Novel Ferrocene Derivatives with PH-Functionalized Phosphanylalkylcyclopentadienyl Ligands: Syntheses and Molecular Structures of *rac*-[Fe{(η^5-C_5H_4)CMe_2PHR}$_2$] (R = Ph, Mes) and *rac*-[Fe{(η^5-C_5H_4)$CMe_2PHPh(Cp^*TaCl_4)$}$_2$][‡]

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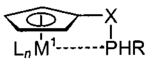
Dedicated to Professor Joachim Strähle on the occasion of his 65th birthday

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

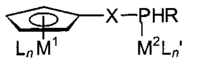
6,6-Dimethylfulvene reacts with LiPHMes (Mes = 2,4,6-$Me_3C_6H_2$) to give Li[(C_5H_4)CMe_2PHMes] (**1**). The ferrocene derivatives *rac*-[Fe{(η^5-C_5H_4)CMe_2PHR}$_2$] [R = Ph (**2**), Mes (**3**)] are obtained in high yield from the lithium reagents Li[(C_5H_4)CMe_2PHR] (R = Ph, Mes) and $FeCl_2$. Compound **2** reacts with [Cp^*TaCl_4] to give the heterotrinuclear complex *rac*-[Fe{(η^5-C_5H_4)$CMe_2PHPh(Cp^*TaCl_4)$}$_2$] (**4**). Compounds **1**–**4** were characterized spectroscopically, and crystal structure determinations were carried out on **2**–**4**.

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-$SiMe_2PHCy$-2,3,4,5-Me_4C_5H, Li_2[(C_5Me_4)$SiMe_2PR$] [R = Cy, 2,4,6-$Me_3C_6H_2$ (Mes)], Li[(C_5H_4)CMe_2PHR] (R = Ph, *t*Bu) and Li_2[(C_5H_4)CH_2CH_2PPh].[4,5] The molecular structures of [Li(tmeda)]$_2$[(C_5H_4)CMe_2PPh][6] and [Li(tmeda)][(C_5H_4)CMe_2PR_2][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, $M^1 = M^2$ or $M^1 \neq M^2$, L = ligands, X = spacer (alkylidene, arylidene), R = alkyl, aryl).



A



B

We have recently shown that Li_2[(C_5Me_4)$SiMe_2PR$] (R = Cy, Mes) reacts with $ZrCl_4$ to give [{(η^5-C_5Me_4)$_2SiMe_2$}$ZrCl_2$] and $(PCy)_4$ or $(PHMes)_2$, while Li[(C_5H_4)CMe_2PHR] reacts with $ZrCl_4$ or [$TiCl_3(THF)_3$] to yield [{(η^5-C_5H_4)CMe_2PHR}$_2ZrCl_2$] or [{(η^5-C_5H_4)CMe_2PHR}$_2TiCl$] (R = Ph, *t*Bu).[5] However, these complexes slowly decompose in solution with formation of [{(η^5-C_5H_4)$_2CMe_2$}MCl_2] (M = Zr, Ti).[5] Erker et al. reported that the complexes [{$CyPCMe_2$(η^5-C_5H_4)}M$(NR_2)_2$] (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{(η^5-C_5H_4)CMe_2PHR}$_2$] [R = Ph (**2**), Mes (**3**)] and the heterotrinuclear complex *rac*-[Fe{(η^5-C_5H_4)$CMe_2PHPh(Cp^*TaCl_4)$}$_2$] (**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]

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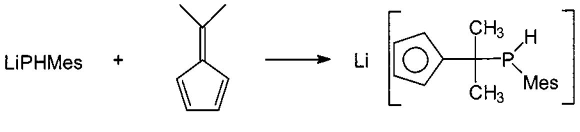
Results and Discussion

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 Et_2O at room temperature to give the highly air and water sensitive compound $Li[(C_5H_4)CMe_2PHMes]$ (**1**) [Equation (1)].

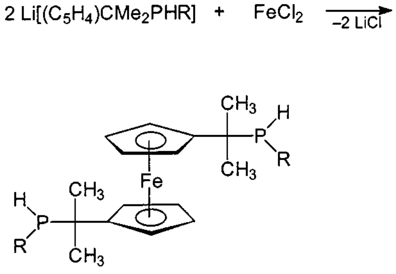


(1)

1

The ^1H NMR spectrum of **1** indicates that the methyl groups in P−C(*Me*$_2$) are prochiral and thus diastereotopic. Therefore, the two nonequivalent Me groups appear as two doublets due to P−H coupling [$\delta = 1.43$ ($^3J_{P-H} = 8.8$ Hz); $\delta = 1.41$ ($^3J_{P-H} = 13.0$ Hz)]. However, in the ^{31}P NMR spectrum, the two Me groups are equivalent, and a doublet of septets is observed. As was observed for $Li[(C_5H_4)CMe_2PHR]$ (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**: $\delta = -45.6$ ($^1J_{P-H} = 216$ Hz); PH_2Mes:[10] $\delta = -154.8$ ($^1J_{P-H} = 203$ 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**: $\delta = 4.36$; PH_2Mes:[10] $\delta = 3.53$). Compared with the signals of 6,6-dimethylfulvene (Me: $\delta = 2.19$; C_5H_4: $\delta = 6.53-5.45$),[11] the corresponding signals in **1** are shifted to high field ($\delta = 1.41$, 1.43 and 5.56).

The ferrocene derivatives $[Fe\{(\eta^5\text{-}C_5H_4)CMe_2PHR\}_2]$ [R = Ph (**2**), Mes (**3**)] are obtained in high yield from the lithium reagents $Li[(C_5H_4)CMe_2PHR]$ (R = Ph, Mes (**1**)] and $FeCl_2$ in THF at room temperature [Equation (2)].



(2)

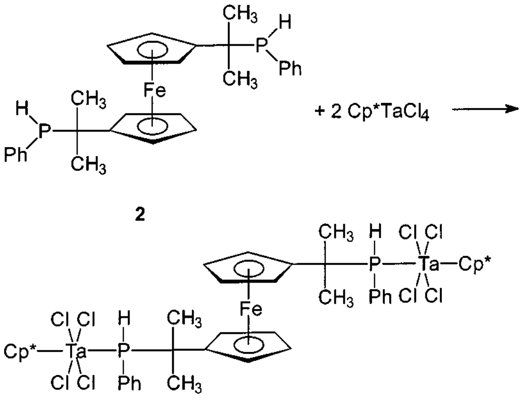
R = Ph (**2**), Mes (**3**)

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 racemic 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 ^{31}P NMR spectra of the reaction mixture could be obtained due to the presence of small amounts of $FeCl_2$. However, the ^{31}P NMR spectra recorded for **2** at different stages of workup always indicated the presence of only one diastereomer. Thus, in the $^{31}P\{^1H\}$ NMR spectrum of crystalline **2**, only one signal is observed. However, in the ^{31}P 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 ^{31}P NMR spectrum of **2** and **3**, a doublet of multiplets is observed [**2**: $\delta = 8.8$ ($^1J_{P-H} = 207$ Hz); **3**: $\delta = -32.8$ ($^1J_{P-H} = 214$ Hz)], which are shifted to low field by ca. 10−13 ppm relative to $Li[(C_5H_4)CMe_2PHR]$ (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(*Me*$_2$) are prochiral and thus diastereotopic. Thus, the two nonequivalent Me groups appear as two doublets due to P−H coupling [**2**: $\delta = 1.32$ ($^3J_{P-H} = 12.0$ Hz), 1.38 ($^3J_{P-H} = 12.4$ Hz); **3**: $\delta = 1.39$ ($^3J_{P-H} = 13.0$ Hz), 1.45 ($^3J_{P-H} = 8.8$ 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



2

(3)

4

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 ($\Delta G^{\#} = 56 \pm 1$ 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_5H_4)CMe_2PHPh}$_2$] (**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_5H_4)CMe_2PHMes}$_2$] (**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_5H_4)CMe_2PHPh(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 [Cp*TaCl$_4$] in toluene at room temperature to give the heterotrinuclear complex *rac*-[Fe{(η^5-C$_5$H$_4$)CMe$_2$PHPh(Cp*TaCl$_4$)}$_2$] (**4**) [Equation (3)].

The trinuclear 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 ([D$_8$]toluene or [D$_6$]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 δ = 8.5 and 57.6 (ratio ca. 1:2), which collapse into one broad singlet at room temperature (δ = 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 [Fe{(η^5-C$_5$H$_4$)CH$_2$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)°]. 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.

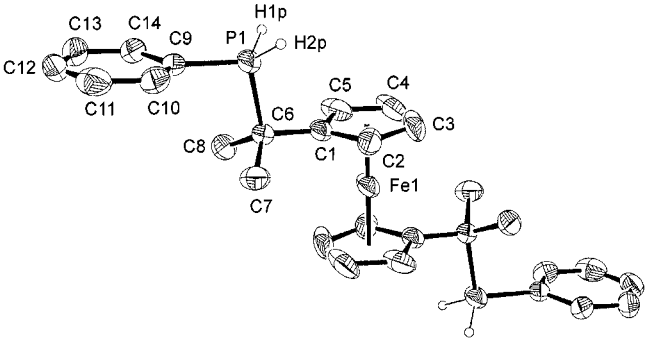


Figure 1. Molecular structure of *rac*-[Fe{(C$_5$H$_4$)CMe$_2$PHPh}$_2$] (**2**) showing the atom numbering scheme employed (ORTEP plot, 50% probability, SHELXTL PLUS; XP[23]); hydrogen atoms (other than P−H) are omitted for clarity; the P−H proton is disordered

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.

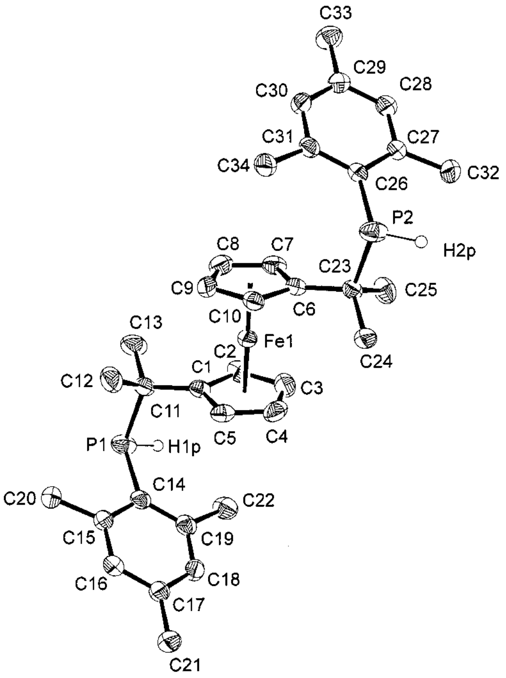


Figure 2. Molecular structure of *rac*-[Fe{(C$_5$H$_4$)CMe$_2$PHMes}$_2$] (**3**) showing the atom numbering scheme employed (ORTEP plot, 50% probability, SHELXTL PLUS; XP[23]); hydrogen atoms (other than P−H) are omitted for clarity; only the *R*,*R* isomer is shown.

In **3** and **4**, the aryl rings and the cyclopentadienyl rings adopt an angle of 31.2(1)° and 34.1(1)° (**3**) or 31.4(2)° and 33.3(2)° (**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 [Cp*TaCl$_4$(PH$_2$Ph)] [2.651(3) Å].[15] Apparently, replacement of the small H substituent by the bulky (C$_5$H$_4$)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 [Cp*TaCl$_4$(PH$_2$Ph)] [0.602(2) Å] and smaller than that observed for [Cp*TaCl$_4$] [0.806(2) Å],[15] due to the higher steric demand of the phosphane ligands in [Cp*TaCl$_4$(PH$_2$Ph)] and **4**. Only one other trinuclear bis(phosphanylmethyl)ferrocene complex, namely [Fe{(η^5-C$_5$H$_4$)CH$_2$PPh$_2$[RuCl$_2$(η^6-1,2,3,4-Me$_4$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$^{R}_{center}$ 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.

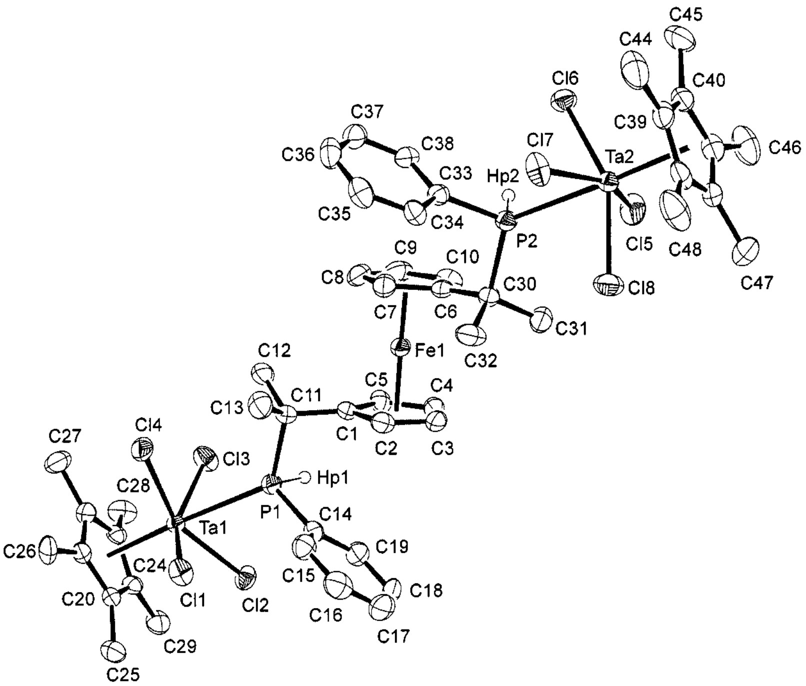


Figure 3. Molecular structure of *rac*-[Fe{(C_5H_4)CMe$_2$PHPh(Cp*TaCl$_4$)}$_2$] (**4**) showing the atom numbering scheme employed (ORTEP plot, 50% probability, SHELXTL PLUS; XP[23]); hydrogen atoms (other than P−H) are omitted for clarity; only the *S*,*S* isomer is shown

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), ^{1}H NMR (400 MHz): internal standard solvent, external standard TMS. ^{13}C NMR (100.6 MHz): external standard TMS, internal standard solvent. ^{31}P NMR (162 MHz): external standard 85% H_3PO_4. 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[(C_5H_4)CMe$_2$PHPh][4] and [Cp*TaCl$_4$][21] were prepared according to the literature procedures. FeCl$_2$ is commercially available (Aldrich).

Synthesis of Li[(C_5H_4)CMe$_2$PHMes] (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 Et$_2$O (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 Et$_2$O, 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.). ^{1}H NMR ([D$_8$]THF): δ = 1.41 (d, $^3J_{P-H}$ = 13.0 Hz, 3 H, CH$_3$ in CMe$_2$), 1.43 (d, $^3J_{P-H}$ = 8.8 Hz, 3 H, CH$_3$ in CMe$_2$), 2.19 (s, 3 H, *p*-CH$_3$ in Mes), 2.26 (s, 6 H, *o*-CH$_3$ in Mes), 4.36 (d, $^1J_{P-H}$ = 215.6 Hz, 1 H, PH), 5.56 (s, 4 H, CH in C_5H_4), 6.78 (s, 2 H, *m*-CH in Mes). ^{13}C NMR ([D$_8$]THF): δ = 21.0 (s, 1C, *p*-CH$_3$ in Mes), 23.9 (m, 2C, *o*-CH$_3$ in Mes), 30.4 (d, $^2J_{P-C}$ = 17.8 Hz, 1C, *C*H$_3$-C), 31.5 (d, $^2J_{P-C}$ = 9.7 Hz, 1C, *C*H$_3$−C), 37.2 (d, $^1J_{P-C}$ = 12.5 Hz, 1C, *C*−CH$_3$), 101.7 (d, $^3J_{P-C}$ = 3.5 Hz, 2C, C2, C5 in C_5H_4), 102.7 (s, 2C, C3, C4 in C_5H_4), 127.1 (d, $^2J_{P-C}$ = 9.6 Hz, 1C, C1 in C_5H_4), 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). ^{31}P NMR ([D$_8$]THF): δ = −45.6 (d of m, $^1J_{P-H}$ = 216 Hz). IR (KBr): $\tilde{\nu}$ = 2337 (νPH, m), 1463 (νC=C m, br) cm^{-1}.

Synthesis of *rac*-[Fe{(η^5-C_5H_4)CMe$_2$PHPh}$_2$] (2): A solution of Li[(C_5H_4)CMe$_2$PHPh] (3.5 g, 15.6 mmol) in THF (30 mL) was slowly added to a suspension of FeCl$_2$ (1.0 g, 7.8 mmol) in THF. During the addition, FeCl$_2$ 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 Et$_2$O. The rust-brown powder was separated from the yellow solution by filtration and extracted repeatedly with Et$_2$O. The Et$_2$O 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). ^{1}H NMR (C_6D_6): δ = 1.32 (d, $^3J_{P-H}$ = 12.0 Hz, 3 H, CH$_3$ in CMe$_2$), 1.38 (d, $^3J_{P-H}$ = 12.4 Hz, 3 H, CH$_3$ in CMe$_2$), 3.75−3.61 (m, 2 H, CH in C_5H_4), 3.95−3.91 (m, 2 H, CH in C_5H_4), 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). ^{13}C NMR (C_6D_6): δ = 28.4 (d, $^2J_{P-C}$ = 16.3 Hz, 1C, *C*H$_3$−C), 28.9 (d, $^2J_{P-C}$ = 16.0 Hz, 1C, *C*H$_3$−C), 33.6 (d, $^1J_{P-C}$ = 12.6 Hz, 1C, *C*−CH$_3$), 66.6 (s, 1C, C4 in C_5H_4), 67.1 (s, 1C, C3 in C_5H_4), 68.3 (d, $^3J_{P-C}$ = 21.0 Hz, 2C, C2, C5 in C_5H_4), 99.6 (d, $^2J_{P-C}$ = 7.2 Hz, 1C, C1 in C_5H_4), 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). ^{31}P NMR (C_6D_6): δ = 8.8 (d of m, $^1J_{P-H}$ = 207 Hz). IR (KBr): $\tilde{\nu}$ = 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 − CMe$_2$], and fragmentation products thereof. $C_{28}H_{32}FeP_2$ (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{(η^5-C_5H_4)CMe$_2$PHMes}$_2$] (3): A solution of Li[(C_5H_4)CMe$_2$PHMes] (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	$C_{28}H_{32}FeP_2$	$C_{34}H_{44}FeP_2$	$C_{48}H_{62}Cl_8FeP_2Ta_2$
M_r	486.33	570.48	1402.27
Temperature (K)	220(2)	220(2)	220(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)
a [Å]	6.1170(3)	8.0117(2)	15.2794(7)
b [Å]	21.2473(9)	17.7373(5)	14.8736(6)
c [Å]	9.6680(4)	20.7827(6)	22.925(1)
β [°]	102.292(1)	93.602(1)	95.607(1)
V [Å^3]	1227.74(9)	2947.5(1)	5184.9(4)
Z	2	4	4
$\rho_{calcd.}$ [Mg m^{-3}]	1.316	1.286	1.796
F(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
R_{int}	0.0283	0.0440	0.0495
Parameters	192	510	780
R [$I > 2\sigma(I)$]	0.0673	0.0387	0.0339
$wR2$ (all data)	0.1641	0.1212	0.0618
$(\Delta/\rho)_{min.}$ [e Å^{-3}]	0.246	0.571	1.007
$(\Delta/\rho)_{max.}$ [e Å^{-3}]	−0.528	−0.379	−1.424

slowly added to a suspension of $FeCl_2$ (0.4 g, 3.0 mmol) in THF (30 mL). During the addition, $FeCl_2$ 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 Et_2O (20 mL). The insoluble rust-brown powder was separated from the orange solution by filtration and extracted repeatedly with Et_2O. The Et_2O 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 (C_6D_6): $\delta = 1.39$ (d, $^3J_{P-H} = 13.0$ Hz, 3 H, CH_3 in CMe_2), 1.45 (d, $^3J_{P-H} = 8.8$ Hz, 3 H, CH_3 in CMe_2), 2.08 (s, 3 H, *p*-CH_3 in Mes), 2.27 (br. s, 6 H, *o*-CH_3 in Mes), 3.87−3.60 (m, 4 H, CH in C_5H_4), 4.4 (d, $^1J_{P-H} = 216.1$ Hz, 1 H, PH), 6.76 (s, 2 H, *m*-H in Mes). ^{13}C NMR (C_6D_6): $\delta = 21.7$ (s, 1C, *p*-CH_3 in Mes), 24.8 (br. s, 2C, *o*-CH_3 in Mes), 29.3 (br. s, 1C, $\mathit{C}H_3{-}C$), 29.6 (br, 1C, $\mathit{C}H_3{-}C$), 35.7 (d, $^1J_{P-C} = 15.2$ Hz, 1C, $\mathit{C}{-}CH_3$), 66.8 (s, 1C, C3 in C_5H_4), 67.3 (s, 1C, C4 in C_5H_4), 68.5 (d, $^3J_{P-C} = 12.2$ Hz, 2C, C2, C5 in C_5H_4), 127.1 (d, $^2J_{P-C} = 9.6$ Hz, 1C, C1 in C_5H_4), 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 im Mes), 143.8 (s, 2C, br, *o*-C in Mes). ^{31}P NMR (C_6D_6): $\delta = -32.8$ (d of m, $^1J_{P-H} = 214$ Hz). IR (KBr): $\tilde{\nu} = 2345$ and 2310 (νPH, m) cm^{-1}. EI MS: *m*/*z* (%) = 570 (10) [M$^+$], 418 (8) [M$^+$ − PHMes], 313 (5) [M$^+$ − $C_5H_4CMe_2PHMes$], 266 (100) [M$^+$ − 2 PHMes], and fragmentation products thereof. $C_{34}H_{44}FeP_2$ (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{(η^5-C_5H_4)CMe_2PHPh(Cp*$TaCl_4$)}$_2$] (4): A solution of **2** (0.7 g, 1.4 mmol) in toluene (15 mL) was added dropwise to a suspension of [Cp*$TaCl_4$] (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*$TaCl_4$], which was also separated by filtration. The solvent was evaporated under vacuum, and the resulting brown residue was extracted with CH_2Cl_2. 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 ([D$_8$]toluene): $\delta = 1.65$ (d, $^3J_{P-H} = 12.0$ Hz, 6 H, CH_3 in CMe_2), 2.24 (s, 30 H, CH_3 in Cp*), 3.49 (m, 4 H, CH in C_5H_4), 3.75 (m, 2 H, CH in C_5H_4), 4.32 (m, 2 H, CH in C_5H_4), 6.97−7.01 (m, 10 H, C*H* in Ph). ^{13}C NMR ([D$_8$]toluene and C_6D_6): $\delta = 13.7$ (s, CH_3 in Cp*), 27.4 [br. s, C($\mathit{C}H_3$)], 27.6 (br. s, C($\mathit{C}H_3$)], 37.8 [s, C(CH_3)], 54 (br. s, ?), 67.2 (s, C3 and C4 in C_5H_4), 68.6 (s, C2 and C5 in C_5H_4), 100.4 (br., C1 in C_5H_4), 128.9 (s, $\mathit{C}{-}CH_3$ 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. ^{31}P NMR ([D$_8$]toluene): $T = 230$ K: $\delta = 57.6$ (d, $^1J_{P-H} = 364$ Hz), 8.5 (d, $^1J_{P-H} = 204$ Hz); $T = 300$ K: $\delta = 33.6$ (br). IR (KBr): $\tilde{\nu} = 2965$ (CH_3, 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/conts/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].

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