7(2)
C(1)–C(11)	149.9(3)
C(11)–P(1)–C(11)'	101.4(2)
C(1)–C(11)–P(1)	113.0(2)

passes through atoms C(1), C(7), Fe(1), C(4) and P(1). Accordingly, the atom C(9), the hydrogen atoms at C(9) and the hydroxyl group O(2)–H(1o2) are disordered over two positions. As the two positions of C(9) could not be treated or refined separately, a rather short C–O bond of 124.7(4) pm results. The other two C–O bond lengths are in the expected range [23].

Hydrogen bonding is observed in **3** and **4**. Whereas **3** has only one hydrogen bond between the OH group and the iodide ion ($O(1) \cdots I(1) = 343.4$ pm), in **4** a one-dimensional chain (along the b -axis) is formed by hydrogen bonding between the chloride anion and three OH groups (one being disordered) from three different $[P(CH_2Fc)(CH_2OH)_3]$ cations ($O(1) \cdots Cl(1)$) and $O(1)' \cdots Cl(1) = 312.5$ pm; $O(2) \cdots Cl(1)$ and $O(2)' \cdots Cl(1) = 307.0$ pm (Fig. 4).

The molecular structure of **8** is shown in Fig. 5, and selected bond lengths and angles are given in Table 6. The

Table 2
 ^{31}P NMR spectroscopic data of ferrocenylphosphines and ferrocenylphosphonium salts in Scheme 1

Compound	δ (ppm)	$^1J_{PH}$ (Hz)	Reference
Primary phosphines	PH_2CH_2Fc (IV) ^a	-129.1	[3,4]
Secondary phosphines	$PH(CH_2Fc)(CH_2OH)$ (III)	-51.4	[3]
	$PH(CH_2Fc)_2$ (1)	-53.3	
Tertiary phosphines	$P(CH_2Fc)(CH_2OH)_2$ (II)	-19.3	[31]
	$P(CH_2Fc)_2(CH_2OH)$ (VI)	-23.5	
	$P(CH_2Fc)_3$ (2)	-17.2	
Quaternary phosphonium salts	$[P(CH_2Fc)(CH_2OH)_3]I$ ^b (I)	$+23.4$	
	$[P(CH_2Fc)_2(CH_2OH)_2]I$ (V)	$+24.7$	
	$[P(CH_2Fc)_3(CH_2OH)]I$ (3)	$+20.6$	
	$[P(CH_2Fc)_4]I$ (8)	$+17.6$	

^a Numbering scheme according to Scheme 1.

^b The ^{31}P NMR data of $[P(CH_2Fc)(CH_2OH)_3]I$ (**I**) and $[P(CH_2Fc)(CH_2OH)_3]Cl$ (**4**) are identical (**4** in D_2O : 25.1 ppm).

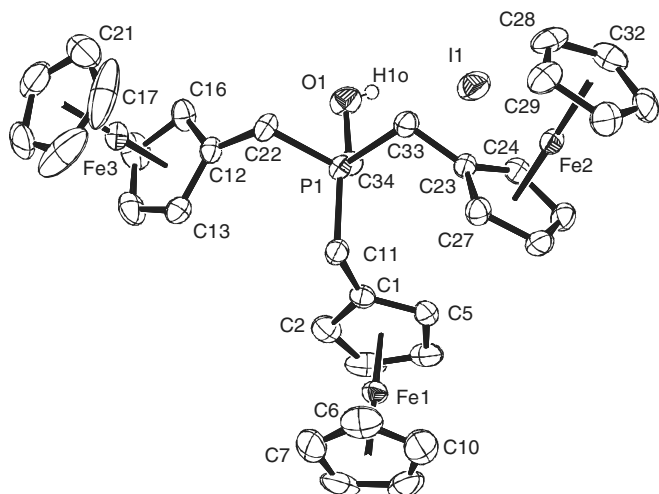


Fig. 2. Molecular structure of **3**. Hydrogen atoms (other than OH) are omitted for clarity.

Table 4
Selected bond lengths (pm) and angles ($^{\circ}$) for $[P(CH_2Fc)_3(CH_2OH)]I$ (**3**)

P(1)–C(11)	181.2(3)
P(1)–C(22)	181.0(3)
P(1)–C(33)	181.5(3)
P(1)–C(34)	181.3(3)
O(1)–C(34)	140.7(3)
C(11)–P(1)–C(33)	111.5(1)
C(11)–P(1)–C(34)	109.4(1)
C(22)–P(1)–C(11)	109.3(1)
C(22)–P(1)–C(33)	108.2(1)
C(22)–P(1)–C(34)	108.7(1)
C(34)–P(1)–C(33)	109.7(2)
O(1)–C(34)–P(1)	107.5(2)

Table 5
Selected bond lengths (pm) and angles ($^{\circ}$) for $[P(CH_2Fc)(CH_2OH)_3]Cl$ (**4**)

P(1)–C(7)	180.2(3)
P(1)–C(8)	181.9(2)
P(1)–C(9)	181.8(3)
O(1)–C(8)	140.4(2)
O(2)–C(9)	124.7(4)
O(1)–H(1o1)	82(3)
O(2)–H(1o2)	83(3)
C(7)–P(1)–C(8)	110.3(1)
C(7)–P(1)–C(9)	108.9(1)
C(8)–P(1)–C(8')	108.7(1)
C(7)–P(1)–C(8)	110.3(1)
C(9)–P(1)–C(8)	109.4(1)
C(1)–C(7)–P(1)	111.9(2)
O(2)–C(9)–P(1)	118.1(2)
O(2)–C(9)–O(2')	76.5(4)

the monophosphine complex $[Mo(CO)_5\{PH(CH_2Fc)_2\}]$ (**5**) exclusively. In contrast to the primary phosphine PH_2CH_2Fc no bis-phosphine complex $[Mo(CO)_4\{PH(CH_2Fc)_2\}_2]$ was observed in a 2:1 reaction under identical conditions [3]. Crystals of **5** are air-stable, whereas solutions decompose in air with formation of a blue oxidation product.

The molecular structure of **5** is shown in Fig. 6, and selected bond lengths and angles are given in Table 7.

Due to the *trans* influence, the shortest Mo–C bond (2(1) pm) is that *trans* to the phosphine ligand. Accordingly, this group has the weakest CO bond, and the CO vibration at lowest wavenumber (1900 cm^{-1}) can be assigned to this group.

In contrast to other tertiary phosphines, sterically demanding tertiary phosphine **2** did not react with $[Cp^*TaCl_4]$ ($Cp^* = C_5H_4Me$) or $[Cp^*TaCl_4]$ ($Cp^* = C_5Me_5$) at $25\text{ }^{\circ}C$ in Et_2O or toluene and no phosphine complex was formed on reaction with $[MI_2(CO)_3(NCMe)_2]$, whereas in the analogous reaction between $[MI_2(CO)_3(NCMe)_2]$ ($M = Mo, W$) and the sterically demanding PPh_3 , the complexes $[MI_2(CO)_3(PPh_3)_2]$ were formed and could be spectroscopically identified prior to their final rearrangement to $[PPh_3][MI_3(CO)_3(PPh_3)]$ [24].

$[Wl_2(CO)_3(NCMe)_2]$ reacts with $[P(CH_2Fc)_3(CH_2OH)]I$ (**3**) or with $[PH(CH_2Fc)_3]I$, prepared in situ from **3** and $Na_2S_2O_5$, with formation of the phosphonium salts

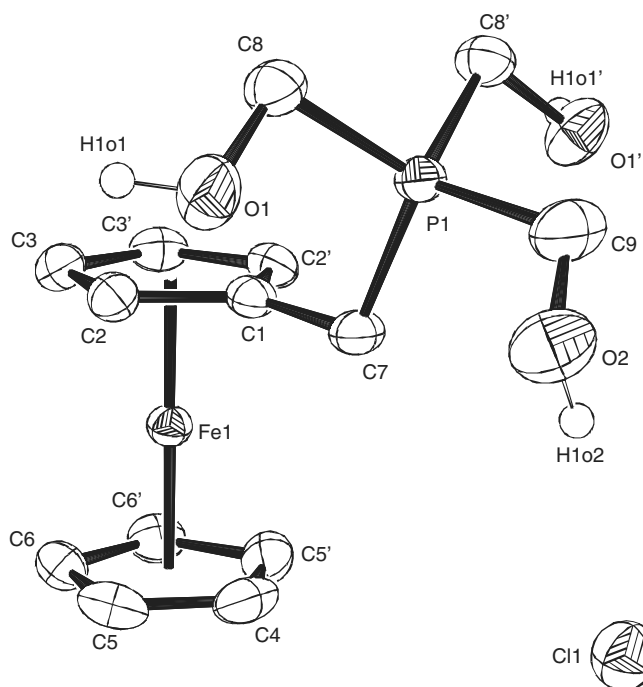


Fig. 3. Molecular structure of **4**. H atoms (other than CH_2OH) are omitted for clarity. The hydroxyl group $O2-H1o2$ is disordered over two positions of which only one is shown.

coordination sphere of the P centre of the large cation of **8** is tetrahedral, but the orientation of the ferrocenyl groups corresponds to their optimum stacking in the lattice. The iodide anion is situated in a pocket formed by four ferrocenyl units whose Fe centres all lie in a distance of 500–600 pm, thus excluding their direct interaction with the iodide anion.

2.4. Coordination chemistry of $PH(CH_2Fc)_2$ (**1**), $P(CH_2Fc)_3$ (**2**) and $[P(CH_2Fc)_3(CH_2OH)]I$ (**3**)

Secondary phosphine **1** reacts with an excess of $[Mo(CO)_6]$ in boiling toluene almost quantitatively to give

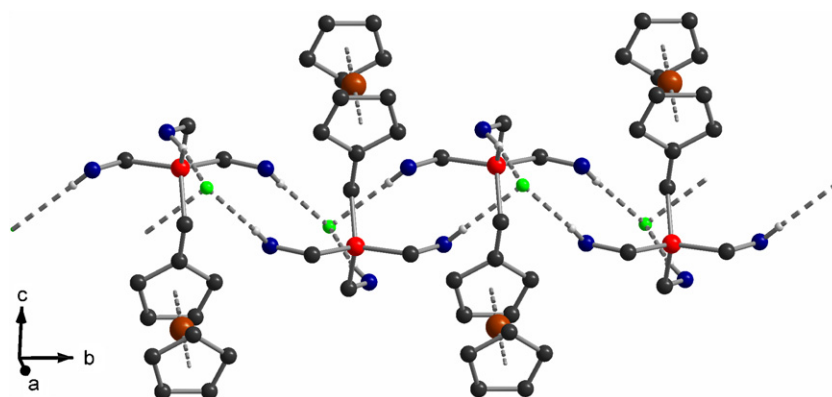


Fig. 4. A one-dimensional chain (along the *b*-axis) is formed by hydrogen bonding between the chloride anion and three OH groups in $[\text{P}(\text{CH}_2\text{Fc})(\text{CH}_2\text{OH})_3]\text{Cl}$ (**4**).

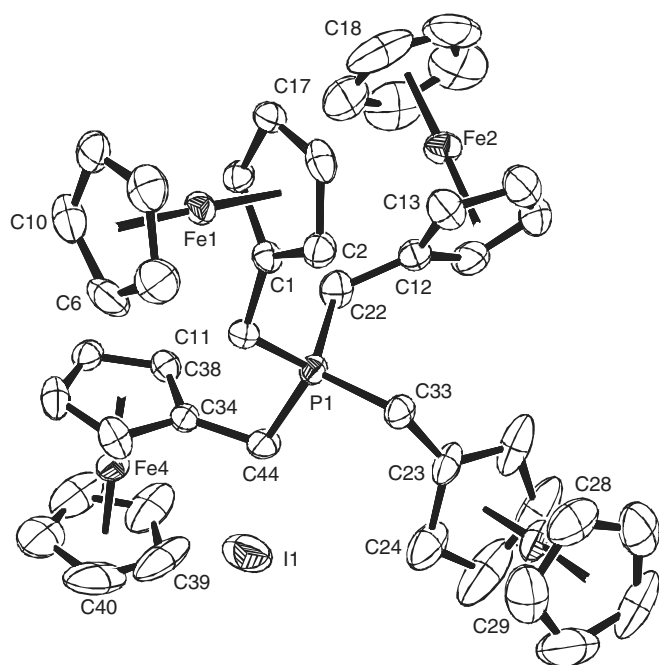


Fig. 5. Molecular structure of **8**. All H atoms are omitted for clarity.

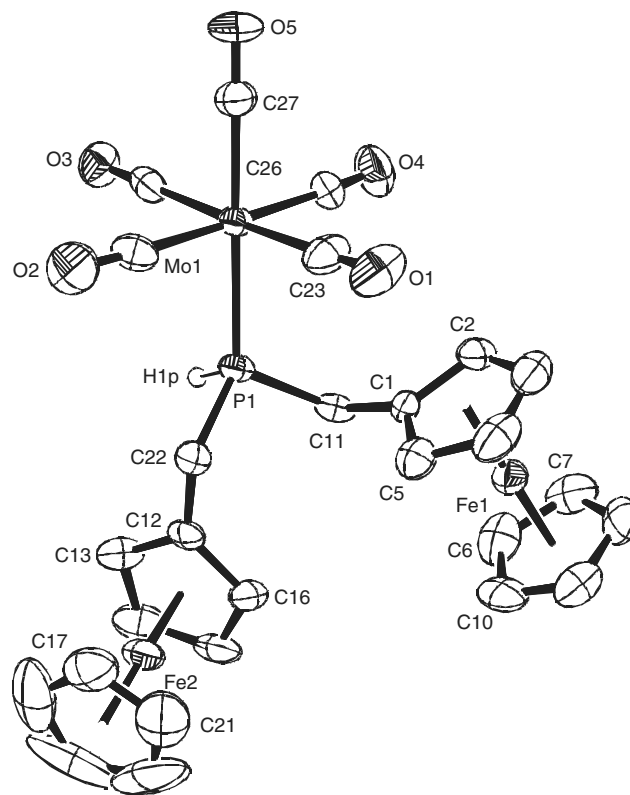


Fig. 6. Molecular structure of **5**.

Table 6
Selected bond lengths (pm) and angles ($^\circ$) for $[\text{P}(\text{CH}_2\text{Fc})_4]\text{I}$ (**8**)

P(1)–C(11)	180.3(5)
P(1)–C(22)	181.6(5)
P(1)–C(33)	180.7(4)
P(1)–C(44)	181.4(4)
C(22)–P(1)–C(11)	108.7(2)
C(33)–P(1)–C(11)	108.9(2)
C(44)–P(1)–C(11)	106.4(2)
C(33)–P(1)–C(22)	113.0(2)
C(44)–P(1)–C(22)	109.4(2)
C(44)–P(1)–C(33)	110.2(2)
C(1)–C(11)–P(1)	116.3(4)
C(12)–C(22)–P(1)	115.7(3)
C(23)–C(33)–P(1)	115.2(3)
C(34)–C(44)–P(1)	110.6(3)

$[\text{P}(\text{CH}_2\text{Fc})_3(\text{CH}_2\text{OH})][\text{Wl}_3(\text{CO})_4]$ (**6**) and $[\text{PH}(\text{CH}_2\text{Fc})_3][\text{Wl}_3(\text{CO})_4]$ (**7**), respectively. Formation of the $[\text{Wl}_3(\text{CO})_4]^-$ anion via ligand exchange in tungsten complexes was already observed in other reactions [25,26], and we propose a similar ligand exchange here (Scheme 2). Accordingly, a higher yield of **6** and **7** was obtained when two equivalents of $[\text{Wl}_2(\text{CO})_3(\text{NCMe})_2]$ were employed in the reaction.

The molecular structures of **6** and **7** are shown in Figs. 7 and 8, and selected bond lengths and angles are given in Tables 8 and 9.

In both salts, the $[\text{Wl}_3(\text{CO})_4]^-$ anion (Fig. 9) has almost C_{3v} symmetry and can be regarded as a monocapped octahe-

Table 7
Selected bond lengths (pm) and angles (°) for [Mo(CO)₅{PH(CH₂Fc)₂}]
(5)

Mo(1)–C(23)	206(1)
Mo(1)–C(24)	204(1)
Mo(1)–C(25)	204(1)
Mo(1)–C(26)	207(1)
Mo(1)–C(27)	202(1)
Mo(1)–P(1)	250.7(2)
C(23)–Mo(1)–C(24)	92.8(4)
C(23)–Mo(1)–C(25)	176.8(4)
C(23)–Mo(1)–C(26)	90.7(4)
C(23)–Mo(1)–C(27)	89.0(4)
C(24)–Mo(1)–C(25)	85.9(4)
C(24)–Mo(1)–C(26)	176.4(4)
C(24)–Mo(1)–C(27)	90.6(4)
C(25)–Mo(1)–C(26)	90.6(4)
C(25)–Mo(1)–C(27)	88.1(4)
C(26)–Mo(1)–C(27)	90.1(4)
C(23)–Mo(1)–P(1)	90.8(3)
C(24)–Mo(1)–P(1)	89.8(3)
C(25)–Mo(1)–P(1)	92.1(3)
C(26)–Mo(1)–P(1)	89.5(3)
C(27)–Mo(1)–P(1)	179.5(3)

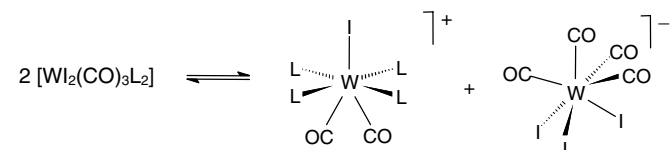
dron. The analogous bromo complex anion [WBr₃(CO)₄][−] was used by Drew et al. [27,28] as standard for definition of the conventional monocapped octahedron. The structure of the [P(CH₂Fc)₃(CH₂OH)]⁺ cation is similar to that of the starting material **3**; however, a different orientation of the ferrocenylmethyl groups is observed in the two cations.

3. Prospect

We are now trying to employ the bulky tertiary phosphine **2** for the stabilisation of transition metal complexes in unusual oxidation states and coordination numbers. Additionally, the P–H functionalised secondary phosphine **1** should allow the synthesis of unusual transition metal phosphanido complexes [29], and the “superbulky” phosphonium cation of compound **8** should find applications due to its four redox-active ferrocenyl centres.

4. Experimental

General Remarks: All manipulations were carried out with standard high-vacuum and dry-nitrogen techniques. Solvents were purified and dried according to standard procedures. NMR spectra in CDCl₃ at 25 °C: Avance DRX 400 (Bruker), standards: ¹H NMR (400 MHz):



Scheme 2. Proposed equilibrium for formation of the tetracarbonyltriiodotungstate(II) anion (L = CH₃CN, PR₃, (R = H, CH₂OH, CH₂Fc)).

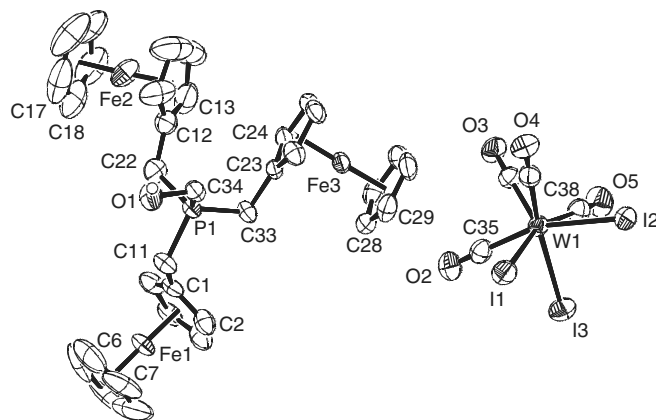


Fig. 7. Molecular structure of **6**.

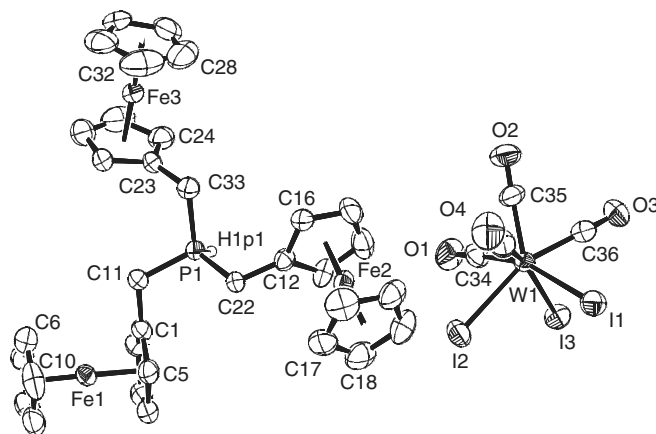


Fig. 8. Molecular structure of **7**. H atoms (other than PH) are omitted for clarity.

TMS, ¹³C NMR (100.6 MHz): TMS, ³¹P NMR (162 MHz): external 85% H₃PO₄. The IR spectra were recorded as KBr mulls on a Perkin–Elmer System 2000 FT-IR spectrometer in the range 350–4000 cm^{−1}. Mass spectra were obtained with a Varian MAT 711 Spectrometer (FAB, 70 eV, source temperature 180 °C, matrix 3-NBA). Elemental analysis was performed on a VARIO EL (Heraeus) with handling of the samples in air. The melting points were determined in sealed capillaries and are uncorrected. Tetrakis(hydroxymethyl)phosphonium chloride was provided by CYTEC; [Mo(CO)₆] is commercially available. [FcCH₂NMe₃]I [30], P(CH₂Fc)(CH₂OH)₂ [31,32] and [Wl₂(CO)₃(NCMe)₂] [33] were prepared according to the literature; the latter was recrystallised from CH₂Cl₂ prior to use.

5. X-ray crystallography

X-ray diffraction data were collected on a Siemens SMART CCD diffractometer (Radiation: Mo K α , λ = 71.073 pm; Method: ω scans rotation). Absorption correction was performed using the program SADABS [34]. The structures were solved by direct methods, and all

Table 8

Selected bond lengths (pm) and angles (°) for the $[\text{P}(\text{CH}_2\text{Fc})_3(\text{CH}_2\text{OH})]^+$ cation and the $[\text{WI}_3(\text{CO})_4]^-$ anion in $[\text{P}(\text{CH}_2\text{Fc})_3(\text{CH}_2\text{OH})][\text{WI}_3(\text{CO})_4]$ (**6**)

Cation			
P(1)–C(11)	180.8(5)	P(1)–C(34)	180.9(5)
P(1)–C(22)	181.6(5)	O(1)–C(34)	140.1(6)
P(1)–C(33)	179.5(5)		
C(11)–P(1)–C(22)	106.1(3)	C(34)–P(1)–C(22)	110.3(3)
C(11)–P(1)–C(34)	106.3(3)	C(1)–C(11)–P(1)	114.2(4)
C(33)–P(1)–C(11)	110.4(3)	C(12)–C(22)–P(1)	115.6(4)
C(33)–P(1)–C(34)	108.6(2)	C(23)–C(33)–P(1)	112.8(4)
C(33)–P(1)–C(22)	114.9(3)	O(1)–C(34)–P(1)	109.8(3)
Anion			
W(1)–C(36)	196.4(6)	W(1)–I(3)	287.0(1)
W(1)–C(37)	201.0(7)	O(2)–C(35)	114.0(7)
W(1)–C(35)	201.8(7)	O(3)–C(36)	114.3(6)
W(1)–C(38)	202.5(7)	O(4)–C(37)	114.0(7)
W(1)–I(1)	285.7(1)	O(5)–C(38)	112.8(7)
W(1)–I(2)	286.0(1)	C(35)–W(1)–I(2)	161.1(2)
C(36)–W(1)–C(37)	74.1(2)	C(38)–W(1)–I(2)	76.5(2)
C(36)–W(1)–C(35)	75.5(2)	C(36)–W(1)–I(3)	126.0(2)
C(37)–W(1)–C(35)	113.0(2)	C(37)–W(1)–I(3)	159.9(2)
C(36)–W(1)–C(38)	74.5(2)	C(35)–W(1)–I(3)	75.9(2)
C(37)–W(1)–C(38)	114.5(2)	C(38)–W(1)–I(3)	75.6(2)
C(35)–W(1)–C(38)	112.4(2)	I(1)–W(1)–I(2)	88.9(1)
C(36)–W(1)–I(1)	126.7(2)	I(1)–W(1)–I(3)	89.5(1)
C(37)–W(1)–I(1)	75.6(2)	I(2)–W(1)–I(3)	91.0(1)
C(35)–W(1)–I(1)	77.6(2)	O(2)–C(35)–W(1)	177.6(6)
C(38)–W(1)–I(1)	158.8(2)	O(3)–C(36)–W(1)	179.8(6)
C(36)–W(1)–I(2)	123.5(2)	O(4)–C(37)–W(1)	179.7(6)
C(37)–W(1)–I(2)	75.5(2)	O(5)–C(38)–W(1)	177.4(5)

Table 9

Selected bond lengths (pm) and angles (°) for the $[\text{PH}(\text{CH}_2\text{Fc})_3]^+$ cation in $[\text{PH}(\text{CH}_2\text{Fc})_3][\text{WI}_3(\text{CO})_4]$ (**7**)

P(1)–C(11)	180.9(8)
P(1)–C(22)	179.9(8)
P(1)–C(33)	180.2(8)
C(22)–P(1)–C(11)	109.7(4)
C(33)–P(1)–C(11)	110.0(4)
C(22)–P(1)–C(33)	110.9(4)
C(1)–C(11)–P(1)	112.3(5)
C(12)–C(22)–P(1)	112.7(5)
C(23)–C(33)–P(1)	112.9(5)

non-hydrogen atoms were refined anisotropically (SHELX97) [35]. H atoms bonded to carbon were mostly calculated on idealised positions and were refined isotropically. Crystal data, structure refinement for compounds **1**, **3–8** are given in Table 1.

The atom labelling scheme for the NMR assignments is as follows:

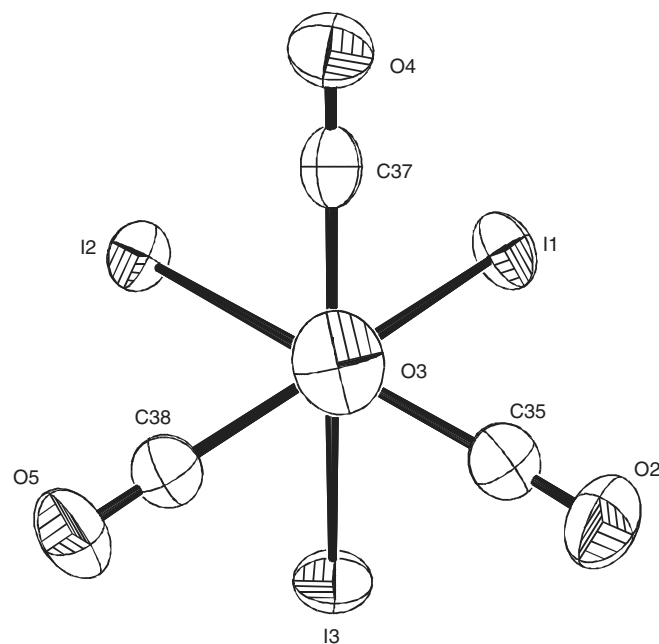
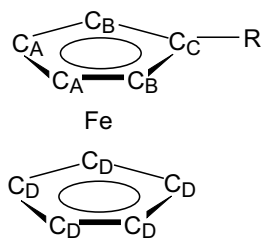


Fig. 9. Molecular structure of the $[\text{WI}_3(\text{CO})_4]^-$ anion in **6**. The W atom and C36 are obscured by the atom O3.

6. Preparations

6.1. $\text{PH}(\text{CH}_2\text{Fc})_2$ (**1**)

An aqueous solution of tetrakis(hydroxymethyl)phosphonium chloride (10.3 g, 43.2 mmol, 7.62 mL of an 80% solution) was mixed with methanol (40 mL) and cooled with an ice bath. KOH (2.41 g, 43.0 mmol) was added, and the mixture was stirred at rt for 1 h. The mixture was then added to a suspension of $[\text{FcCH}_2\text{NMe}_3]\text{I}$ (11.09 g, 28.8 mmol) in ethanol (150 mL), refluxed for 24 h and then concentrated until a solid precipitated. The solid was isolated and dissolved in a mixture of H_2O (15 mL), NET_3 (18 mL) and diethyl ether (80 mL), and the solution was stirred for 1 h. The aqueous phase was separated and extracted with diethyl ether (3×30 mL). Compound **3** was extracted from the aqueous phase using CH_2Cl_2 (*vide infra*).

The combined ethereal phases were washed with H_2O (3×20 mL) and then dried over sodium sulfate. Filtration and evaporation of the solvent gave an orange solid (7.68 g), which was dried in vacuum.

This solid was dissolved in hot *n*-heptane (100 mL), and H_2O (50 mL) was added. The two-phase mixture was refluxed, $\text{Na}_2\text{S}_2\text{O}_5$ (3.5 g, 18.4 mmol) in H_2O (30 mL) was slowly added over 2 h and the solution was refluxed for 1 h. The hot mixture was separated in a separating funnel. After cooling to rt the aqueous phase was extracted with hot *n*-heptane or hot petroleum ether (3×30 mL). The combined organic phases were washed with H_2O (3×30 mL) and dried over sodium sulfate. Filtration and evaporation of the solvent gave a mixture of $\text{PH}_2\text{CH}_2\text{Fc}$

(52 mol%, $\delta = -129.1$), $\text{PH}(\text{CH}_2\text{Fc})_2$ (**1**) (44 mol%, $\delta = -53.4$) and $\text{P}(\text{CH}_2\text{Fc})_3$ (**2**) (4 mol%, $\delta = -17.4$) (determined by ^{31}P NMR).

$\text{PH}_2\text{CH}_2\text{Fc}$ was separated by sublimation (oil bath temperature 40°C , $p = 0.1$ Pa). The remaining solid was dissolved in hot *n*-pentane (4 mL) and crystallised at 0°C . This was repeated four times. The solid was treated with hot *n*-hexane, in which **1** dissolved and **2** remained as a solid. Filtration and evaporation of the solvent gave 1.3 g (3.0 mmol, 21%) of **1** as an orange powder. Slow evaporation of a concentrated solution in acetone gave crystals of **1** suitable for X-ray diffraction. Compound **2** was recrystallised from acetone to give 0.09 g (0.15 mmol, 1.5%) of an orange powdery solid.

1: mp: 79°C ; ^1H NMR: δ 4.11 (s, 10 H, H_D), 4.08 (s, 8H, H_AB), 3.31 (d/quint, $^1J_\text{PH} = 198$ Hz (d), $^3J_\text{PH} = 7.2$ Hz (quint), 1H, PH), 2.63 (m, CH_2); ^{31}P NMR: δ -53.3 (d, $^1J_\text{PH} = 196$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 87.1 (d, $^2J_\text{PC} = 6.6$ Hz, C_C), 69.4 (s, C_D), 69.3 and 68.8 (2 d, $^3J_\text{PC} = 4.0$ Hz/2.7 Hz, C_B), 68.1 and 67.9 (2 s, C_A), 22.3 (d, $^1J_\text{PC} = 12.7$ Hz, CH_2); $^{13}\text{C}\{^{31}\text{P}, ^1\text{H}\}$ NMR (25°C , C_6D_6): δ 87.5 (s, C_C), 69.8 (s, C_D), 69.6 and 69.2 (2 s, C_B), 68.5 and 68.3 (2 s, C_A), 22.6 (s, CH_2); MS: $m/z = 430.0$ [$\text{M}]^+$ (10.8%), 231.0 [$\text{FcCH}_2\text{PH}]^+$ (8.8%), 199.0 [FcCH_2] $^+$ (100%). IR (cm^{-1}): 3920 w, 3096 m, 3080 m, 2927 m, 2884 m, 2285 m, 1637 w, 1461 m, 1409 m, 1388 m, 1250 m, 1228 m, 1176 m, 1134 w, 1118 m, 1102 s, 1056 m, 1039 m, 1026 m, 1002 s, 952 m, 922 m, 911 m, 818 s, 716 m, 680 m, 475 s. Anal. Calc. for $\text{C}_{22}\text{H}_{23}\text{Fe}_2\text{P}$: C, 61.44; H, 5.39. Found: C, 60.80; H, 5.06%.

2: mp: $75\text{--}79^\circ\text{C}$; ^1H NMR: δ 4.11 (s, 15H, H_D), 4.09 and 4.07 (2 s, 6H each, H_AB), 2.62 (m, 6H, CH_2); ^{31}P NMR: δ -17.2 (br); $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 85.0 (d, $^2J_\text{PC} = 9.9$ Hz, C_C), 69.5 (s, C_D), 69.5–69.1 (m, C_B), 68.4, 68.3 and 68.1 (3 s, C_A), 25.2 (d, $^1J_\text{PC} = 15.8$ Hz, CH_2). MS: $m/z = 628.5$ [$\text{M}]^+$ (3.8%), 614.5 [$\text{M}-\text{CH}_2$] $^+$ (2.9%), 231.0 [$\text{FcCH}_2\text{PH}]^+$ (27.8%), 199.0 [FcCH_2] $^+$ (66.8%). IR: 3923 w, 3419 m, 3094 m, 2895 m, 1622 m, 1499 m, 1456 m, 1409 m, 1260 m, 1213 w, 1105 s, 1041 s, 1026 s, 1002 m, 922 m, 821 s, 757 s, 591 w, 550 w, 502 m, 483 m, 429 m.

6.2. [$\text{P}(\text{CH}_2\text{Fc})_3(\text{CH}_2\text{OH})$]**I** (**3**)

The aqueous phase which remained after extraction of **1** and **2** from the reaction mixture with diethyl ether (*vide supra*) was extracted with CH_2Cl_2 (3×30 mL). The combined organic phases were washed with H_2O (3×20 mL) and dried over sodium sulfate. Filtration and evaporation of the solvent gave a dark brown tarry residue. The residue was dissolved in hot acetone, and the acetone solution was subjected to column chromatography [column: silica gel 60 (0.063–0.100 mm), eluent: acetone]. The first fraction gave 0.9 g of [$\text{P}(\text{CH}_2\text{Fc})_3(\text{CH}_2\text{OH})$]**I**· H_2O (**3**· H_2O), which was obtained as crystals by slow evaporation of the solvent. These crystals melt in hot toluene, and the melt releases water vapour above 100°C with formation of a bright orange powder of water-free **3**, which is insoluble

in toluene. Recrystallisation from acetone gave orange crystals of **3**.

3· H_2O : mp: 76°C , $>100^\circ\text{C}$ decomp. with evaporation of H_2O ; MS: $m/z = 659.1$ [$\text{P}(\text{CH}_2\text{Fc})_3(\text{CH}_2\text{OH})$] $^+$ (17%), 628.1 [$\text{P}(\text{CH}_2\text{Fc})_3$] $^+$ (3.5%), 199.1 [FcCH_2] $^+$ (100%). IR (cm^{-1}): 3922 w, 3440 s, 3171 s, 3095 s, 2927 m, 2872 s, 1708 s, 1627 m, 1460 w, 1408 m, 1394 m, 1361 m, 1242 w, 1221 m, 1120 w, 1103 s, 1054 m, 1039 s, 1024 s, 999 s, 923 m, 892 m, 874 m, 832 s, 810 s, 601 w, 574 w, 530 s, 502 s, 485 s, 429 m. Anal. Calc. for $\text{C}_{34}\text{H}_{38}\text{Fe}_3\text{O}_2\text{PI}$: C, 50.79; H, 4.76. Found: C, 50.6; H, 4.93%.

3 (water-free): mp: 174.5°C ; ^1H NMR: δ 5.08 (br, 1H, OH), 4.26 (br d, $^2J_\text{PH} = 3.4$ Hz, 2H, PCH_2O), 4.22 and 4.20 (2 br s, each 6H, H_AB), 4.19 (s, 15H, H_D), 3.42 (d, $^2J_\text{PH} = 11$ Hz, 6H, PCH_2Fc); ^{31}P NMR: δ 20.6 (non, $^2J_\text{PH} = 11$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR: δ ca. 81 (v br, C_C), 71.3, 70.9, 69.5 and 69.1 (4 v br m, C_ABD), ca. 30 (v br, PCH_2O), 21.5 (br, PCH_2Fc); MS: $m/z = 659.1$ [$\text{P}(\text{CH}_2\text{Fc})_3(\text{CH}_2\text{OH})$] $^+$ (23.5%), 628.1 [$\text{P}(\text{CH}_2\text{Fc})_3$] $^+$ (5.8%), 199.1 [FcCH_2] $^+$ (85.1%); IR (cm^{-1}): 3211 s, 3093 m, 3063 m, 2927 m, 2885 m, 2286 w, 1634 w, 1494 w, 1461 m, 1384 m, 1303 w, 1242 m, 1221 w, 1207 w, 1192 w, 1139 m, 1103 s, 1051 s, 1040 s, 1025 m, 1000 m, 923 m, 892 m, 847 m, 816 s, 732 m, 695 w, 579 w, 501 s, 483 s, 428 m, 420 m.

6.3. [$\text{P}(\text{CH}_2\text{Fc})(\text{CH}_2\text{OH})_3$]**Cl** (**4**)

A solution of paraformaldehyde (0.3 g, 10 mmol) in 18% HCl (2 mL) was added to a conc. solution of $\text{P}(\text{CH}_2\text{Fc})(\text{CH}_2\text{OH})_2$ (0.5 g, 1.7 mmol) in methanol. After 10 h orange crystals had formed, which are highly soluble in acetone and water. The crystals were isolated, washed with diethyl ether and dried. Yield: 0.49 g (80%); mp: 90°C (decomp.); ^1H NMR (D_2O): δ 4.47 (d, $^2J_\text{PH} = 1.6$ Hz, 6H, PCH_2O), 4.35 (s, 2H, $\text{CH}_\text{A/B}$), 4.30 (t, $^4J_\text{PH} = 1.8$ Hz, 2H, $\text{CH}_\text{A/B}$), 4.26 (s, 5H, CH_D), 3.61 (d, $^2J_\text{PH} = 12.8$ Hz, 2H, PCH_2Fc), OH signal not observed; ^{31}P NMR (D_2O): δ 25.1 (t, $^2J_\text{PH} = 12.5$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (D_2O): δ 74.1 (d, $^2J_\text{PC} = 2.5$ Hz, C_C), 70.2 and 70.0 (2 s, C_AB), 70.1 (s, C_D), 50.4 (d, $^1J_\text{PC} = 54$ Hz, 3 C, PCH_2O), 16.0 (d, $^1J_\text{PC} = 36$ Hz, PCH_2Fc). IR (cm^{-1}): 3225 s, 2917 w, 2407 m, 1615 w, 1429 m, 1394 m, 1276 w, 1224 w, 1103 m, 1062 s, 1037 s, 997 m, 933 m, 844 m, 820 m, 566 w, 505 m, 481 m, 430 m, 415 m.

6.4. [$\text{Mo}(\text{CO})_5\{\text{PH}(\text{CH}_2\text{Fc})_2\}$]**Cl** (**5**)

$\text{PH}(\text{CH}_2\text{Fc})_2$ (0.12 g, 0.28 mmol) and $[\text{Mo}(\text{CO})_6]$ (1.7 g; 6.4 mmol) were refluxed in toluene (10 mL) for 10 h. The mixture was cooled to 0°C and the precipitated excess $[\text{Mo}(\text{CO})_6]$ was removed by filtration. The solvent was evaporated and the remaining solid (0.18 g) was heated to 50°C for 2 h to separate excess $[\text{Mo}(\text{CO})_6]$ by sublimation. Recrystallisation of the remaining solid from toluene gave orange rhombohedral crystals at 0°C . Yield: 0.16 g (86%); mp: 174.5°C ; ^1H NMR: δ 4.11 (s, 10H, H_D), 4.18 and 4.16

(2 s, 8H, H_{AB}), 4.39 (d of quint, ¹J_{PH} = 318 Hz (d), ³J_{PH} = 6.1 Hz (quint), 1H, PH), 2.63 (m, 4 H, CH₂); ³¹P NMR: δ 0.6 (d, ¹J_{PH} = 318 Hz); ¹³C{¹H} NMR: δ 210.1 (d, ²J_{PC} = 23.8 Hz, (CO)_{ax}), 206.0 (d, ²J_{PC} = 9.0 Hz, (CO)_{äq}), 83.4 (s, C_C), 69.7, 69.6, 69.1 and 68.8 (4 s, C_{AB} and C_D), 28.3 (d, ¹J_{PC} = 18.6 Hz, CH₂); ¹³C{³¹P, ¹H} NMR: 210.1 (s, (CO)_{ax}), 206.0 (s, (CO)_{äq}), 83.4 (s, C_C), 69.7, 69.6, 69.1 and 68.8 (4 s, C_{AB} and C_D), 28.4 (s, CH₂); MS: *m/z* = 667.9 [M⁺] (3.4%), 527.8 [Mo{PH(CH₂Fc)₂}]⁺ (1.6%), 429.9 [PH(CH₂Fc)₂]⁺ (3.9%), 231.0 [FcCH₂PH]⁺ (5.0%), 199.0 [FcCH₂]⁺ (49%). IR (cm⁻¹): 3096 m, 2963 w, 2919 w, 2319 m, 2072 s, 1997 s, 1966 s, 1935 s, 1900 s, 1638 w, 1461 m, 1411 m, 1307 w, 1237 m, 1193 m, 1115 w, 1103 m, 1040 w, 1027 m, 999 s, 952 m, 941 w, 924 m, 880 m, 844 w, 820 m, 715 m, 693 m, 665 w, 609 s, 578 s, 498 m, 479 m, 425 m, 410 w. Anal. Calc. for C₂₇H₂₃Fe₂MoO₅P: C, 48.69; H, 3.48; O, 12.01. Found: C, 48.1; H, 3.07; O, 11.6%.

6.5. [P(CH₂Fc)₃(CH₂OH)][WI₃(CO)₄] (6)

[P(CH₂Fc)₃(CH₂OH)]I (3) (0.23 g, 0.3 mmol) was added to a solution of [WI₂(CO)₃(NCMe)₂] (0.18 g, 0.3 mmol) in CH₂Cl₂ (10 mL) and stirred for 24 h. The solid was separated by filtration and washed with CH₂Cl₂. The solvent was evaporated, and the residue dissolved in CHCl₃ (2 mL). After 2 weeks at rt single crystals of 6 had formed. Yield: ca. 0.04 g (10%); mp: 160 °C (decomp.); ¹H NMR: δ 4.26 and 4.17 (2 s, each 6H, H_{AB}), 4.23 (s, 15H, H_D), 3.37 (d, ²J_{PH} = 11.6 Hz, 6H, PCH₂Fc), signal of PCH₂O not observed (presumably obscured by Fc signals at 4.3 ppm), OH signal not observed; ³¹P NMR: δ 19.9 (sept or non, ²J_{PH} = 11.3 Hz). ¹³C{¹H} NMR: no signals observed due to low concentration. IR: 3427 m, 3089 w, 2915 w, 2066 m, 2020 s, 1941 s, 1640 w, 1462 w, 1407 m, 1261 w, 1238 w, 1203 m, 1104 m, 1038 m, 1026 m, 1000 m, 922 m, 876 w, 821 m, 734 w, 570 w, 531 m, 482 m, 427 w. Anal. Calc. for C₃₈H₃₆Fe₃I₃O₅PW: C, 34.17; H, 2.72. Found: C, 33.5; H, 3.12%.

6.6. [PH(CH₂Fc)₃][WI₃(CO)₄] (7)

To a solution of 3 (0.1 g, 0.12 mmol) in CH₂Cl₂ (10 mL) was slowly added a solution of Na₂S₂O₅ (20 mg, 0.13 mmol) in H₂O (5 mL). The liquid was heated with intense stirring for several hours to give a solution of [PH(CH₂Fc)₃]I (³¹P NMR 53.0 ppm (br)). The organic layer was isolated, dried over sodium sulfate, and filtered. Under stirring [WI₂(CO)₃(NCMe)₂] (0.15 g, 0.25 mmol) was dissolved in the mixture, which was then filtered. After 2 h at rt without stirring, orange single crystals of 7 had formed, which are nearly insoluble in chlorinated solvents. Yield: 0.13 g (83%); mp: 160 °C (decomp.); ¹H, ³¹P and ¹³C{¹H} NMR: no signals observed due to very low solubility; IR: 3428 m, 3093 w, 2887 w, 2066 s, 1997 s, 1928 s, 1634 m, 1458 w, 1405 w, 1251 w, 1103 m, 1039 m, 1026 m, 999 m, 928 w, 825 m, 737 w, 532 m, 484 m, 427

w, 413 w. Anal. Calc. for C₃₇H₃₄Fe₃I₃O₄PW: C, 34.04; H, 2.63; O, 4.90. Found: C, 33.8; H, 2.42; O, 4.73%.

6.7. [P(CH₂Fc)₄]I (8)

[FcCH₂NMe₃]I (8.81 g, 22.88 mmol) and PH₂CH₂Fc (1.69 g, 7.27 mmol) were dissolved in ethanol (150 mL) and refluxed for 72 h. The solvent was partly removed, and the solid precipitate was recrystallised from ethanol to give 6.61 g (6.93 mmol, 91%) of crystalline orange 8. Apart from PH₂CH₂Fc, other phosphine derivatives could not be observed as side products. Recrystallisation from CHCl₃ gave crystals of 8 · CHCl₃ that could be analysed by X-ray crystallography. ¹H NMR: δ 4.14 (s, 8H, H_{AB}), 4.11 (s, 20H, H_D), 3.40 (d, ²J_{PH} = 11.7 Hz, 8H, H_{AB}), 2.83 (d, ²J_{PH} = 4.9 Hz, 8H, CH₂); ¹³C{¹H} NMR: δ 74.2 (s, C_C), 69.8 (d, ¹J_{CP} = 1.5 Hz, C_{AB}), 69.5 (s, C_D) 69.0 (s, C_{AB}), 22.0 (d, ¹J_{PC} = 38.7 Hz, CH₂); ³¹P NMR: δ 17.6 (non, ²J_{PH} = 11.7 Hz). MS: *m/z* = 827.0 [P(CH₂Fc)₄]⁺ (82.3%), 199.0 [FcCH₂]⁺ (100%). IR: 3431 s, 3091 m, 2872 m, 1637 s, 1459 m, 1407 m, 1243 m, 1136 s, 1105 s, 1040 m, 1025 m, 1001 m, 923 w, 874 m, 815 s, 503 s, 429 m.

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