

Novel Ferrocene Derivatives with PH-Functionalized Phosphanylalkylcyclopentadienyl Ligands: Syntheses and Molecular Structures of *rac*-[Fe{(η⁵-C₅H₄)CMe₂PHR}₂] (R = Ph, Mes) and *rac*-[Fe{(η⁵-C₅H₄)CMe₂PHPh(Cp*TaCl₄)}₂]^[‡]

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Dedicated to Professor Joachim Strähle on the occasion of his 65th birthday

Keywords: Metallocenes / P ligands / Bridging ligands / Secondary phosphanes / Tantalum

6,6-Dimethylfulvene reacts with LiPHMes (Mes = 2,4,6-Me₃C₆H₂) to give Li[(C₅H₄)CMe₂PHMes] (**1**). The ferrocene derivatives *rac*-[Fe{(η⁵-C₅H₄)CMe₂PHR}₂] [R = Ph (**2**), Mes (**3**)] are obtained in high yield from the lithium reagents Li[(C₅H₄)CMe₂PHR] (R = Ph, Mes) and FeCl₂. Compound **2** reacts with [Cp*TaCl₄] to give the heterotrinnuclear complex

rac-[Fe{(η⁵-C₅H₄)CMe₂PHPh(Cp*TaCl₄)}₂] (**4**). Compounds **1–4** were characterized spectroscopically, and crystal structure determinations were carried out on **2–4**.

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Introduction

Since the first report of a cyclopentadienyl transition metal complex in which the cyclopentadienyl ligand bears a donor-functionalized side chain, by Mathey et al. in 1978,^[1] this area has expanded rapidly.^[2] While numerous *O*- and *N*-functionalized cyclopentadienyl ligands are known, the number of cyclopentadienes with a *P*-functionalized alkyl or silyl side chain is still small,^[1,3] and only recently have we reported the first such compounds in which the P atom has a reactive P–H bond, namely, 1-SiMe₂PHCy-2,3,4,5-Me₄C₅H, Li₂[(C₅Me₄)SiMe₂PR] [R = Cy, 2,4,6-Me₃C₆H₂ (Mes)], Li[(C₅H₄)CMe₂PHR] (R = Ph, *t*Bu) and Li₂[(C₅H₄)CH₂CH₂PPh].^[4,5] The molecular structures of [Li(tmeda)]₂[(C₅H₄)CMe₂PPh]^[6] and [Li(tmeda)]-[(C₅H₄)CMe₂PR₂]^[7] (R = Ph, Me) were also reported. Such compounds are useful precursors for mono- or dianionic bifunctional ligands in transition metal chemistry. Thus, the monoanionic phosphanylalkylcyclopentadienyl ligands can act as chelating ligands towards one metal center (**A**) or

they can bridge two (different) metal centers (**B**) (M = metal, M¹ = M² or M¹ ≠ M², L = ligands, X = spacer (alkylidene, arylidene), R = alkyl, aryl).



We have recently shown that Li₂[(C₅Me₄)SiMe₂PR] (R = Cy, Mes) reacts with ZrCl₄ to give [(η⁵-C₅Me₄)₂SiMe₂]₂ZrCl₂ and (PCy)₄ or (PHMes)₂, while Li[(C₅H₄)CMe₂PHR] reacts with ZrCl₄ or [TiCl₃(THF)₃] to yield [(η⁵-C₅H₄)CMe₂PHR]₂ZrCl₂ or [(η⁵-C₅H₄)CMe₂PHR]₂TiCl (R = Ph, *t*Bu).^[5] However, these complexes slowly decompose in solution with formation of [(η⁵-C₅H₄)₂CMe₂]₂MCl₂ (M = Zr, Ti).^[5] Erker et al. reported that the complexes [(CyPCMe₂(η⁵-C₅H₄))M(NR₂)₂] (M = Ti, R = Me; M = Zr, R = Et) are active catalysts for the polymerization of α-olefins.^[8]

We now report the synthesis of the novel stable PH-functionalized ferrocene derivatives *rac*-[Fe{(η⁵-C₅H₄)CMe₂PHR}₂] [R = Ph (**2**), Mes (**3**)] and the heterotrinnuclear complex *rac*-[Fe{(η⁵-C₅H₄)CMe₂PHPh(Cp*TaCl₄)}₂] (**4**) of type **B**.

Ferrocene derivatives usually show enhanced stability and are generally nontoxic. Thus, their industrial applications range from additives for heating oil to reduce formation of soot, iron-containing fertilizers, UV absorbers and protective coatings for rockets and satellites.^[9]

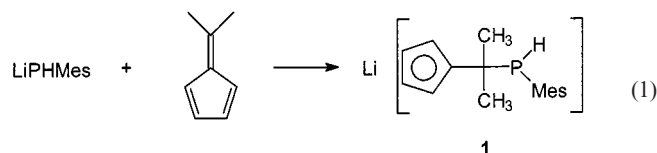
[‡] Parts of this work were presented as a poster at the 34th International Conference on Coordination Chemistry, Edinburgh, 9–14 July 2000 (abstract no. P0600) and at the XVth International Conference on Phosphorus Chemistry, Sendai, 29 July – 3 August 2001 (abstract no. PB065).

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Results and Discussion

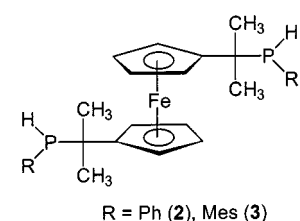
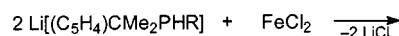
Syntheses of Compounds 1–4.

As a general synthetic route to cyclopentadienes with *P*-functionalized side chains, the addition of alkali metal phosphanides to fulvenes has been employed.^[3a–3c,4,5] Accordingly, 6,6-dimethylfulvene reacts with LiPHMes in Et₂O at room temperature to give the highly air and water sensitive compound Li[(C₅H₄)CMe₂PHMes] (**1**) [Equation (1)].



The ¹H NMR spectrum of **1** indicates that the methyl groups in P–C(Me₂) are prochiral and thus diastereotopic. Therefore, the two nonequivalent Me groups appear as two doublets due to P–H coupling [$\delta = 1.43$ (³*J*_{P–H} = 8.8 Hz); $\delta = 1.41$ (³*J*_{P–H} = 13.0 Hz)]. However, in the ³¹P NMR spectrum, the two Me groups are equivalent, and a doublet of septets is observed. As was observed for Li[(C₅H₄)CMe₂PHR] (R = Ph,^[4] Cy^[5]), the signal is shifted to low field by ca. 110 ppm, and the P–H coupling constant increases by ca. 10–15 Hz relative to the primary phosphane [**1**: $\delta = -45.6$ (¹*J*_{P–H} = 216 Hz); PH₂Mes:^[10] $\delta = -154.8$ (¹*J*_{P–H} = 203 Hz)]. Similarly, the signal of the PH group is shifted to low field in the ¹H NMR spectrum by ca. 0.2–0.9 ppm relative to the phosphane (**1**: $\delta = 4.36$; PH₂Mes:^[10] $\delta = 3.53$). Compared with the signals of 6,6-dimethylfulvene (Me: $\delta = 2.19$; C₅H₄: $\delta = 6.53$ – 5.45),^[11] the corresponding signals in **1** are shifted to high field ($\delta = 1.41$, 1.43 and 5.56).

The ferrocene derivatives [Fe{(η^5 -C₅H₄)CMe₂PHR}₂] [R = Ph (**2**), Mes (**3**)] are obtained in high yield from the lithium reagents Li[(C₅H₄)CMe₂PHR] (R = Ph, Mes (**1**)) and FeCl₂ in THF at room temperature [Equation (2)].



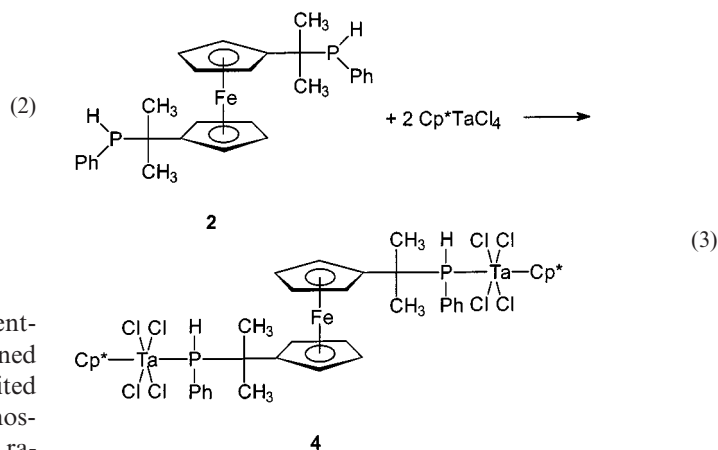
After workup and repeated recrystallization from *n*-pentane (**2**) or toluene (**3**), the ferrocene derivatives are obtained as orange solids, which are air-stable, at least for a limited period of time. Due to the presence of two chiral phosphanyl groups, two diastereomers can be formed: the *rac*-

cemic form (*R,R* and *S,S* enantiomer) and the *meso* form (*S,R* enantiomer). As bulky substituents are present on the cyclopentadienyl rings, the antiperiplanar conformation is favored (see X-ray crystal structure determinations of **2**–**4** below).

No meaningful ³¹P NMR spectra of the reaction mixture could be obtained due to the presence of small amounts of FeCl₂. However, the ³¹P NMR spectra recorded for **2** at different stages of workup always indicated the presence of only one diastereomer. Thus, in the ³¹P{¹H} NMR spectrum of crystalline **2**, only one signal is observed. However, in the ³¹P NMR spectrum of **3**, obtained from *n*-hexane, two overlapping doublets of different intensity (ca. 4:1) are observed at $\delta = -33.4$ and -33.9 with P–H coupling constants of 219 and 213 Hz, respectively, even at elevated temperature (340 K); this indicates the formation of both diastereomers, one of which is preferred. Recrystallization from toluene yields the preferred isomer (which was shown to be the *rac* isomer by crystal structure determination) as orange rod-like crystals. The *meso* isomer could not be obtained in pure form.

In the proton-coupled ³¹P NMR spectrum of **2** and **3**, a doublet of multiplets is observed [**2**: $\delta = 8.8$ (¹*J*_{P–H} = 207 Hz); **3**: $\delta = -32.8$ (¹*J*_{P–H} = 214 Hz)], which are shifted to low field by ca. 10–13 ppm relative to Li[(C₅H₄)CMe₂PHR] (R = Ph, Mes). The complex coupling pattern in **2** arises from coupling of the protons of the Me and Ph groups. As was already observed for **1**, the ¹H NMR spectra of **2** and **3** indicate that the methyl groups in P–C(Me₂) are prochiral and thus diastereotopic. Thus, the two nonequivalent Me groups appear as two doublets due to P–H coupling [**2**: $\delta = 1.32$ (³*J*_{P–H} = 12.0 Hz), 1.38 (³*J*_{P–H} = 12.4 Hz); **3**: $\delta = 1.39$ (³*J*_{P–H} = 13.0 Hz), 1.45 (³*J*_{P–H} = 8.8 Hz)]. These signals and those of the P–H group are only slightly shifted relative to those of the lithium reagents, while a shift to high-field of ca. 1.8 ppm is observed for the C–H protons of the cyclopentadienyl rings.

At room temperature, the *ortho*-Me groups of the mesityl ring in **3** give a broad signal at $\delta = 2.27$ in the ¹H NMR



spectrum, indicating that rotation around the P–C(mesityl) bond is hindered. At 340 K, only one sharp signal is observed for the Me groups, while below 263 K two separate

signals are observed. From the coalescence temperature [$T_c = 291(2)$ K] the activation enthalpy ($\Delta G^\ddagger = 56 \pm 1$ kJ/mol)^[12] was determined by using the Eyring equa-

Table 1. Selected bond lengths [Å] and bond angles [°] for **2–4**

[Fe{(η^5 -C ₅ H ₄)CMe ₂ PhPh} ₂] (2)			
Fe–C	2.045(5)–2.064(5)	P(1)–C(9)	1.823(3)
P(1)–C(6)	1.891(3)	P(1)–H(2P)	1.7(2)
P(1)–H(1P)	1.43(8)		
C(9)–P(1)–C(6)	103.3(1)	C(9)–P(1)–H(1P)	116(3)
C(6)–P(1)–H(1P)	101(3)	C(9)–P(1)–H(2P)	105(5)
C(6)–P(1)–H(2P)	119(5)	C(10)–C(9)–P(1)	120.8(3)
C(14)–C(9)–P(1)	120.7(3)	C(1)–C(6)–P(1)	103.4(2)
C(7)–C(6)–P(1)	109.4(3)	C(8)–C(6)–P(1)	110.8(3)
[Fe{(η^5 -C ₅ H ₄)CMe ₂ PhMes} ₂] (3)			
Fe–C	2.042(2)–2.085(2)		
P(1)–C(14)	1.848(2)	P(1)–C(11)	1.903(2)
P(1)–H(1P)	1.25(3)	P(2)–C(26)	1.838(2)
P(2)–C(23)	1.901(2)	P(2)–H(2P)	1.0(1)
C(14)–P(1)–C(11)	107.55(9)	C(14)–P(1)–H(1P)	100(1)
C(11)–P(1)–H(1P)	98(1)	C(26)–P(2)–C(23)	106.87(9)
C(26)–P(2)–H(2P)	111(8)	C(23)–P(2)–H(2P)	99(8)
C(15)–C(14)–P(1)	117.7(2)	C(19)–C(14)–P(1)	123.2(2)
C(31)–C(26)–P(2)	122.7(2)	C(27)–C(26)–P(2)	118.8(2)
C(1)–C(11)–P(1)	110.7(1)	C(12)–C(11)–P(1)	108.8(2)
C(13)–C(11)–P(1)	103.3(2)	C(6)–C(23)–P(2)	110.3(1)
C(25)–C(23)–P(2)	109.4(1)	C(24)–C(23)–P(2)	103.8(1)
[Fe{(η^5 -C ₅ H ₄)CMe ₂ PhPh(Cp*TaCl ₄) ₂] (4)			
Ta–C	2.446(5)–2.530(4)	Fe–C	2.040(5)–2.070(4)
Ta(1)–Cl(1)	2.400(1)	Ta(1)–Cl(2)	2.390(1)
Ta(1)–Cl(3)	2.404(1)	Ta(1)–Cl(4)	2.402(1)
Ta(2)–Cl(5)	2.393(1)	Ta(2)–Cl(6)	2.402(1)
Ta(2)–Cl(7)	2.388(1)	Ta(2)–Cl(8)	2.401(1)
Ta(1)–P(1)	2.758(1)	Ta(2)–P(2)	2.798(1)
P(1)–C(14)	1.829(4)	P(1)–C(11)	1.899(5)
P(1)–H(1P)	1.45(5)	P(2)–C(33)	1.821(4)
P(2)–C(30)	1.909(5)	P(2)–H(2P)	1.29(4)
Cl(2)–Ta(1)–Cl(1)	87.39(4)	Cl(2)–Ta(1)–Cl(4)	151.90(4)
Cl(1)–Ta(1)–Cl(4)	85.32(5)	Cl(2)–Ta(1)–Cl(3)	87.39(4)
Cl(1)–Ta(1)–Cl(3)	152.81(4)	Cl(4)–Ta(1)–Cl(3)	86.83(5)
Cl(2)–Ta(1)–P(1)	71.78(4)	Cl(1)–Ta(1)–P(1)	78.37(4)
Cl(4)–Ta(1)–P(1)	80.16(4)	Cl(3)–Ta(1)–P(1)	74.66(4)
C(14)–P(1)–Ta(1)	116.9(2)	C(11)–P(1)–Ta(1)	127.9(1)
C(14)–P(1)–C(11)	105.3(2)	C(14)–P(1)–H(1P)	99(2)
C(11)–P(1)–H(1P)	96(2)	Ta(1)–P(1)–H(1P)	106(2)
C(1)–C(11)–P(1)	104.7(3)	C(13)–C(11)–P(1)	112.6(4)
C(12)–C(11)–P(1)	106.8(3)	C(19)–C(14)–P(1)	118.8(4)
C(15)–C(14)–P(1)	123.1(4)	Cl(7)–Ta(2)–Cl(5)	152.66(4)
Cl(7)–Ta(2)–Cl(8)	86.34(5)	Cl(5)–Ta(2)–Cl(8)	88.10(5)
Cl(7)–Ta(2)–Cl(6)	86.91(4)	Cl(5)–Ta(2)–Cl(6)	85.19(5)
Cl(8)–Ta(2)–Cl(6)	151.24(4)	Cl(5)–Ta(2)–P(2)	74.66(4)
Cl(6)–Ta(2)–P(2)	72.44(4)	Cl(7)–Ta(2)–P(2)	78.01(4)
Cl(8)–Ta(2)–P(2)	78.80(4)	Ta(2)–P(2)–H(2P)	103(2)
C(33)–P(2)–Ta(2)	117.4(2)	C(30)–P(2)–Ta(2)	127.3(2)
C(30)–P(2)–H(2P)	100(2)	C(33)–P(2)–H(2P)	101(2)
C(6)–C(30)–P(2)	105.2(3)	C(31)–C(30)–P(2)	107.9(3)
C(32)–C(30)–P(2)	110.0(3)	C(38)–C(33)–P(2)	120.3(4)
C(34)–C(33)–P(2)	121.9(3)	C(33)–P(2)–C(30)	103.5(2)

tion.^[13] Compound **2** reacts with $[\text{Cp}^*\text{TaCl}_4]$ in toluene at room temperature to give the heterotrimeric complex *rac*- $[\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{CMe}_2\text{PPh}(\text{Cp}^*\text{TaCl}_4)\}_2]$ (**4**) [Equation (3)].

The trimeric complex **4** is unstable in solution at room temperature. When brown crystals of **4** are dissolved in benzene or toluene at room temperature, a white precipitate forms after only a few minutes. Thus, for the NMR spectroscopic studies the crystals were cooled to -195°C in an NMR tube and the solvent ($[\text{D}_8]\text{toluene}$ or $[\text{D}_6]\text{benzene}$) was added at this temperature. The sample was warmed to ca. -50°C prior to the NMR spectroscopic studies.

At -50°C , two doublets are observed in the ^{31}P NMR spectrum at $\delta = 8.5$ and 57.6 (ratio ca. 1:2), which collapse into one broad singlet at room temperature ($\delta = 33.7$). Recrystallization from dichloromethane and toluene yielded small brown crystals suitable for crystal structure determination, which showed this to be the *rac* isomer.

Molecular Structures of 2–4

The ferrocene derivatives crystallize in the centrosymmetric monoclinic space group no. 14 $[P2_1/n]$ (**2**, **3**) and $P2_1/c$ (**4**). For **2**, two molecules are present in the unit cell, while for **3** and **4**, four molecules are present.

In all three complexes, the substituted cyclopentadienyl rings adopt an antiperiplanar conformation, as expected for bulky substituents (see Table 1 for bond lengths and angles). An antiperiplanar conformation was also observed for $[\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{CH}_2\text{PPh}_2\}_2]$.^[14]

In **2**, the Ph and cyclopentadienyl rings are almost coplanar [angle between plane of Ph ring and cyclopentadienyl ring $6.0(3)^\circ$]. The Fe atom is located on a crystallographic center of inversion. As the P–H proton is disordered over two positions (Figure 1), the configuration of the phosphanyl group could not be determined.

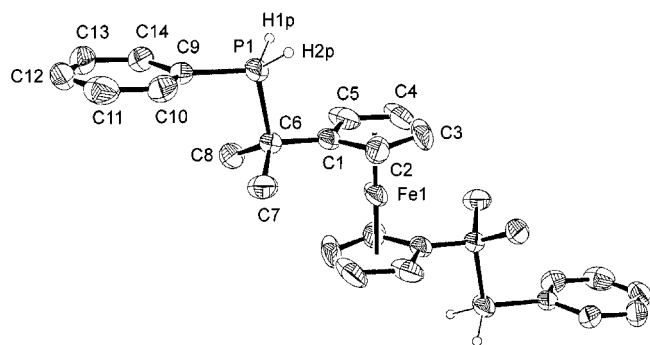


Figure 1. Molecular structure of *rac*- $[\text{Fe}\{(\text{C}_5\text{H}_4)\text{CMe}_2\text{PPh}\}_2]$ (**2**) showing the atom numbering scheme employed (ORTEP plot, 50% probability, SHELXTL PLUS; XP^[23]); hydrogen atoms (other than P–H) are omitted for clarity; the P–H proton is disordered

In **3** (Figure 2) and **4** (Figure 3), the PH protons were located in the difference Fourier synthesis and refined isotropically. Only the *rac* isomer is present in the unit cell. As **4** is derived from **2**, in which the configuration could not

be determined, the presence of the *rac* isomer can be deduced for **2**, too.

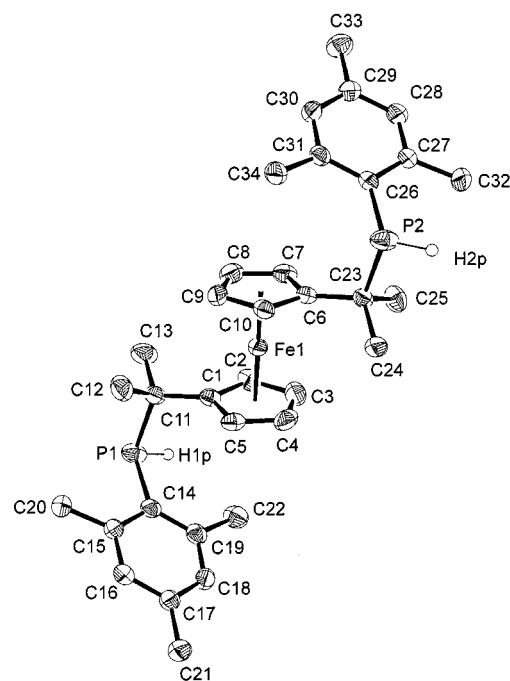


Figure 2. Molecular structure of *rac*- $[\text{Fe}\{(\text{C}_5\text{H}_4)\text{CMe}_2\text{PMe}\}_2]$ (**3**) showing the atom numbering scheme employed (ORTEP plot, 50% probability, SHELXTL PLUS; XP^[23]); hydrogen atoms (other than P–H) are omitted for clarity; only the *R,R* isomer is shown.

In **3** and **4**, the aryl rings and the cyclopentadienyl rings adopt an angle of $31.2(1)^\circ$ and $34.1(1)^\circ$ (**3**) or $31.4(2)^\circ$ and $33.3(2)^\circ$ (**4**). In **4**, the Ta–P bond lengths of 2.758(1) and 2.798(1) Å are longer than those in the phosphane complex $[\text{Cp}^*\text{TaCl}_4(\text{PH}_2\text{Ph})]$ [2.651(3) Å].^[15] Apparently, replacement of the small H substituent by the bulky $(\text{C}_5\text{H}_4)\text{CMe}_2$ substituent at the P atom weakens the Ta–P bond. In **4**, the Ta atom is located 0.573(1) Å above the plane formed by the four Cl atoms. This distance is similar to that in $[\text{Cp}^*\text{TaCl}_4(\text{PH}_2\text{Ph})]$ [0.602(2) Å] and smaller than that observed for $[\text{Cp}^*\text{TaCl}_4]$ [0.806(2) Å].^[15] due to the higher steric demand of the phosphane ligands in $[\text{Cp}^*\text{TaCl}_4(\text{PH}_2\text{Ph})]$ and **4**. Only one other trimeric bis(phosphanylmethyl)ferrocene complex, namely $[\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{CH}_2\text{PPh}_2[\text{RuCl}_2(\eta^6\text{-1,2,3,4-Me}_4\text{C}_6)]\}_2]$, has been structurally characterized.^[16,17]

The Fe–C bond lengths of 2.04–2.08 Å and the distance Fe–Cp_{center}^R of ca. 1.65–1.67 Å in **2–4** are in good agreement with those of related ferrocene derivatives.^[14,16–19]

We are now extending these synthetic approaches to other cyclopentadienes with *P*-functionalized side chains and investigating their coordination properties towards other transition metals and main group metals.

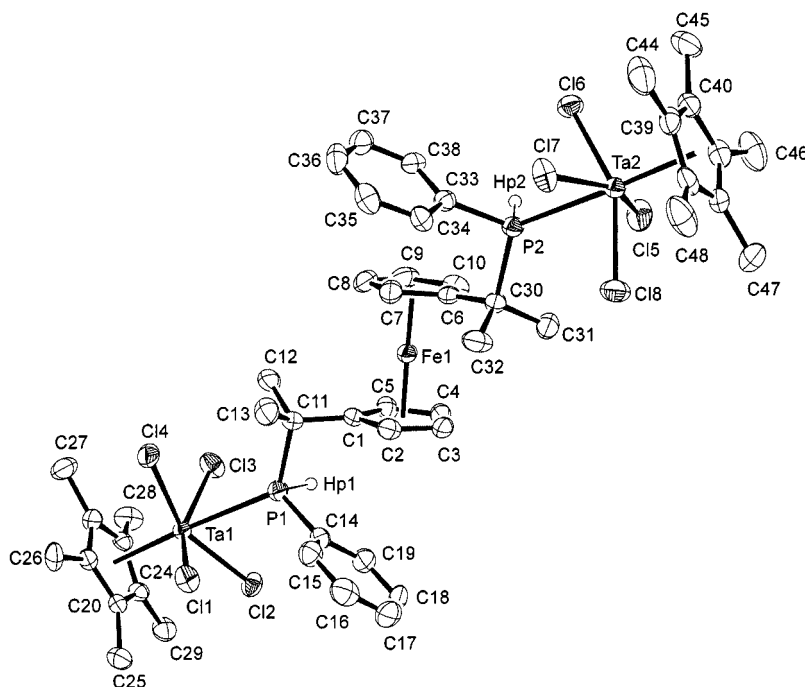


Figure 3. Molecular structure of *rac*-[Fe{(C₅H₄)CMe₂PHPh(Cp*TaCl₄)}₂] (**4**) showing the atom numbering scheme employed (ORTEP plot, 50% probability, SHELXTL PLUS; XP^[23]); hydrogen atoms (other than P–H) are omitted for clarity; only the *S,S* isomer is shown

Experimental Section

General: All experiments were carried out under purified dry argon. Solvents were dried and freshly distilled under argon. The NMR spectra were recorded with an AVANCE DRX 400 spectrometer (Bruker), ¹H NMR (400 MHz): internal standard solvent, external standard TMS. ¹³C NMR (100.6 MHz): external standard TMS, internal standard solvent. ³¹P NMR (162 MHz): external standard 85% H₃PO₄. The IR spectra were recorded on an FT-IR spectrometer Perkin–Elmer System 2000 in the range 350–4000 cm^{−1}. MS: MAT 212 (Varian). The melting points were determined in sealed capillaries under argon and are uncorrected. 6,6-dimethylfulvene,^[11] LiPHMes,^[20] Li[(C₅H₄)CMe₂PHPh]^[4] and [Cp*TaCl₄]^[21] were prepared according to the literature procedures. FeCl₂ is commercially available (Aldrich).

Synthesis of Li[(C₅H₄)CMe₂PHMes] (1**):** 6,6-Dimethylfulvene (0.8 mL, 6.7 mmol) was added slowly in 0.1 mL portions to an orange suspension of LiPHMes (1.1 g, 6.7 mmol) in Et₂O (30 mL), and the resulting pale yellow reaction mixture stirred for 12 h. The resulting solid was isolated by filtration and washed twice with ca. 20 mL Et₂O, then twice with ca. 20 mL *n*-hexane and dried under vacuum to yield **1** as a white powder (1.4 g, 63%). M.p. 220 °C (dec.). ¹H NMR ([D₈]THF): δ = 1.41 (d, ³J_{P–H} = 13.0 Hz, 3 H, CH₃ in CMe₂), 1.43 (d, ³J_{P–H} = 8.8 Hz, 3 H, CH₃ in CMe₂), 2.19 (s, 3 H, *p*-CH₃ in Mes), 2.26 (s, 6 H, *o*-CH₃ in Mes), 4.36 (d, ¹J_{P–H} = 215.6 Hz, 1 H, PH), 5.56 (s, 4 H, CH in C₅H₄), 6.78 (s, 2 H, *m*-CH in Mes). ¹³C NMR ([D₈]THF): δ = 21.0 (s, 1C, *p*-CH₃ in Mes), 23.9 (m, 2C, *o*-CH₃ in Mes), 30.4 (d, ²J_{P–C} = 17.8 Hz, 1C, CH₃–C), 31.5 (d, ²J_{P–C} = 9.7 Hz, 1C, CH₃–C), 37.2 (d, ¹J_{P–C} = 12.5 Hz, 1C, C–CH₃), 101.7 (d, ³J_{P–C} = 3.5 Hz, 2C, C₅ in C₅H₄), 102.7 (s, 2C, C₃, C₄ in C₅H₄), 127.1 (d, ²J_{P–C} = 9.6 Hz, 1C, C₁ in C₅H₄), 129.1 (d, ³J_{P–C} = 2.5 Hz, 2C, *m*-C in Mes), 132.6 (d, ¹J_{P–C} = 29.1 Hz, 1C, *ipso*-C in Mes), 137.3 (s, 1C, *p*-C in Mes), 143.8 (s, 2C, br, *o*-C in Mes). ³¹P NMR ([D₈]THF):

δ = −45.6 (d of m, ¹J_{P–H} = 216 Hz). IR (KBr): ν̃ = 2337 (νPH, m), 1463 (νC=C m, br) cm^{−1}.

Synthesis of *rac*-[Fe{(η⁵-C₅H₄)CMe₂PHPh}₂] (2**):** A solution of Li[(C₅H₄)CMe₂PHPh] (3.5 g, 15.6 mmol) in THF (30 mL) was slowly added to a suspension of FeCl₂ (1.0 g, 7.8 mmol) in THF. During the addition, FeCl₂ slowly dissolved, and the initially pale pink solution turned first yellow and finally red-brown. The solution was stirred for 16 h. The solvent was then evaporated under vacuum and the brown residue treated with Et₂O. The rust-brown powder was separated from the yellow solution by filtration and extracted repeatedly with Et₂O. The Et₂O fractions were combined and the solvent was evaporated under vacuum. The yellow residue was recrystallized repeatedly from *n*-hexane or *n*-pentane. At −20 °C orange needles of **2** were obtained. Yield: 2.2 g (59%), m.p. 97–100 °C (from *n*-pentane). ¹H NMR (C₆D₆): δ = 1.32 (d, ³J_{P–H} = 12.0 Hz, 3 H, CH₃ in CMe₂), 1.38 (d, ³J_{P–H} = 12.4 Hz, 3 H, CH₃ in CMe₂), 3.75–3.61 (m, 2 H, CH in C₅H₄), 3.95–3.91 (m, 2 H, CH in C₅H₄), 4.08 (d, ¹J_{P–H} = 206.7 Hz, 1 H, PH), 7.05 (m, 3 H, *o*- and *p*-CH in Ph), 7.16 (m, 2 H, *m*-CH in Ph). ¹³C NMR (C₆D₆): δ = 28.4 (d, ²J_{P–C} = 16.3 Hz, 1C, CH₃–C), 28.9 (d, ²J_{P–C} = 16.0 Hz, 1C, CH₃–C), 33.6 (d, ¹J_{P–C} = 12.6 Hz, 1C, C–CH₃), 66.6 (s, 1C, C₄ in C₅H₄), 67.1 (s, 1C, C₃ in C₅H₄), 68.3 (d, ³J_{P–C} = 21.0 Hz, 2C, C₂, C₅ in C₅H₄), 99.6 (d, ²J_{P–C} = 7.2 Hz, 1C, C₁ in C₅H₄), 126.6 (s, 1C, *p*-C in Ph), 129.3 (d, ³J_{P–C} = 5.6 Hz, 2C, *m*-C in Ph), 135.5 (d, ¹J_{P–C} = 17.8 Hz, 1C, *ipso*-C in Ph), 137.0 (d, ²J_{P–C} = 15.5 Hz, 2C, *p*-C in Ph). ³¹P NMR (C₆D₆): δ = 8.8 (d of m, ¹J_{P–H} = 207 Hz). IR (KBr): ν̃ = 2283 (νPH, m), 1463 and 1432 (νC=C, Ph, m), 741 and 697 (δC=C, Ph, st) cm^{−1}. EI MS: *m/z* (%) = 486 (15) [M⁺], 377 (10) [M⁺ − PHPh], 266 (100) [M⁺ − 2 PHPh], 226 (5) [M⁺ − 2 PHPh − CMe₂], and fragmentation products thereof. C₂₈H₃₂FeP₂ (486.3): calcd. C 69.1, H 6.6, P 12.7; found C 68.7, H 6.3, P 12.1.

Synthesis of *rac*-[Fe{(η⁵-C₅H₄)CMe₂PHMes}₂] (3**):** A solution of Li[(C₅H₄)CMe₂PHMes] (1.6 g, 6.0 mmol) in THF (20 mL) was

Table 2. Crystal data and structure refinement for **2**, **3**, and **4**

	2	3	4
Empirical formula	C ₂₈ H ₃₂ FeP ₂	C ₃₄ H ₄₄ FeP ₂	C ₄₈ H ₆₂ Cl ₈ FeP ₂ Ta ₂
<i>M_r</i>	486.33	570.48	1402.27
Temperature (K)	220(2)	220(2)	220(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i> (no. 14)	<i>P</i> 2 ₁ / <i>n</i> (no. 14)	<i>P</i> 2 ₁ / <i>c</i> (no. 14)
<i>a</i> [Å]	6.1170(3)	8.0117(2)	15.2794(7)
<i>b</i> [Å]	21.2473(9)	17.7373(5)	14.8736(6)
<i>c</i> [Å]	9.6680(4)	20.7827(6)	22.925(1)
β [°]	102.292(1)	93.602(1)	95.607(1)
<i>V</i> [Å ³]	1227.74(9)	2947.5(1)	5184.9(4)
<i>Z</i>	2	4	4
ρ _{calcd.} [Mg m ^{−3}]	1.316	1.286	1.796
<i>F</i> (000)	512	1216	2752
Crystal size [mm]	0.50 × 0.40 × 0.20	0.40 × 0.40 × 0.40	0.20 × 0.10 × 0.05
Abs. coeff. [mm ^{−1}]	0.758	0.642	4.993
Θ range [°]	1.92 to 28.85	1.51 to 28.81	1.34 to 28.29
Refl. collected	12421	29937	32451
Independent reflections	2994	7185	12325
<i>R_{int}</i>	0.0283	0.0440	0.0495
Parameters	192	510	780
<i>R</i> [<i>I</i> > 2σ(<i>I</i>)]	0.0673	0.0387	0.0339
<i>wR</i> 2 (all data)	0.1641	0.1212	0.0618
(Δ/ρ) _{min.} [e Å ^{−3}]	0.246	0.571	1.007
(Δ/ρ) _{max.} [e Å ^{−3}]	−0.528	−0.379	−1.424

slowly added to a suspension of FeCl₂ (0.4 g, 3.0 mmol) in THF (30 mL). During the addition, FeCl₂ slowly dissolved, and the initially pale pink solution turned first yellow and finally red-brown. The solution was stirred for 16 h. Then the solvent was evaporated under vacuum, and the brown residue treated with Et₂O (20 mL). The insoluble rust-brown powder was separated from the orange solution by filtration and extracted repeatedly with Et₂O. The Et₂O fractions were combined and the solvent was evaporated under vacuum. The yellow residue was recrystallized repeatedly from *n*-hexane, *n*-pentane or toluene. At −20 °C yellow platelets (from hexane) or orange rod-like crystals (from toluene) of **3** were obtained. Yield: 0.9 g (55%), m.p. 162 °C (from toluene). ¹H NMR (C₆D₆): δ = 1.39 (d, ³*J*_{P-H} = 13.0 Hz, 3 H, CH₃ in CMe₂), 1.45 (d, ³*J*_{P-H} = 8.8 Hz, 3 H, CH₃ in CMe₂), 2.08 (s, 3 H, *p*-CH₃ in Mes), 2.27 (br. s, 6 H, *o*-CH₃ in Mes), 3.87–3.60 (m, 4 H, CH in C₅H₄), 4.4 (d, ¹*J*_{P-H} = 216.1 Hz, 1 H, PH), 6.76 (s, 2 H, *m*-H in Mes). ¹³C NMR (C₆D₆): δ = 21.7 (s, 1C, *p*-CH₃ in Mes), 24.8 (br. s, 2C, *o*-CH₃ in Mes), 29.3 (br. s, 1C, CH₃–C), 29.6 (br, 1C, CH₃–C), 35.7 (d, ¹*J*_{P-C} = 15.2 Hz, 1C, C–CH₃), 66.8 (s, 1C, C3 in C₅H₄), 67.3 (s, 1C, C4 in C₅H₄), 68.5 (d, ³*J*_{P-C} = 12.2 Hz, 2C, C2, C5 in C₅H₄), 127.1 (d, ²*J*_{P-C} = 9.6 Hz, 1C, C1 in C₅H₄), 129.1 (d, ³*J*_{P-C} = 2.5 Hz, 2C, *m*-C in Mes), 132.6 (d, ¹*J*_{P-C} = 29.1 Hz, 1C, *ipso*-C in Mes), 137.3 (s, 1C, *p*-C in Mes), 143.8 (s, 2C, br. *o*-C in Mes). ³¹P NMR (C₆D₆): δ = −32.8 (d of m, ¹*J*_{P-H} = 214 Hz). IR (KBr): $\tilde{\nu}$ = 2345 and 2310 (ν_{PH}, m) cm^{−1}. EI MS: *m/z* (%) = 570 (10) [*M*⁺], 418 (8) [*M*⁺ − PHMes], 313 (5) [*M*⁺ − C₅H₄CMe₂PHMes], 266 (100) [*M*⁺ − 2 PHMes], and fragmentation products thereof. C₃₄H₄₄FeP₂ (570.5): calcd. C 71.6, H 7.8, P 10.9; found C 71.1, H 8.3, P 10.3.

Synthesis of *rac*-[Fe{(η⁵-C₅H₄)CMe₂PHPh(Cp*TaCl₄)}₂] (4**):** A solution of **2** (0.7 g, 1.4 mmol) in toluene (15 mL) was added dropwise to a suspension of [Cp*TaCl₄] (1.3 g, 2.8 mmol) in toluene (30 mL). The color of the reaction mixture changed from orange to brown. The mixture was then heated to 70 °C for 2 h, allowed to cool, and stirred at room temperature overnight. The solid was

separated from the solution by filtration. Cooling to −20 °C gave unconverted [Cp*TaCl₄], which was also separated by filtration. The solvent was evaporated under vacuum, and the resulting brown residue was extracted with CH₂Cl₂. The dichloromethane solution was concentrated. Cooling to −20 °C gave a fine brown solid, which was recrystallized repeatedly from toluene. Finally, small brown crystals were obtained together with a brown powder. Yield: 0.9 g (45%), m.p. 162–167 °C (from toluene). ¹H NMR ([D₈]toluene): δ = 1.65 (d, ³*J*_{P-H} = 12.0 Hz, 6 H, CH₃ in CMe₂), 2.24 (s, 30 H, CH₃ in Cp*), 3.49 (m, 4 H, CH in C₅H₄), 3.75 (m, 2 H, CH in C₅H₄), 4.32 (m, 2 H, CH in C₅H₄), 6.97–7.01 (m, 10 H, CH in Ph). ¹³C NMR ([D₈]toluene and C₆D₆): δ = 13.7 (s, CH₃ in Cp*), 27.4 [br. s, C(CH₃)], 27.6 (br. s, C(CH₃)], 37.8 [s, C(CH₃)], 54 (br. s, ?), 67.2 (s, C3 and C4 in C₅H₄), 68.6 (s, C2 and C5 in C₅H₄), 100.4 (br., C1 in C₅H₄), 128.9 (s, C–CH₃ in Cp*), 129.7 (s, *m*-C in Ph), 133.9 (s, *ipso*-C in Ph), 137.3 (s, *o*-C in Ph); *p*-C in phenyl obscured by solvent. ³¹P NMR ([D₈]toluene): *T* = 230 K: δ = 57.6 (d, ¹*J*_{P-H} = 364 Hz), 8.5 (d, ¹*J*_{P-H} = 204 Hz); *T* = 300 K: δ = 33.6 (br). IR (KBr): $\tilde{\nu}$ = 2965 (CH₃, m), 2286 (PH, m), 1463 and 1435 (C=C Ph, m), 742 and 697 (C=C Ph, st) cm^{−1}.

Data Collection and Structural Refinement of **2, **3**, and **4**:** Data (Mo-*K*_α = 0.71073 Å) were collected with a Siemens CCD (SMART) diffractometer. All observed reflections were used for refinement (SAINT) of the unit cell parameters. Empirical absorption correction with SADABS.^[22] The structures were solved by direct methods (SHELXTL PLUS).^[23] Fe, Ta, P, Cl, and C atoms were refined anisotropically; H atoms were located by difference maps and refined isotropically. Table 2 lists crystallographic details.

CCDC-173678 (**2**), -173679 (**3**) and -173680 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/contents/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft.

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Received October 25, 2001
[101420]