DOI: 10.1002/ejic.200600914

Synthesis, Structure and Reactivity of Trimethylsilyl-Substituted Phosphametallocenes

Rebekka Loschen,[a] Christoph Loschen,[a][‡] and Walter Frank,[a][‡‡] and Christian Ganter*[a]

Dedicated to Prof. Dr. Gerhard E. Herberich on the occasion of his 70th birthday

Keywords: Metallocenes / P ligands / Silicon / Phosphaferrocenes / Conformation analysis

New sterically crowded phosphaferrocene and -ruthenocene derivatives were synthesized via the 2,5-bis(trimethylsilyl)-phospholide anion **5**. Their reactivity with regard to the exchange of the Me_3Si groups for other functional groups was examined. X-ray structures were determined for the mono- (**6**) and the 1,1′-diphosphaferrocene (**8**). The activation barrier for ring–ring rotation in **8** was determined by NMR spectroscopy and supported by DFT calculations. Attempts to prepare 2,5-difunctional phosphaferrocenes through electrophilic substitutions were unsuccessful, but yielded en route a new bidentate P,P ligand (**3**) and its $Mo(CO)_4$ complex, which were both characterized by X-ray diffraction.

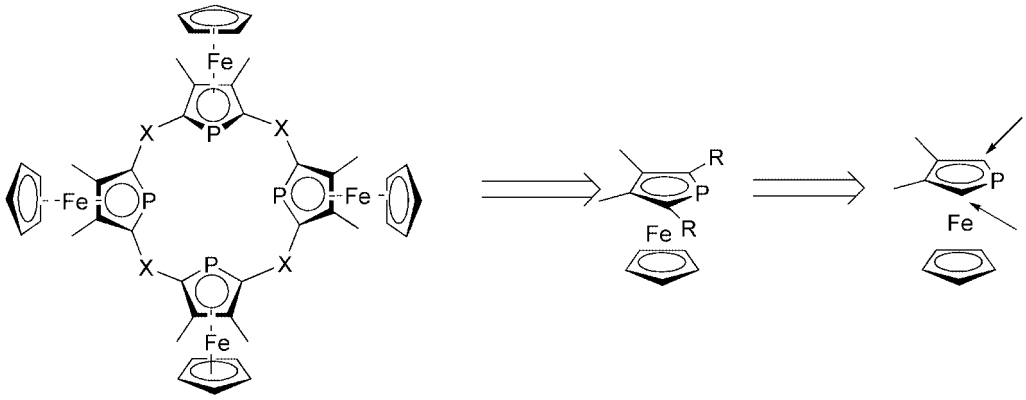
Introduction

Phosphametallocenes are interesting compounds that show remarkable equivalence with their carbocyclic analogues regarding some of the physical and chemical properties but also show markedly different behaviour with regard to other properties. The Fe containing phosphaferrocenes are by far the most intensively studied phosphametallocenes, which were discovered in 1977 and still continue to be of interest.[1] In particular, the use of phosphaferrocene building blocks for the construction of multidentate, chiral chelate ligands has brought about a renewed interest within the last decade.[2] The chemical reactivity of phosphaferrocenes in view of synthetically useful transformations is restricted to electrophilic aromatic substitutions, which provide access to derivatives with one additional functional group attached to the phosphole ring, thereby rendering the phosphaferrocene a planar-chiral moiety. In this paper we report our attempts to prepare phosphaferrocene and phospharuthenocene derivatives with two functional groups at the 2,5-position of the phosphole ring. Related compounds were prepared earlier by converting suitable phosphole precursors into the respective phosphametallocenes[3] and this strategy was successfully employed in this work. The sought-after 2,5-difunctionalized phosphaferrocenes are synthetically interesting compounds and may be used for the assembly of extended structures like macrocycles containing several individual phosphaferrocene units. Such compounds would significantly expand the class of known macrocyclic ligands, which mainly consist of oxygen, sulfur or nitrogen containing derivatives.[4] In contrast, much less is known about phosphorus containing macrocycles although the first example was prepared as early as 1975.[5,6] While the O, N and S containing compounds feature strong σ-donor properties, the P derivatives are of special interest because they may exhibit a more or less pronounced π-acceptor character, depending on the nature of the phosphorus subunit. For example, a macrocycle comprising four phosphinine rings with strong acceptor properties[7] has been reported by Mathey et al.[8] This ligand formed stable complexes with low-valent transition-metal fragments of Rh^I, Ir^I, Au^I and Au^0.[8a,9] Phosphaferrocenes also feature sp^2-hybridized P atoms with a significant π-acceptor capacity[1] and have been used recently as building blocks for the construction of bi- and oligodentate chiral chelate ligands. In view of their potential use for the assembly of macrocycles we decided to elaborate on the synthesis of 2,5-disubstituted phosphaferrocenes.

Results and Discussion

A potential retrosynthetic fragmentation of a phosphaferrocene containing macrocycle is presented in Scheme 1. Disconnection leads to 2,5-disubstituted phosphaferrocene derivatives with suitable functional groups. Thus, a 2,5-diformyl or diacyl derivative, or compounds derived thereof, appear to be attractive synthetic targets.

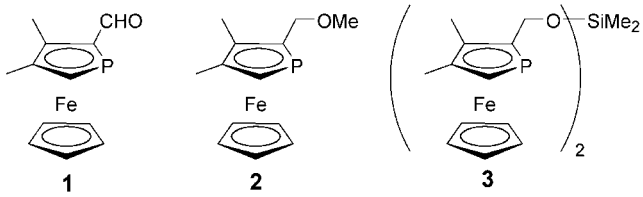
[a] Institut für Anorganische Chemie, Heinrich-Heine-Universität Düsseldorf,
Universitätsstrasse 1, 40225 Düsseldorf, Germany
E-Mail: christian.ganter@uni-duesseldorf.de
[‡] DFT calculations.
[‡‡] X-ray structure determinations.



Scheme 1.

Modification of an Existent Phosphaferrocene

In contrast to ferrocene, which can be deprotonated and treated with a great variety of electrophiles, this protocol is not applicable to phosphaferrocenes,[10] thus preventing an easy and general access to functionalized derivatives. As mentioned above, electrophilic substitution is the only reported method for the introduction of a substituent into the phosphole ring of a given phosphaferrocene unit. For example, the electrophilic formylation,[11] acylation[12] and carboxylation[13] of 3,4-dimethylphosphaferrocene under Friedel–Crafts or Vilsmeyer conditions have been reported to occur selectively on the phosphole ring giving the monofunctionalized products with the additional substituent at the 2-position in good yield, thereby rendering the phosphaferrocene a planar-chiral moiety. The deactivating nature of the formyl, acyl and carboxylic ester functional groups prevents the formation of disubstituted derivatives. We thought that transformation of these functional groups into less deactivating or even activating ones might overcome this situation and allow the introduction of a second functional group via electrophilic substitution. Therefore, we prepared the ether derivatives **2** and **3** in good yield after initial reduction of the aldehyde **1** to the corresponding alcohol (Scheme 2).



Scheme 2.

The spectroscopic characterization revealed that compound **3** was obtained as a *rac*/*meso* mixture in the ratio of 2:1 because of the racemic nature of the starting aldehyde **1**. The *rac* isomer of **3** could be characterized by an X-ray diffraction analysis. It crystallizes in the triclinic space group $P\bar{1}$ with both enantiomers in the asymmetric unit (Z = 4). The geometrical data for the two independent molecules are identical within experimental precision and values are reported for one molecule only. Bond lengths and angles fall in the range typically observed for phosphaferrocene derivatives. The suitability of the dinuclear phosphaferrocene **3** to act as a bidentate-P,P ligand was demonstrated by the formation of the complex **3**·Mo(CO)$_4$. Again, the X-ray structure of the complex containing the *rac*-ligand could be determined and the two structures are depicted in Figure 1 and Figure 2, relevant geometrical data are compiled in Table 1 and Table 2. The Mo complex lacks any molecular symmetry in the solid state (point group C_1), but features effective C_2 symmetry in solution leading to a singlet resonance for the two phosphorus atoms in the ^{31}P NMR spectrum. A Similar behaviour has been observed before for other Mo(CO)$_4$ complexes with C_2-symmetric bisphosphaferrocenes.[14,15] The deviations of the central MoL$_6$ core from regular octahedral symmetry in terms of bond angles are rather small since the P,P ligand is highly flexible because of the extended backbone. The Mo–P and Mo–CO distances are in agreement with values observed for related complexes with phosphaferrocene or other π-acidic P-ligands.[16] The changes of intra-ligand geometrical parameters upon coordination are small but typical and mainly

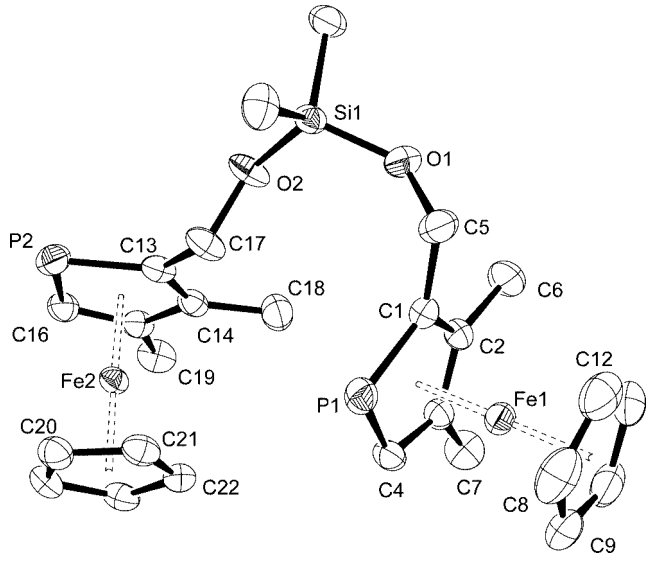


Figure 1. Molecular structure of complex **3**.

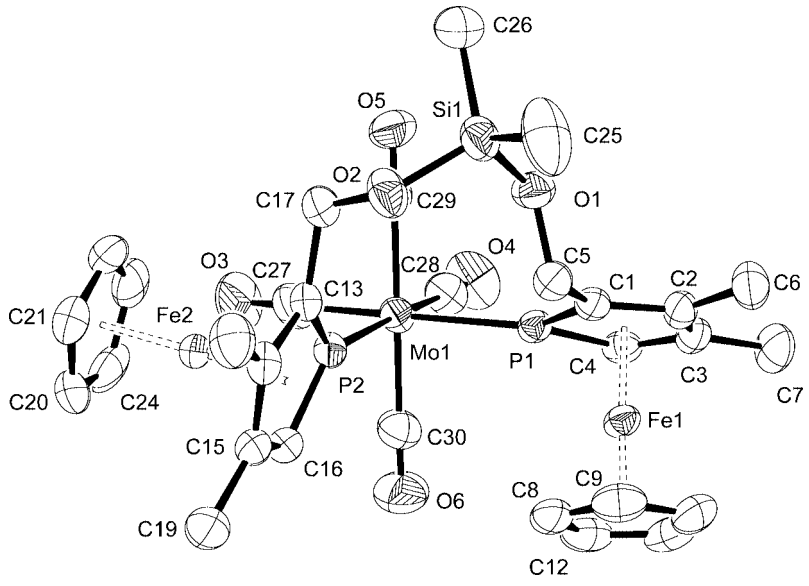


Figure 2. Molecular structure of complex (*rac*-**3**)·[$Mo(CO)_4$].

involve the increase of the C–P–C angle in the phosphole ring from 88.3 to 90.2°.

Table 1. Selected bond lengths [Å] and angles [°] for complexes **3** and **3**·$Mo(CO)_4$.

	3	**3**·$Mo(CO)_4$
P1–C4	1.753(4)	1.737(5)
P1–C1	1.775(4)	1.756(5)
P2–C16	1.766(4)	1.756(5)
P2–C13	1.778(4)	1.758(5)
C1–C2	1.410(5)	1.420(6)
C3–C4	1.402(5)	1.416(7)
C2–C3	1.414(4)	1.419(7)
C13–C14	1.412(5)	1.435(6)
C15–C16	1.406(5)	1.396(7)
C14–C15	1.420(5)	1.423(7)
Si1–O1	1.622(2)	1.629(4)
Si1–O2	1.631(2)	1.632(4)
C4–P1–C1	88.35(17)	90.2(2)
C16–P2–C13	88.17(17)	90.2(2)
C2–C1–C5	123.2(3)	124.4(4)
C14–C13–C17	123.6(3)	122.7(5)
O1–Si1–O2	112.89(14)	109.13(19)

Table 2. Unique bond lengths [Å] and angles [°] for complex **3**·$Mo(CO)_4$.

Mo1–P1	2.4938(14)	Mo1–P2	2.5187(14)
Mo1–C27	1.989(7)	Mo1–C28	1.959(7)
Mo1–C30	2.010(7)	Mo1–C29	2.019(7)
O3–C27	1.174(7)	O4–C28	1.167(7)
O5–C29	1.152(6)	O6–C30	1.151(7)
C30–Mo1–C29	178.9(3)	C27–Mo1–P1	174.6(2)
C28–Mo1–P2	177.9(2)	P1–Mo1–P2	92.93(4)

Unfortunately, all attempts to introduce a second functional group into the derivatives **2** and **3** by electrophilic formylation or acylation have met with failure. Furthermore, the dinuclear derivative 1,1′-bis[(3,4-dimethylphosphaferrocene-2-yl)methyl]ferrocene[15] could also neither be formylated nor acylated.

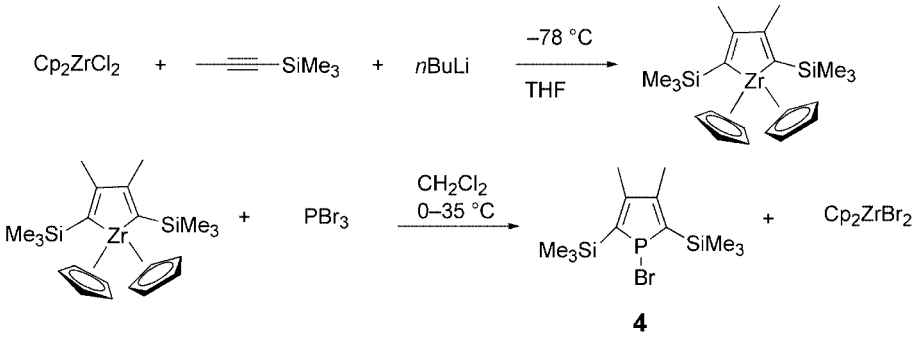
2,5-Disubstituted Phosphaferrocenes from Preformed Phospholes

Because of the unsuccessful attempts described in the preceding paragraph a different synthetic approach was envisaged. An alternative access to 2,5-disubstituted phosphaferrocenes is the synthesis of a suitable 2,5-disubstituted phospholide anion in a first step and subsequent coordination to a CpFe source. For this purpose we chose the well-known zirconocene-mediated coupling of alkynes: with 1-trimethylsilylpropyne as a coupling partner, the zirconacyclopentadiene with the Me_3Si groups in α-positions is formed regioselectively in high yield and can be converted into the corresponding bromophosphole (**4**) by treatment with PBr_3 (Scheme 3).[17,18]

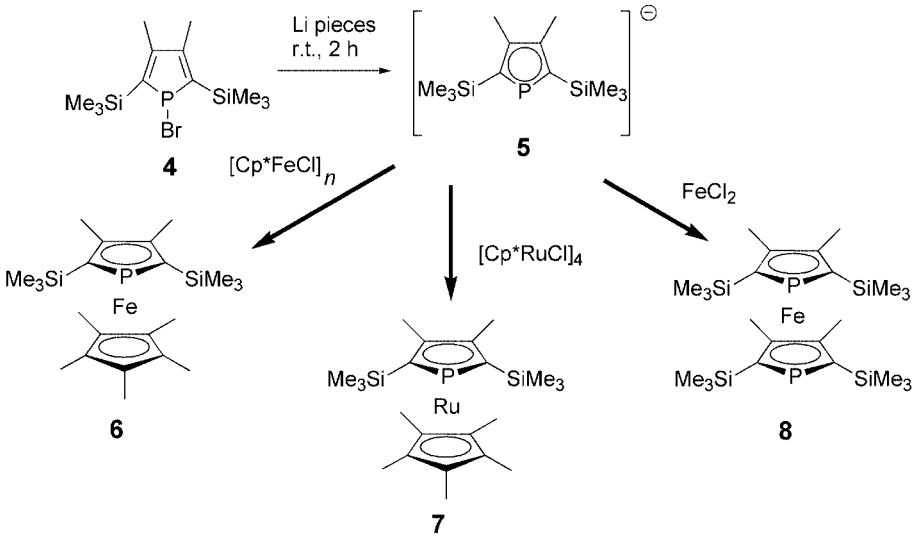
Reduction of bromophosphole (**4**) by elemental lithium proceeds straightforwardly to the corresponding phospholide anion **5**, the conversion can easily be monitored by ^{31}P NMR spectroscopy [δ = 141 (**5**), 78 ppm (**4**)]. Subsequent coordination of anion **5** to suitable Cp-metal fragments gave access to new TMS-substituted phosphametallocenes (Scheme 4): 2,5-bis(trimethylsilyl)-3,4-dimethylphosphaferrocene (**6**), the analogous ruthenocene (**7**) and 2,2′,5,5′-tetrakis(trimethylsilyl)-3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene (**8**), which has been synthesized before but was only characterized by ^1H NMR spectroscopy.[19]

2,5-Bis(trimethylsilyl)-3,4-dimethylphosphaferrocene (6)

In order to prepare 2,5-bis(silyl)monophosphaferrocene derivatives the phospholide anion **5** was treated with different iron precursors. While the reaction with [(mesitylene)$FeCp^+$]PF_6 was unsuccessful, treatment with $[Cp^*FeCl]_n$ (Scheme 3) – prepared in situ from Cp*Li and $FeCl_2$ in THF according to the literature[2g] – proceeded straightforwardly to produce the Cp*-phosphaferrocene **6** in 55% yield as red crystals after crystallization from MeOH, which was completely characterized by NMR spectroscopy, mass spectroscopy, elemental analysis and X-ray diffraction. An



Scheme 3.



Scheme 4.

ORTEP plot of the molecular structure of **6** is depicted in Figure 3, relevant geometrical data can be found in Table 3. Complex **6** features a typical sandwich-type structure with an almost planar phospholyl ring parallel to the Cp* ring. The distances between the Fe atom and the phospholyl centroid Ct1 (1.668 Å) and the Cp* centroid Ct2 (1.690 Å), respectively, are very similar. As is usually observed in phosphametallocene complexes, the C1–P1–C4 angle (91.4°) is close to 90°, the mean P–C distances are 1.790 Å and the C–C bonds in the phospholyl ring are very similar. The steric bulk of the $SiMe_3$ groups becomes apparent from the angles Fe–Ct1–Si (95.7°, 96.8°), which exceed the ideal value of 90°, while the deviation for the β-Me groups is significantly smaller (90.9°, 91.1°). In conclusion, the structural parameters of the parent compound differ only very slightly from those observed for the related phosphaferrocene and ruthenocene ([Cp*M{(2,5-tBu$_2$)C_4H_2P}], M = Fe,[20] Ru[21]) with tBu groups in place of the Me_3Si groups. A closely related molecule with alkynyldimethylsilyl substituents was obtained by Mathey et al. via [CpFe(η^6-C_9H_{12})][PF_6].[18]

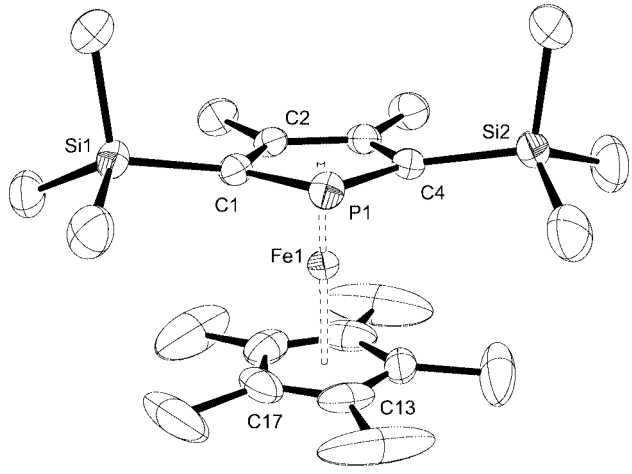


Figure 3. Molecular structure of complex **6**.

The bis(trimethylsilyl) complex **6** may serve as a source for other 2,5-difunctionalized phosphaferrocenes suitable for macrocyclization reactions by exchange of the Me_3Si

Table 3. Selected bond lengths [Å] and angles [°] for complexes **6** and **8**.

	6	**8**
P1–C1	1.792(3)	1.750(4)
P1–C4	1.788(3)	1.751(3)
C1–C2	1.430(4)	1.401(5)
C2–C3	1.437(4)	1.390(5)
C3–C4	1.439(4)	1.421(5)
Fe1–Ct(C_4P)	1.668(2)	1.672(2)
Fe1–Ct(C_5)	1.690(2)	
C4–P1–C1	91.42(13)	92.5(2)
Fe1–Ct(C_4P)–Si1	96.8(2)	95.0(2)
Fe1–Ct(C_4P)–Si2	95.7(2)	97.6(2)

groups for other functional groups, although the small polarity of the C–Si bond limits the reaction bandwidth.[22] For example, the conversion of an *i*Pr_3Si group attached to a phosphametallocene into a trifluoroacetyl group has recently been reported[23] and the bis(trifluoroacetyl) derivative derived from **6** would be of high synthetic value. However, upon treatment of complex **6** with trifluoroacetic anhydride and BF_3·OEt_2 only one TMS group is substituted, the other one is protodesilylated by the acid formed during the reaction.

An even simpler approach to 2,5-difunctionalized phosphaferrocenes with substituents suitable for further transformation might involve the preparation of 2,5-diacyl- or dicarboxylic ester derivatives. Although the syntheses of the appropriate phospholide anions with two acyl or ester groups have been elaborated by Mathey et al.,[24] we were unsuccessful in transforming these functional phospholide anions into the respective Fe or Ru sandwich complexes.

2,5-Bis(trimethylsilyl)-3,4-dimethylphospharuthenocene (7)

Phospharuthenocenes are much less investigated than phosphaferrocenes. The first example, [Cp*Ru{(2,5-*t*Bu_2)-C_4P}], was prepared by Carmichael et al. in 1994[21] and some mixed Ru/Fe tripledecker[25] complexes were reported later. Meanwhile, a couple of additional derivatives with bulky groups in 2,5-positions like naphthyl,[26] triisoproplylsilyl,[23] cyclohexyl or menthyl[27] could be prepared as well. To prevent η^1-P-coordination in the complexation reaction, the phosphole has to bear either bulky substituents at the α-position or, as was found out later, an electron-withdrawing group.[28] Once the phosphole is coordinated to ruthenium, the α-substituents can be transformed into other sterically less demanding functional groups. Treatment of anion **5** with $[Cp^*RuCl]_4$ afforded the new 2,5-bis(trimethylsilyl)ruthenocene (**7**) (Scheme 4) as a brown solid after chromatographic workup. Interestingly, the ^{31}P resonance of complex **7** (δ = 0.95 ppm) is drastically shifted to lower field as compared to the 2,5-*t*Bu_2 analogue (δ = –63.0 ppm).[21]

In analogy to **6** the reactivity of **7** towards electrophilic desilylation was tested in a trifluoroacylation reaction. However, the only product isolated from this reaction was the protodesilylated complex, as was evident from the appearance of a doublet in the ^{1}H NMR spectrum due to the α protons.

2,2′,5,5′-Tetrakis(trimethylsilyl)-3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene (8)

This compound has been synthesized before, but was only poorly characterized.[19] We found that treatment of anion **5** with anhydrous $FeCl_2$ in THF at low temperature provides ready access to complex **8**, which was completely characterized by NMR and mass spectroscopy, elemental analysis and X-ray diffraction. An ORTEP view of the molecular structure is given in Figure 4 and selected geometrical data are given in Table 3. The compound crystallizes in the orthorhombic space group *Pnna* with the Fe atom sitting on a crystallographic twofold axis (Z = 4). Bond lengths and angles are within the range of values usually observed for 1,1′-diphosphaferrocenes in general and compare well in particular with the closely related molecules [{2,5-($SiMe_2CCMe$)$_2$-3,4-Me_2-C_4P}$_2$Fe] (**A**)[18] and [{2,5-Cy_2-C_4H_2P}$_2$Fe] (**B**).[27] Again, as observed for compound **6**, the deviation of the Fe–Ct–Si angles from 90° (95.0 and 97.6°) is more pronounced than that for the β-Me groups (91.1 and 91.5°), reflecting the increased steric bulk of the silyl groups. The most interesting feature of the structure is the conformation of the two phospholyl rings with a P–Ct–Ct′–P′ torsion angle of α = 85.4°, which means that the P atom of one ring is roughly eclipsing the α-C atom of the other (P/C_α-conformation). Several conformations are conceivable for 1,1′-diphosphaferrocenes:[29] the limiting high-symmetry conformations C_{2v} and C_{2h}, with the P atoms in a *syn* (α = 0°) or *anti* (α = 180°) arrangement, respectively, and two C_2-symmetric conformations in which the P atoms are superposed either with the α carbon (P/C_α, α = 90–100°) or with the β carbon of the other ring (P/C_β, α = 140–145°). Indeed, examples for all of these conformations have been observed in the solid state and the question of which conformation is preferred has been addressed on various levels of theory. Both extended Hückel[30] and Fenske–Hall[31] calculations indicated that the C_{2h}-symmetric conformation has the highest relative energy for the unsubstituted derivative, lying some 10 kcal/mol above a C_2-symmetric arrangement with $\alpha > 100°$. However, for substituted derivatives the substitution pattern may also influence the relative stability of conformers by the avoidance of sterically unfavourable interactions of the substituents. For example, for the 3,3′,4,4′-tetramethyl derivative the P/C_β conformation is found in the solid state in accordance with theory,[11] minimizing the steric interference of the Me groups. For 2,2′,5,5′-tetraphenyl-1,1′-diphosphaferrocene, however, an exceptional P,P-*syn* conformation is found (α = 0°), which is stabilized presumably by additional π–π interactions between the two pairs of parallel phenyl rings.[29] This contradicts nicely with the structure of the 2,2′,5,5′-tetracyclohexyl derivative, for which a P,P-*anti* arrangement has been identified.[27] However, this conformation seems to be the exception rather than the rule, because many other 1,1′-diphosphaferrocenes with sterically demanding groups in the 2,5 positions show the P/C_α conformation as observed for complex **8**. Examples include the alkynylsilyl derivative **A**,[18] the 2,5-*t*Bu_2-diphosphametallocenes with Sn and Pb,[32] the Sb analogue of **8**[17b] and the parent 1,1′,3,3′-

tetrakis(trimethylsilyl)ferrocene.[33] DFT calculations on a B3LYP level were performed for complex **8** and exhibited a P/C_α minimum energy conformation with a torsion angle of $\alpha \approx 86°$. The highest relative energy (11.6 kcal/mol) was identified for the C_{2v} symmetric conformation ($\alpha = 0°$).

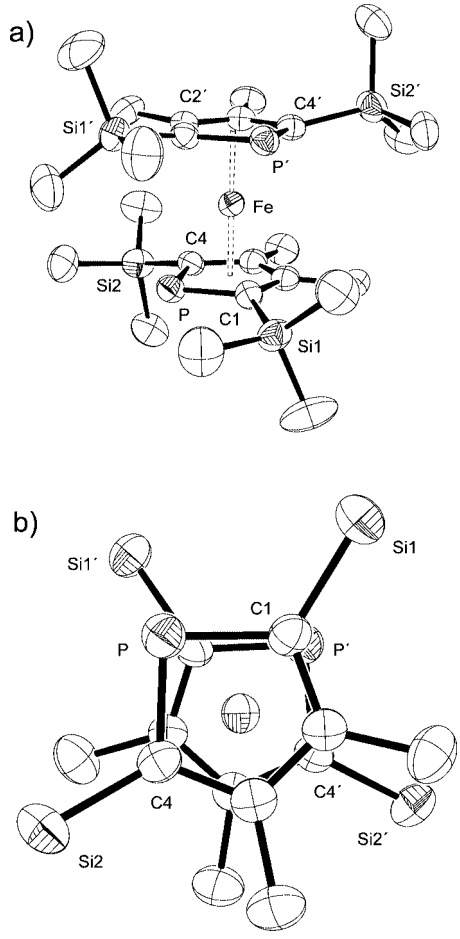


Figure 4. Two views of the molecular structure of complex **8**.

*Solution Dynamics of **8***

The proton NMR spectrum of **8** at room temperature shows two singlets corresponding to the methyl and to the TMS groups in a ratio 6:18. Obviously, ring rotation at ambient temperature is fast on the NMR time-scale. On cooling a sample in [D_8]toluene coalescence was observed (500 MHz) at ca. –5 °C for the $SiMe_3$ signals ($\Delta\nu = 125$ Hz) and at –20 °C for the β-Me signals ($\Delta\nu = 34$ Hz). At –50 °C the signals were clearly separated. The value of 12.6 ± 0.3 kcal/mol for the rotational barrier calculated from these data is in agreement with the value determined by Al-Taweel[19] and lies well within the range of 10–14 kcal/mol observed for other ferrocenes and diphosphaferrocenes with bulky substituents (Table 4) and fits nicely with the value obtained from the DFT calculations of 11.6 kcal/mol. No substantial differences between ferrocenes and diphosphaferrocenes are recognizable.

Table 4. Activation barriers ($\Delta G^{\ddagger}$) for ring rotation in 1,1′-diphosphaferrocenes and ferrocenes with bulky substituents.

Substituents	$\Delta G^{\ddagger}$ [kcal mol^{-1}]	Reference
1,1′-Diphosphaferrocenes		
2,2′,5,5′-$(TMS)_4$-3,3′,4,4′-Me_4	12.6	this work[a]
	12.5	[19][a]
	11.6	this work[b]
None	8.8	[30][d]
2,2′,5,5′-Ph_4	< 6.5	[29][c]
2,2′,5,5′-[(–)-menthyl]$_4$	12.9	[44][a]
Ferrocenes		
1,1′3,3′-$(TMS)_4$	11.0	[33][a]
1,1′,2,2′,4,4′-$(TMS)_6$	11.0	[45][a]
1,1′,2,2′,3,3′,4,4′-(*i*Pr)$_8$	13.7	[46][a]
1,1′,2,2′-$(TMS)_4$-4,4′-(*t*Bu)$_2$	9.8	[47][a]

[a] Low-temperature NMR spectroscopy. [b] DFT calculation. [c] Calculated value. [d] EHT calculation.

Treatment of **8** with DMSO/KOtBu[34] in order to examine the reactivity of the complex towards desilylation resulted in decomposition of the starting material and no product could be isolated.

Experimental Section

DFT Calculations: In order to determine the rotational barrier B3LYP[35] single point energies with Ahlrichs TZVP basis set[36] on top of BP86[37] geometries, optimized with a SVP basis set[38] have been carried out, as implemented in the program package Turbomole.[39] For the BP86 calculations the resolution of the identity (RI) approach has been used to fit the density within the Coulomb potential with an auxiliary basis set.[40] The phosphaferrocene backbone has been kept frozen at different torsional orientations of the two rings whereas the remainder of the molecule has been relaxed to its equilibrium geometry. The minimum structure has been characterized by calculating the Hessian matrix.

Reactions were carried out under an atmosphere of dry nitrogen by means of conventional Schlenk techniques. Solvents were dried and purified by standard methods. Alumina was heated at 220 °C for 12 h, cooled to room temp. under high vacuum, deactivated with 5% water and stored under nitrogen. NMR spectra were recorded with a Bruker Avance DRX 500 (^{1}H NMR, 500 MHz; ^{31}P{^{1}H} NMR, 202 MHz; ^{13}C{^{1}H} NMR, 126 MHz) and a Bruker Avance DRX 200 spectrometer (^{1}H NMR, 200 MHz; ^{31}P{^{1}H} NMR, 81 MHz). ^{1}H NMR spectra are referenced to the residual solvent signal and ^{31}P NMR spectra to external H_3PO_4 (85%). Mass spectra were recorded with a Varian MAT 311A spectrometer (EI, 70 eV electron energy). 2,5-Bis(trimethylsilyl)-3,4-dimethyl-1,1-bis(cyclopentadienyl)zirconacyclopentadiene,[17] **4**,[18] [Cp*FeCl]$_n$,[2g] 2-Hydroxymethyl-3,4-dimethyl-1-phosphaferrocene[11] and [Cp*RuCl]$_4$[41] were prepared according to the literature.

Synthesis of 2: A suspension of NaH (60 wt.-% in mineral oil, 0.21 g, 5.25 mmol) in THF was added dropwise to a mixture of 2-hydroxymethyl-3,4-dimethyl-1-phosphaferrocene (1.01 g, 3.86 mmol) and methyliodide (2.4 mL, 38.6 mmol) in THF at –55 °C. The mixture was slowly warmed to room temp. while stirring overnight and was subsequently heated to reflux for 30 min. After cooling to room temp. water (10 mL) was added and the product was extracted with dichloromethane. The organic phase was dried with Na_2SO_4, filtered and the solvent was removed under high vacuum. Column chromatography on alumina (hexane/ether, 5:1) gave pure

2 as an orange oil (1.003 g, 95%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.215, 2.222 (s, 6 H, 3,4-CH_3), 3.35 (s, 3 H, O-CH_3), 3.78 (d, $^2J_{CP}$ = 35.89 Hz, 1 H, α-H), 4.12 (s, 5 H, Cp), 3.86–4.24 (m, 2 H, CH_2) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 13.48 and 16.86 (s, 3,4-CH_3), 57.78 (s, OCH_3), 71.02 (d, $^2J_{CP}$ = 21.80 Hz, CH_2), 71.85 (s, Cp), 76.92 (d, $^1J_{CP}$ = 58.13 Hz, α-CH), 92.69 (d, $^1J_{CP}$ = 55.71 Hz, α-C), 94.20 (d, $^2J_{CP}$ = 4.84 Hz, β-C), 96.75 (d, $^2J_{CP}$ = 7.26 Hz, β-C) ppm. ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ = –73.24 (s) ppm. $C_{13}H_{17}FePO$ (276.10), EI-MS: *m*/*z* = 276 (M^+), 246 (M^+ – 2 CH_3), 231 (M^+ – CH_2OMe). Calcd. C 56.55, H 6.21; found C 56.57, H 6.30.

Synthesis of 3: Triethylamine (328 μL, 2.36 mmol) was added to a solution of 2-hydroxymethyl-3,4-dimethyl-1-phosphaferrocene (620 mg, 2.36 mmol) in THF (20 mL) at room temp. Dichlorodimethylsilane (143 μL, 1.18 mmol) was added slowly via syringe and the mixture was refluxed for 3 h. After cooling to room temp. water was added and the product extracted with diethyl ether and dried with Na_2SO_4. Filtration and removal of the solvent under high vacuum gave the *rac*/*meso* mixture of **3** in a 2:1 ratio as an analytically pure orange oil (411 mg, 0,71 mmol, 60%). Cooling an ether solution gave the pure *rac* isomer as orange crystals suitable for X-ray diffraction. ^{1}H NMR (200 MHz, $CDCl_3$); *rac*/*meso* mixture: δ = 0.115 (s, 3 H, $SiCH_3$), 0.122 (s, 3 H, $SiCH_3$), 2.173, 2.183, 2.193, 2.205 (4s, 12 H, CCH_3), 3.75 (d(br), $^1J_{HP}$ = 35.89 Hz, 2 H, α-H), 4.114, 4.121 (2s, 10 H, Cp), 4.155–4.365 (m, 4 H, CH_2-O) ppm; *rac* isomer: δ = 0.121 (s, 6 H, $SiCH_3$), 2.173 (s, 6 H, CCH_3), 2.184 (s, 6 H, CCH_3), 3.75 (d, 2 H, α-H, $^2J_{HP}$ = 35.89 Hz), 4.120 (s, 10 H, Cp), 4.26 (m, 4 H, CH_2-O) ppm. ^{13}C NMR (125 MHz, $CDCl_3$); *rac*/*meso* mixture: δ = –2.53 (br. s, $SiCH_3$), –0.597 (br. s, $SiCH_3$), 13.54 (s, CH_3), 16.92 (s, CH_3), 61.18 (d, $^2J_{CP}$ = 24.2 Hz, CH_2), 71.81 (s, Cp), 71.83 (s, Cp), 76.70 (d, $^1J_{CP}$ = 58.1 Hz, α-CH), 76.58 (d, $^1J_{CP}$ = 58.1 Hz, α-CH) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 81 MHz): δ = –74.18 (*rac*); –74.34 (*meso*) ppm. EI-MS (80 eV, 150 °C), *m*/*z* = 580 (M^+), 515 (M^+ – Cp), 262 (PFc – CH_2O^+), 245 ($PFcCH_2^+$), 179 ($PFcCH_2^+$-Cp), 124 (179 – Fe). $C_{26}H_{34}Fe_2O_2P_2Si$ (580.28): calcd. C 53.82, H 5.91; found C 53.00, H 5.83. The too small value for C is probably due to the formation of some SiC, which is rather frequently encountered.

Synthesis of [(*rac*-3)·Mo(CO)$_4$]: A solution of [(nbd)Mo(CO)$_4$] (65 mg, 0.217 mmol) in THF was added to a solution of *rac*-**3** (126 mg, 0.217 mmol) in THF, the mixture was stirred at room temp. for 30 min and subsequently refluxed for two hours. The solvent was removed under high vacuum and the residue was recrystallized from ether. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.06 (s, 6 H, $SiCH_3$), 2.20, 2.21 (s, 6 H, CH_3), 3.84 (d, 2 H, $^2J_{HP}$ = 32.12 Hz, α-H), 4.21 (s, 10 H, Cp), 4.19 (m, 4 H, CH_2) ppm. ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): –22,74 (s) ppm. IR ($CDCl_3$): 2029 (mst), 1935 (st), shoulders at 1920 and 1900 cm^{-1}. $C_{30}H_{34}Fe_2MoO_6P_2Si$ (788.20): calcd. C 45.71, H 4.35; found C 45.49, H 4.50.

Synthesis of 6: Freshly cut lithium pieces (excess) were added to a solution of bromophosphole (**4**) (400 mg, 1.19 mmol) in THF at room temp. After complete conversion of the phosphole to the phospholide anion (monitored by ^{31}P NMR, **5**: 141 ppm, ca. 3 h) the solution was transferred by cannula to a freshly prepared solution of $[Cp^*FeCl]_n$ at 0 °C and the mixture was stirred overnight at room temp. and refluxed for 1 h. Water was added and the product was extracted with diethyl ether. The organic phase was dried with Na_2SO_4, filtered and the solvent was removed under high vacuum. The crude product was purified by column chromatography over alumina (hexane). Recrystallization from methanol yielded bright red crystals (ca. 290 mg, 55%) contaminated with trace amounts of decamethylferrocene. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.20 (d, $^4J_{HP}$ = 0.75 Hz, 18 H, $SiMe_3$), 1.81 (s, 15 H, Cp*), 2.03 (s, 6 H, CH_3) ppm. ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ = –8.18 ppm (s). $C_{22}H_{39}FePSi_2$ (446): calcd. C 59.17, H 8.80; found C 58.99, H 8.88. EI-MS: *m*/*z* = 446 (M^+), 374 (M^+ – TMS + H), 326 (374 – $SiMe_2$).

Synthesis of 7: A solution of phospholide (**5**) was prepared as described above from bromophosphole (**4**) (111 mg, 0.33 mmol). $[Cp^*RuCl]_4$ (90 mg, 0.083 mmol) was suspended in THF and added to the phospholide solution at –78 °C. The reaction mixture turned from red to brown and was warmed to room temp. while stirring overnight. The solvent was removed under high vacuum and the crude product was purified by column chromatography over alumina (hexane/ether = 5:1). Compound **7** (120 mg, 36%) was obtained as a brown powder after the removal of the solvent in vacuo. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.20 (d, $^4J_{HP}$ = 0.75 Hz, 18 H, $SiMe_3$), 1.87, (s, 15 H, Cp*), 1.93 (s, 6 H, 3,4-CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 1.6 (d, $^3J_{CP}$ = 5.5 Hz, $SiMe_3$), 11.6 (s, Cp*-CH_3), 13.8 (d, $^3J_{CP}$ = 1.8 Hz, 3,4-CH_3), 87.4 (s, Cp*-C), 88.6 (d, $^1J_{CP}$ = 79.7 Hz, α-C), 100.1 (d, $^2J_{CP}$ = 4.6 Hz, β-C) ppm. ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ = 0.95 (s) ppm. EI-MS ($C_{22}H_{39}PRuSi_2$, 491.77): *m*/*z* = 492 (M^+), 477 (M^+ – CH_3), 419 (M^+ – $SiMe_3$). Calcd. C 53.73, H 7.99; found C 54.01, H 8.15.

Synthesis of 8: A solution of phospholide (**5**) was prepared as described above from bromophosphole (**4**) (0.51 g, 1.52 mmol). Anhydrous $FeCl_2$ (0.096 g, 0,76 mmol) was added to the phospholide solution at –78 °C. The solution was stirred overnight and warmed to room temp. The solvent was removed under high vacuum and the crude product purified by chromatography over alumina (hexane). Recrystallization from methanol yielded **8** (0.150 g, 35%) as red crystals suitable for X-ray diffraction. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.27 (s, 36 H, $SiMe_3$), 2.08 (s, 12 H, 3,4-CH_3) ppm. ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ = –26.13 (s) ppm. ^{13}C NMR (126 MHz, 298 K, $CDCl_3$): δ = 1.80, 1.82, 1.84, 1.86 (s, $SiMe_3$), 16.5 (br. s, 3,4-CH_3), 103.8 (d, $^2J_{CP}$ = 4.6 Hz, β-C) ppm. EI-MS ($C_{24}H_{48}FeP_2Si_4$, 566.78): *m*/*z* = 566 (M^+), 494 (M^+ – H – $SiMe_3$) 405 (M^+ – H – $SiMe_3$ – CH_3). Calcd. C 50.86, H 8.54; found C 51.02, H 8.50.

X-ray Crystallographic Study: Crystals of compounds **3**, **3**·Mo(CO)$_4$, **6** and **8** suitable for X-ray studies were investigated with a Stoe IPDS using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 291 K. In the cases of **3**·Mo(CO)$_4$ and **6** a space group type of $P2_1/n$ and in the case of **8** the space group *Pnna* were uniquely determined. In the case of **3** the symmetry of the diffraction pattern was compatible with space group types $P1$ and $P\bar{1}$. The latter proved to be the correct one after structure refinement. Lorentz polarization corrections were applied to all the intensity data. In the case of **3**·Mo(CO)$_4$ and **8** absorption corrections using symmetry equivalent reflections and a face-indexed Gaussian integration procedure, respectively, were applied. The structures were solved by direct methods[42] and the positions of all but the H atoms of the pentamethylcyclopentadienyl group of **6** were found via ΔF syntheses. Refinements[43] by full-matrix least-squares calculations on F^2 converged to the indicators given in Table 5. Anisotropic displacement parameters were refined for all atoms heavier than hydrogen. Idealized bond lengths and angles were used for the CH_3, CH_2 and CH groups; the riding model was applied for their H atoms. In addition, the H atoms of the CH_3 groups were allowed to rotate around the neighbouring C–C bonds. The isotropic displacement parameters of the H atoms were kept equal to 120% of the equivalent isotropic displacement parameters of the parent "aromatic" or secondary carbon atom and equal to 150% of the parent primary carbon atom, respectively. A summary of

Table 5. Crystallographic data for compounds **3**, **3·Mo(CO)$_4$**, **6** and **8**.

Compound	**3**	**3·Mo(CO)$_4$**	**6**	**8**
Formula	$C_{26}H_{34}Fe_2O_2P_2Si$	$C_{30}H_{34}Fe_2MoO_6P_2Si$	$C_{22}H_{39}FePSi_2$	$C_{24}H_{48}FeP_2Si_4$
M_r [g mol^{-1}]	580.26	788.24	446.53	566.77
Crystal system	triclinic	monoclinic	monoclinic	orthorhombic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$Pnna$
a [Å]	11.1473(8)	10.9670(16)	9.7586(6)	19.0769(19)
b [Å]	13.9223(10)	17.7718(14)	13.2369(9)	16.6026(11)
c [Å]	17.4988(12)	17.7603(19)	19.9071(13)	10.2037(6)
α [°]	92.111(8)	90	90	90
β [°]	100.862(8)	94.514(18)	93.781(8)	90
γ [°]	90.298(9)	90	90	90
V [Å]^3	2665.1(3)	3450.8(7)	2565.9(3)	3231.8(4)
Z	4	4	4	4
D_c [g cm^{-3}]	1.446	1.517	1.156	1.165
F(000)	1208	1600	960	1216
μ(Mo-K_α) [mm^{-1}]	1.275	1.353	0.748	0.725
$2\theta_{max}$ [°]	50.00	50.00	50.00	50.00
Total reflections	35124	26649	32998	2844
Independent reflections	8846	5984	4516	2844
Observed reflections [$I > 2\sigma(I)$]	5768	3189	3285	906
Parameters refined	607	385	248	149
R_1/wR_2 [$I > 2\sigma(I)$]	0.0337, 0.0764	0.0367, 0.0731	0.0453, 0.1129	0.0336, 0.0456
R_1/wR_2 (all data)	0.0512, 0.0780	0.0709, 0.0759	0.0584, 0.1156	0.0824, 0.0484

further crystallographic data, data collection parameters and refinement parameters is collected in Table 5.

CCDC-622213 (for **3**), -622214 [for **3·Mo(CO)$_4$**], -622216 (for **6**) and -622215 (for **8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

Financial support of this work by the Deutsche Forschungsgemeinschaft (DFG) (GA 597/1) is gratefully acknowledged. We gratefully acknowledge computer time granted by the HRZ Philipps-Universität Marburg and the CSC Frankfurt. We thank M. Schilling and E. Hammes for assistance with the X-ray structure determinations.

[1] For comprehensive reviews see for example: a) F. Mathey, *Coord. Chem. Rev.* **1994**, *137*, 1; b) F. Mathey, *Top. Curr. Chem.* **2002**, *220*, 27; c) P. Le Floch, *Coord. Chem. Rev.* **2006**, *250*, 627.

[2] a) C. Ganter, L. Brassat, C. Glinsböckel, B. Ganter, *Organometallics* **1997**, *16*, 2862; b) C. Ganter, *Chem. Soc. Rev.* **2003**, *32*, 130; c) C. Ganter, *J. Chem. Soc., Dalton Trans.* **2001**, 3541; d) J. Bitta, S. Fassbender, G. Reiss, W. Frank, C. Ganter, *Organometallics* **2005**, *24*, 5176; e) R. Shintani, G. C. Fu, *J. Am. Chem. Soc.* **2003**, *125*, 10778; f) R. Shintani, G. C. Fu, *Angew. Chem.* **2003**, *115*, 4216; g) R. Shintani, G. C. Fu, *Org. Lett.* **2002**, *4*, 3699.

[3] a) S. Holand, M. Jeanjean, F. Mathey, *Angew. Chem.* **1997**, *109*, 117; b) P. Toullec, F. Mathey, *Synlett* **2001**, 1977; c) M. Melaimi, L. Ricard, F. Mathey, P. Le Floch, *Org. Lett.* **2002**, *4*, 1245.

[4] a) J.-M. Lehn, *Angew. Chem.* **1988**, *100*, 91; b) C. J. Pedersen, *Angew. Chem.* **1988**, *100*, 1053; c) D. J. Cram, *Angew. Chem.* **1988**, *100*, 1041; d) R. Cooper (Ed.), *Crown Compounds: Toward Future Application*, Wiley Interscience: New York, **1992**; e) J. S. Bradshaw, R. M. Izatt, *Acc. Chem. Res.* **1997**, *30*, 338; f) J.-M. Lehn, *Acc. Chem. Res.* **1978**, *11*, 49; g) N. S. Pooma, A. V. Baja, *Chem. Rev.* **1979**, *79*, 389.

[5] L. Horner, P. Walach, H. Kunz, *Phosphorus* **1975**, *6*, 63.

[6] a) For a review see: A.-M. Caminade, J. P. Majoral, *Chem. Rev.* **1994**, *94*, 1183; b) S. Ekici, M. Nieger, R. Glaum, E. Niecke, *Angew. Chem.* **2003**, *115*, 451; c) P. G. Edwards, R. Haigh, D. Li, V. Newman, *J. Am. Chem. Soc.* **2006**, *128*, 3818.

[7] F. Mathey, P. Le Floch, *Chem. Ber.* **1996**, *129*, 263.

[8] a) N. Avarvari, N. Mézailles, L. Ricard, F. Mathey, *Science* **1998**, *280*, 1587; b) N. Avarvari, N. Maigrot, L. Ricard, F. Mathey, P. Le Floch, *Chem. Eur. J.* **1999**, *5*, 2109.

[9] N. Mézailles, N. Avarvari, N. Maigrot, L. Ricard, F. Mathey, P. Le Floch, L. Cataldo, T. Berclaz, M. Geoffrey, *Angew. Chem.* **1999**, *111*, 3390.

[10] a) B. Dechamps, J. Fischer, F. Mathey, A. Mitschler, *Inorg. Chem.* **1981**, *20*, 3252; b) B. Dechamps, J. Fischer, F. Mathey, A. Mitschler, L. Ricard, *Organometallics* **1982**, *1*, 312.

[11] G. de Lauzon, B. Deschamps, J. Fischer, F. Mathey, A. Mitschler, *J. Am. Chem. Soc.* **1980**, *102*, 994.

[12] F. Mathey, A. Mitschler, R. Weiss, *J. Am. Chem. Soc.* **1977**, *99*, 3537.

[13] G. de Lauzon, B. Deschamps, F. Mathey, *Nouv. J. Chim.* **1980**, *4*, 683.

[14] S. O. Agustsson, C. Hu, U. Englert, T. Marx, L. Wesemann, C. Ganter, *Organometallics* **2002**, *21*, 2993.

[15] C. Ganter, C. Kaulen, U. Englert, *Organometallics* **1999**, *18*, 5444.

[16] a) ref.[14]; b) ref.[15]; c) C. Ganter, L. Brassat, B. Ganter, *Chem. Ber./Recueil* **1997**, *130*, 1771; d) T. G. Hill, C. Haltiwanger, T. R. Prout, A. D. Norman, *Inorg. Chem.* **1989**, *28*, 3461; e) E. H. Wong, F. C. Bradley, E. J. Gabe, *J. Organomet. Chem.* **1983**, *244*, 235; f) M. S. Balakrishna, T. K. Prakasha, S. S. Krishnamurthy, U. Siriwardane, N. S. Hosmane, *J. Organomet. Chem.* **1990**, *390*, 203.

[17] a) M. Westerhausen, M. H. Digeser, C. Gückel, H. Nöth, J. Knizek, W. Ponikwar, *Organometallics* **1999**, *18*, 2491; b) A. J. Ashe III, J. W. Kampf, S. M. Al-Taweel, *Organometallics* **1992**, *11*, 1491; c) A. J. Ashe III, J. W. Kampf, S. M. Al-Taweel, *J. Am. Chem. Soc.* **1992**, *114*, 372.

[18] X. Sava, N. Mézailles, N. Maigrot, F. Nief, L. Ricard, F. Mathey, P. Le Floch, *Organometallics* **1999**, *18*, 4205.

[19] S. M. Al-Taweel, *Phosphorus, Sulphur Silicon Relat. Elem.* **1997**, *130*, 203.

[20] C. Burney, D. Carmichael, K. Forissier, J. C. Green, F. Mathey, L. Ricard, *Chem. Eur. J.* **2005**, *11*, 5381.

[21] D. Carmichael, L. Ricard, F. Mathey, *J. Chem. Soc., Chem. Commun.* **1994**, 1167.
[22] a) For cross-coupling reactions with aryl-X see: E. Hagiwara, K. Gouda, Y. Hatanaka, T. Hiyama, *Tetrahedron Lett.* **1997**, *38*, 439; b) for silyl-halogen exchange see: B. Bennetau, J. Dunogues, *Synlett* **1993**, 171; c) T. H. Chan, I. Fleming, *Synthesis* **1979**, 761.
[23] D. Carmichael, F. Mathey, L. Ricard, N. Seeboth, *Chem. Commun.* **2002**, 2976.
[24] For the preparation by treatment of the 3,4-dimethylphospholide anion with electrophiles see ref.[3a,3b]; For preparations by CO_2 insertion into the C–Si bonds of phospholide **5** see ref.[3c].
[25] a) G. E. Herberich, B. Ganter, *Organometallics* **1997**, *16*, 522; b) G. E. Herberich, B. Ganter, U. Englert, *Struct. Chem.* **1998**, *9*, 359.
[26] D. Carmichael, L. Ricard, N. Seeboth, J. M. Brown, T. D. W. Claridge, B. Odell, *Dalton Trans.* **2005**, 2173.
[27] M. Ogasawara, T. Nagano, K. Yoshida, T. Hayashi, *Organometallics* **2002**, *21*, 3062.
[28] D. Carmichael, J. Klankermeyer, L. Ricard, N. Seeboth, *Chem. Commun.* **2004**, 1144.
[29] P. B. Hichcock, G. A. Lawless, I. Marziano, *J. Organomet. Chem.* **1997**, *527*, 305.
[30] G. Guimon, D. Gonbeau, G. Pfister-Guillouzo, G. de Lauzon, F. Mathey, *Chem. Phys. Lett.* **1984**, *104*, 560.
[31] N. M. Kostic, R. F. Fenske, *Organometallics* **1983**, *3*, 1008.
[32] K. Forissier, L. Ricard, D. Carmichael, F. Mathey, *Chem. Commun.* **1999**, 1273.
[33] J. Okuda, E. Herdtweck, *J. Organomet. Chem.* **1989**, *373*, 99.
[34] C. Ganter, T. Wagner, *Chem. Ber.* **1995**, *128*, 1157.
[35] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 1372; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785; c) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623.
[36] A. Schäfer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829.
[37] a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098; b) J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822; c) J. P. Perdew, *Phys. Rev. B* **1986**, *34*, 7406.
[38] A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2571.
[39] a) R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, *162*, 165; b) O. Treutler, R. Ahlrichs, *J. Chem. Phys.* **1995**, *102*, 346.
[40] a) K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *240*, 283; b) K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *242*, 652; c) K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, *Theor. Chem. Acc.* **1997**, *97*, 119.
[41] P. J. Fagan, M. D. Ward, J. C. Calabrese, *J. Am. Chem. Soc.* **1989**, *111*, 1698.
[42] G. M. Sheldrick, *SHELXS86. Program for the Solution of Crystal Structures*, University of Göttingen, Germany, **1985**.
[43] G. M. Sheldrick, *SHELXL97. Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.
[44] M. Ogasawara, K. Yoshida, T. Hayashi, *Organometallics* **2003**, *22*, 1783.
[45] J. Okuda, E. Herdtweck, *Chem. Ber.* **1988**, *121*, 1899.
[46] H. Sitzmann, *J. Organomet. Chem.* **1988**, *354*, 203.
[47] J. Okuda, *Chem. Ber.* **1989**, *122*, 1075.

Received: September 28, 2006
Published Online: December 19, 2006

