Synthesis of 1,1′-Ferrocenylene-Bridged Bisdiphosphenes

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A simple synthetic access to the first ferrocenylene-bridged bisdiphosphenes $Fe(C_5H_4-P=P-R)_2$ is reported. The unsaturated P=P units require steric protection by adjacent substituents such as Dmp (2,6-dimesitylphenyl) and Tbt (2,4,6-tris[bis(trimethylsilyl)methyl]phenyl) and should be capable of conjugative interaction with the central metallocene unit. The electronic situation in these molecules has been assessed on the basis of DFT calculations. As a derivative of the Tbt-substituted bisdiphosphene with $Tbt-PH_2$, the resulting ferrocenylene-bridged bis-1,3-dihydrotriphosphane has been characterized by X-ray crystallography

Introduction

Compounds containing phosphorus in low coordination numbers have fascinated chemists for several decades.[1−5] Initially the interest in these compounds was mainly focused on the unusual bond situation present in these molecules.[6] More recently, the incorporation of unsaturated phosphane units such as P=C and P=P connected by phenylene and arylene groups into oligomers and polymers attracted considerable attention as new types of electronic materials.[7−10] Such materials can support electronic communication across extended π-conjugated systems, and a recent review describes the first applications of phosphorus-based materials in optoelectronics (nonlinear optics, organic light-emitting diodes, etc.).[11,12]

Extending this concept by incorporation of low-coordinated phosphorus centers into metallocene-based polymers should provide unique electronic properties and, moreover, the redox activity of the metal centers should allow some control of the electronic and magnetic properties in this type of compounds.[13,14]

However, the knowledge of compounds containing unsaturated phosphane units adjacent to metallocenes is very limited to date. We prepared the first examples of ferrocenyl-substituted diphosphenes, iminophosphanes, and phosphaalkenes.[15−17] In our initial study we employed the Mes* substituent (Mes* = 2,4,6-tri-*tert*-butylphenyl) to protect the reactive P=P unit in **1**.[15] This concept was later extended by the work of Tokitoh et al. employing the more bulky Tbt (Tbt = 2,4,6-tris[bis-(trimethylsilyl)methyl]phenyl) substituent (**2**).[18,19] All these compounds show substantial conjugative interaction of the unsaturated P=E moiety with the ferrocenyl group. Nevertheless the so far reported examples carry only one P=E unit at the metallocene. For diphosphenes, the preparation of molecules containing two or more P=P units has been accomplished with strictly organic linking groups.[8,20] In this contribution we report on the preparation of ferrocenes carrying a diphosphene unit on each of the ferrocene cyclopentadienyl rings (**3**). These compounds are the first 1,1′-ferrocenylene-bridged bisdiphosphenes[21,22] and should open the way to the preparation of more extended analogues.

Results and Discussion

To generate 1,1′-ferrocenylene-bridged bisdiphosphenes, we reacted 1,1′-ferrocenylene bisdihalophosphanes[23,24] with the bulky substituted lithium phosphanides Dmp-PHLi (Dmp = 2,6-dimesitylphenyl)[25] and Tbt-PHLi[26] in ether solution. Subsequent

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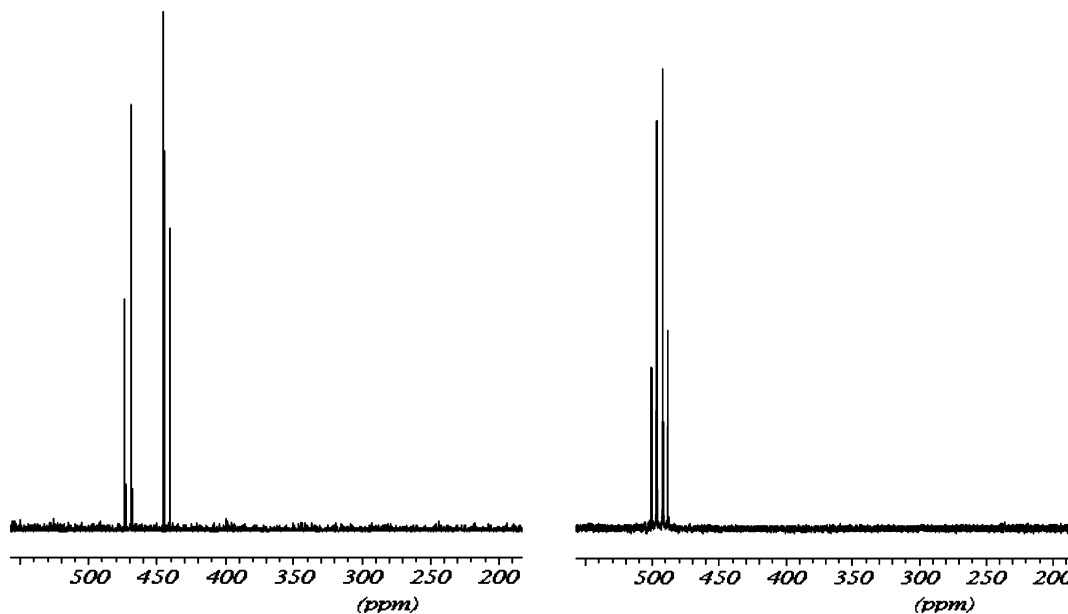
**Figure 1.** ^{31}P NMR spectra of **3a** (left) and **3b** (right).

Table 1. Comparison of the [31]P Data of Diphosphenes Adjacent to Ferrocene (Fc = ferrocenyl; Fc′ = 1,1′-ferrocenylene)

	P_A [ppm]	P_B [ppm]	$^1J_{PP}$ [Hz]	λ_{max} $(n(Fe)-\pi^*)$ [nm]	λ $(\pi-\pi^*)$ [nm]	ref
Fc−P=P−Mes*	471.2	442.6	532	515	357	15
Fc−P=P−Tbt	501.7	479.5	546	542	371	18
Fc′(−P=P−Dmp)$_2$	470.3	444.9	537	542	351	this work
Fc′(−P=P−Tbt)$_2$	500.0	492.5	555	545	380	this work

Scheme 1. First Ferrocenyl Diphosphenes 1[15] and 2[18] and Ferrocenylene Bisdiphosphenes 3a,b
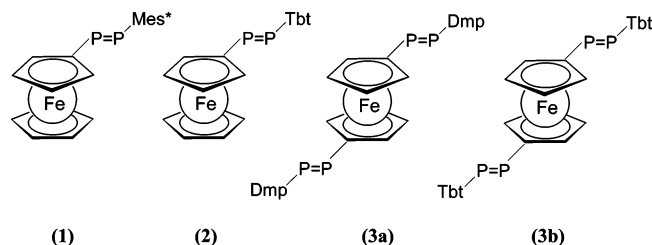
Scheme 2. Synthesis of Ferrocenylene Bisdiphosphenes 3a (R = Dmp) and 3b (R = Tbt)
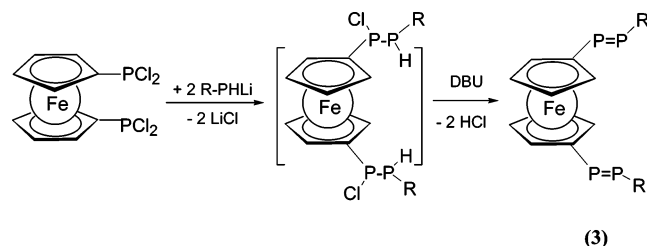
dehydrohalogenation with DBU furnished dark red solutions of the envisaged diphosphenes **3a** (R = Dmp) and **3b** (R = Tbt) (Scheme 2). The presence of the P=P unit in **3a,b** is evident from their ^{31}P NMR spectra, which show a AB spin system at characteristically high chemical shift values with $^1J_{PP}$ coupling constants of 537 Hz (**3a**) and 555 Hz (**3b**) typical for diphosphenes (Figure 1). The values observed for ferrocenylene compounds **3a,b** are quite close to those of the corresponding ferrocenyl analogues reported before (Table 1). As in other π-donor-substituted diphosphenes, the ^{31}P NMR shifts of these compounds appear at rather high field along with rather small

$^1J_{PP}$ coupling constants for diphosphenes, indicating conjugative interaction of the P=P units with the ferrocene core. [27] The comparison of Fc−P=P−Tbt and Fc′(−P=P−Tbt)$_2$ (Fc = ferrocenyl, Fc′ = 1,1′-ferrocenylene) reveals that the attachment of a second identical diphosphene unit has a moderately deshielding effect on the phosphorus atom showing a ^{31}P resonance at higher field. This indicates a slightly reduced π-donation of the ferrocene system into the P=P units of Fc′-(−P=P−Tbt)$_2$ compared to Fc−P=P−Tbt.

For both diphosphenes **3a,b** the λ_{max} absorptions in the UV/vis region at 542 nm (**3a**) and 545 nm (**3b**) indicate electronic interaction of the P=P unit with the ferrocene system. On the basis of quantum chemical calculations these absorptions have been assigned to a metal-to-ligand charge transfer (MLCT) due to the electronic transition from iron-centered d-orbitals to the π^*-orbital of the P=P moiety. [18] As in related diphosphenes, the $\pi-\pi^*$ transition is observed at lower wavelength. For **3a** the corresponding absorption band is observed at 371 nm and for **3b** at 380 nm. The characteristic spectroscopic data of the ferrocenylene bisdiphosphenes correspond well with those of ferrocenyl diphosphenes and are summarized in Table 1.

Both ferrocenylene diphosphenes **3a,b** are very sensitive to air and moisture, but remain unchanged under inert conditions in solution as well as in the solid state. However, the Dmp-substituted diphosphene **3a** is significantly more sensitive toward air than the Tbt-substituted **3b**. The protection provided by the Tbt substituent seems to be significantly more efficient than in the case of Dmp. Preliminary experiments exploring the reactivity of **3a,b** show that addition of water leads to Dmp-PH$_2$ and Tbt-PH$_2$, respectively along with 1,1-ferrocenebisphosphinic acid (and 1,1-ferrocenebisphosphonic acid in the

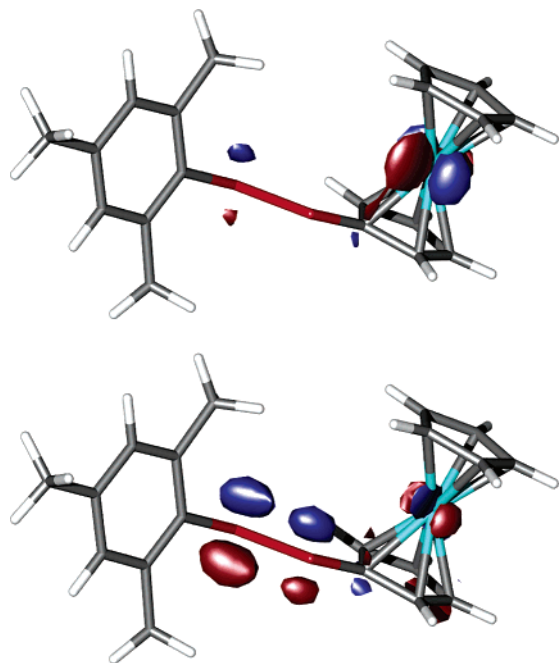(27) Weber, L. *Chem. Rev.* **1992**, *92*, 1839−1906.

Figure 2. Contour plots of the HOMO (top) and the HOMO−3 (bottom) of **4**.

presence of oxygen).[28,29] These findings can be rationalized assuming a polarized P=P double bond in which the π-donor properties of the ferrocene unit, which have been found to be comparable with that of an amino group, increase π-electron density on the phosphorus atom adjacent to the bulky ligand. Such a description is in good agreement with results from ab initio calculations on the simplified model systems Fc−P=P−Mes (**4**) and Fc′(−P=P−Mes)$_2$ (**5**). On the DFT (B3LYP) level employing a LAN2DZ basis set, the HOMO of **4** is mainly an iron d-orbital showing little interaction with the P=P bond. The π(P=P)-orbital (HOMO−3) is clearly polarized with the π-electron density shifted away from the ferrocene system (Figure 2). Attachment of a second diphosphenyl group as in **5** leads to a similar situation, where in addition to a conjugation of the cyclopentadienyl rings with the −P=P− units also direct interaction of Fe d-electrons with the diphosphene units occurs (Figure 3). The LUMO in **4** and **5** is a π^*-orbital located at the P=P unit, which in the case of **5** is significantly augmented with d-states at the Fe center (Figure 4).

A comparison of the calculated NBO charges (Table 2) shows that the net polarization of the P=P-π-system is only small (0.1 electron). Also the electron-donating capacity of the ferrocenyl system is not significantly lowered by interacting with one P=P system. Thus, interaction with a second P=P unit raises the positive charge on Fe only marginally and shows even less effect on the Cp carbon atoms (Table 2). This as well as the net positive charge of the P atoms indicates that the P=P units in **4** and **5** act as an acceptor on the π-level, but as a donor on the σ-level toward the ferrocene system. Therefore, the electron-releasing capacity of the ferrocene system is not exhausted by a single diphosphene unit, and on attachment of a second such unit the characteristic polarization of the P=P π-system is retained.

On treatment with Tbt-PH$_2$, bisdiphosphene **3b** reacts under formation of bistriphosphane **6**. This reaction is reversible, and
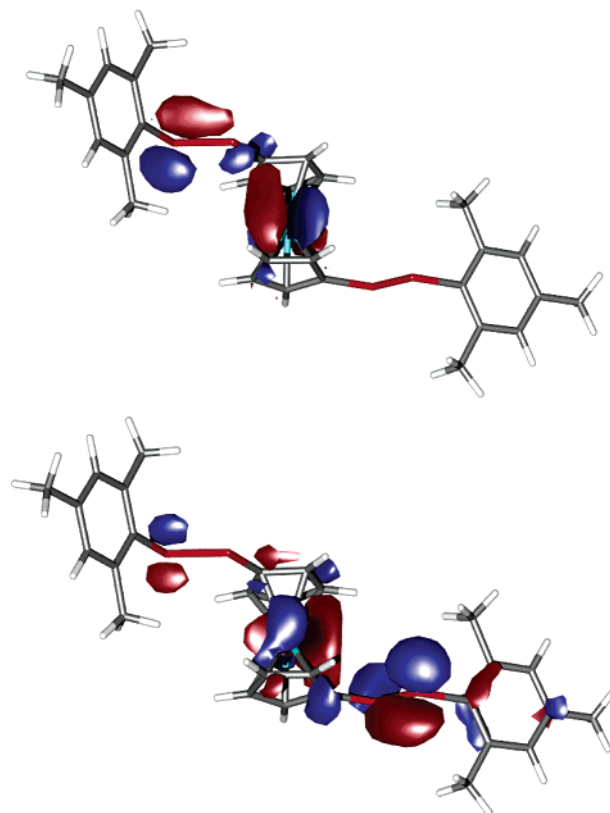
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Figure 3. Contour plots of the HOMO (top) and the HOMO−1 (bottom) of **5**.

Scheme 3. Formation of 6

(3b)   (6)
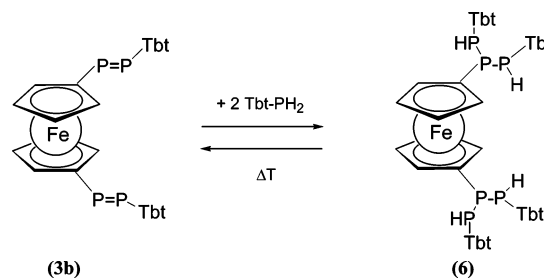
Table 2. Comparison of the NBO Charges Calculated for Fc−P=P−Mes (4) and Fc′(−P=P-Mes)$_2$ (5) (B3LYP/LANL2DZ)

	Fc−P=P−Mes (**4**)		Fc′(−P=P−Mes)$_2$ (**5**)		
Cp−*P*=P−R	+0.209	$\Delta q = 0.109$	+0.206	+0.218	$\Delta q = 0.095$
Cp−P=*P*−R	+0.318	$\Delta q = 0.109$	+0.324	+0.313	$\Delta q = 0.095$
C$_\alpha$	−0.428		−0.422	−0.423	
Fe	+0.242			+0.257	
C$_{ipso}$	−0.341		−0.340	−0.341	

heating of neat **6** to approximately 100 °C leads to elimination of Tbt-PH$_2$ and liberation of the initial bisdiphosphene **3b** (Scheme 3), in analogy with what has been observed for the related monodiphosphene. [19] Therefore, **6** can be considered as a less sensitive storage form of **3b** in the presence of Tbt-PH$_2$. In solution the resonances of the 16 possible stereoisomers of **6** are observed in a range between −18 and −85 ppm in the ^{31}P NMR spectra, which is close to what has been reported for the related compound with only one triphosphane unit at the metallocene. As in the latter case the NMR signals of the mixture of diastereomers are broadened due to hindered rotation at the Tbt moieties at room temperature. In contrast to the previously reported ferrocenyl 1,3-dihydrotriphosphane, heating of a toluene solution of **6** to 95 °C does not lead to coalescence
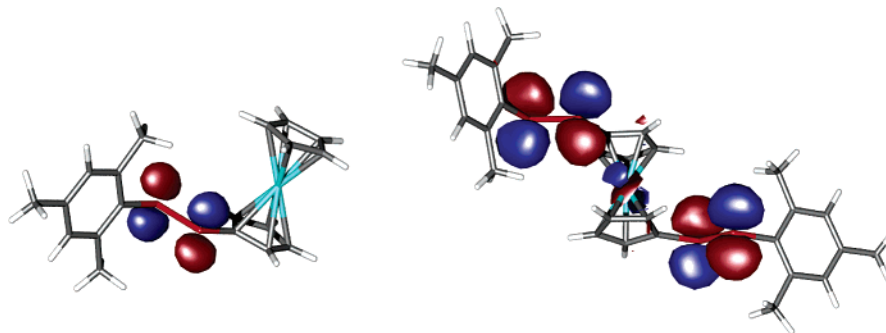
Figure 4. Contour plots of the LUMOs of **4** (left) and **5** (right).
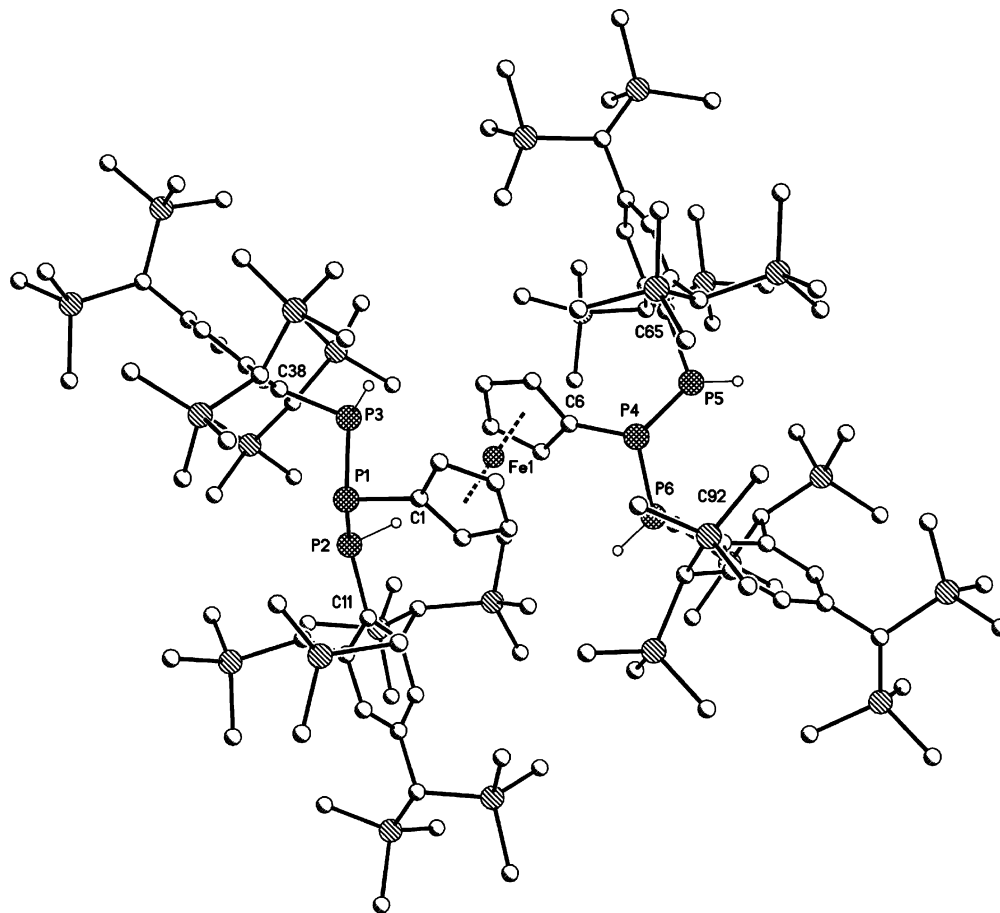

Figure 5. Molecular structure of **6** in the solid state. Hydrogen atom and solvent molecules are omitted for clarity.

of the signals in the ^{31}P NMR spectra. We have been able to determine the crystal structure of **6** (Table 3), and a drawing of the molecule and selected structural parameters are shown in Figure 5 and Table 4, respectively. Since the position of the phosphorus-bonded hydrogen atoms could be localized by electron density determination, the molecular structure of this particular single crystal could be assigned to the isomer of **6** with 2*S*,3*R*,5*R*,6*R* configuration at the phosphorus atoms (space group: $P2_12_12_1$ (No. 19), Flack parameter $x = -0.01(2)$). As expected all six phosphorus atoms show a pyramidal coordination environment. The phosphorus atoms adjacent to the ferrocenyl moiety show the strongest pyramidalization, with a sum of angles of 295° (P1) and 294° (P4). These values are close to the 293° found for the only other structurally character-ized 1,3-dihydrotriphosphane in the literature.[19] For the other phosphorus atoms in **6**, the sum of angles is somewhat higher

(302° (P5), 309° (P3), 311° (P6)), with the largest value found for P2 (313°), which is also the phosphorus atom with a configuration opposite of the other ones.

In summary, our results show that ferrocenylene-bridged bisdiphosphenes are synthetically accessible. On the basis of experimental spectroscopic results and ab initio calculations, it is evident that the low-lying π^*-states provided by the P=P unit interact with the ferrocene system in which the latter serves as electron donor. Interestingly, the capacity of this electron reservoir is reduced yet not exceeded on attachment of a second diphosphene unit, as spectroscopic data and ab initio calculations for ferrocenyl diphosphenes and ferrocenylene bisdiphosphenes suggest. In future work we will focus on preparing analogous ferrocenylene-bridged bis-P=C and bis-P=N derivatives in order to gain synthetic access to ferrocene-based oligomers and polymers with such units in the backbone.

Table 3. Crystal Data and Structure Refinement for 6

formula	$C_{118}H_{248}FeP_6Si_{24} \cdot C_6H_6$
fw	2661.1
temp, K	123
wavelength, Å	0.71073
cryst syst	orthorhombic
space group	$P2_12_12_1$ (No. 19)
unit cell dimens	
a, Å	19.6366(2)
b, Å	24.3191(3)
c, Å	34.6941(5)
α, deg	90
β, deg	90
γ, deg	90
volume, Å^3	16568.0(4)
Z	4
density (calcd), Mg/m^3	1.067
μ (mm^{-1})	0.362
goodness-of-fit on F^2	0.849
R1 (obsd data)	0.0558
wR2 (all data)	0.1049
Flack parameter x	−0.01(2)

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 6

P(1)−P(2)	2.219(2)	P(2)−P(1)−P(3)	92.10(7)
P(1)−P(3)	2.234(2)	P(6)−P(4)−P(5)	97.13(7)
P(4)−P(5)	2.244(2)	C(1)−P(1)−P(2)	105.64(19)
P(4)−P(6)	2.233(2)	C(1)−P(1)−P(3)	97.10(16)
C(1)−P(1)	1.836(5)	C(6)−P(4)−P(5)	100.56(16)
C(6)−P(4)	1.814(5)	C(6)−P(4)−P(6)	96.28(17)
C(11)−P(2)	1.852(5)	C(11)−P(2)−P(1)	111.94(17)
C(38)−P(3)	1.830(5)	H(2p)−P(2)−C(11)	102.6(11)
C(65)−P(5)	1.847(5)	H(2p)−P(2)−P(1)	98.9(11)
C(92)−P(6)	1.839(5)	C(38)−P(3)−P(1)	111.36(16)
C(92)−P(6)−P(4)	108.58(16)	H(3p)−P(3)−C(38)	101.2(11)
H(6p)−P(6)−C(92)	103.5(12)	H(3p)−P(3)−P(1)	96.8(10)
H(6p)−P(6)−P(4)	98.6(11)	C(65)−P(5)−P(4)	106.30(16)
		H(5p)−P(5)−C(65)	99.5(11)
		H(5p)−P(5)−P(4)	96.0(10)

Experimental Section

All chemical experiments were performed in an argon atmosphere using standard Schlenk techniques or a glovebox. Solvents were dried over sodium/potassium alloy and stored under argon. ^{1}H, ^{13}C, and ^{31}P NMR spectra have been recorded on Bruker AMX 360 and Varian Unity 400 spectrometers at room temperature. Chemical shift values are given in ppm and are referenced to external standards. Mass spectra have been measured on Kratos MS-50 and Masslab VG 12-250 spectrometers using the EI ionization technique or FAB with an *m*-NBA matrix. Dmp-PH$_2$, Tbt-PH$_2$, and Fc′(PCl$_2$)$_2$ have been prepared according to published procedures.[18,24,30]

Synthesis of 1,1′-Bis(2,6-dimesitylphenyldiphosphenyl)ferrocene (3a). Dmp-PH$_2$ (0.34 g, 0.98 mmol) was dissolved in diethyl ether (10 mL) and cooled to −78 °C. To this mixture was added a solution of *n*-butyllithium in *n*-hexane (1.6 M, 0.6 mL, 0.95 mmol) while stirring. The mixture was warmed to room temperature for 0.5 h and subsequently cooled to −78 °C again. The reaction mixture was added to a solution of Fc′(PCl$_2$)$_2$ (0.19 g, 0.49 mmol) in diethyl ether (5 mL) at −78 °C. After stirring at the same temperature for 1 h, the mixture was allowed to warm to room temperature for 1 h, upon which it turned orange. DBU (0.15 g, 0.98 mmol) was added to the solution at room temperature, and the mixture immediately turned red-violet. After continued stirring for 30 min the solvent is removed. The residue is extracted with *n*-hexane and filtered. Evaporation of the filtrate under reduced pressure afforded diphosphene **3a** (0.36 g, 0.38 mmol, 77%) as a dark red solid (mp: 136.4 °C (dec)). ^{31}P (C$_6$D$_6$): 470.3 (d, $^1J_{PP} =$

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537 Hz), 444.9 (d, $^1J_{PP} =$ 537 Hz). ^{1}H (C$_6$D$_6$): 2.17 (s, 24 H), 2.32 (s, 12 H), 3.85−4.55 (m, 8 H), 6.97 (s, 8 H), 7.10 (d, $^3J_{HH} =$ 7.6 Hz; d, $^4J_{HP} =$ 1.3 Hz; 4 H), 7.36 (t, $^3J_{HH} =$ 7.6 Hz; 2 H). ^{13}C (C$_6$D$_6$): 21.36 (*o*-CH_3), 21.54 (*p*-CH_3), 72.32−75.94 (m, brd, C_5H_4), 128.06 (s, *m*-C_6H_3), 128.86 (s, *m*-C_6H_2), 131.05 (s, *p*-C_6H_3), 136.08 (s, *o*-C_q-Mes), 136.74 (s, C_q-aryl), 139.81 (s, C_q-aryl), 142.30 (s, C_q-aryl),146.26 (d, $J_{CP} =$ 11 Hz, C_q-aryl). Anal. (%) Calcd for C$_{58}$H$_{58}$FeP$_4$ (934.82): C 74.52, H 6.25. Found: C 74.44, H 6.52. UV−vis (benzene): 542 nm, 351 nm. MS (EI): 934,2 (3%, M$^+$), 590.2 (63%, M$^+$ − DmpP), 440.2 (17%, CpHPPDmp$^+$), 331 (100%), 246.0 (19%, M$^+$ − 2DmpP), 151.2 (32%, CpFeP$^+$), 96.2 (17%, CpPH$^+$), 56.2 (4%, Fe$^+$).

Synthesis of 1,1′-Bis(2,4,6-tris[bis(trimethylsilyl)methyl]phenyl)-diphosphenyl)ferrocene (3b). Tbt-PH$_2$ (0.91 g, 1.55 mmol) was dissolved in diethyl ether (10 mL) and cooled to −78 °C. To this mixture was added a solution of *n*-butyllithium in *n*-hexane (1.6 M, 0.97 mL, 1.55 mmol) while stirring. The mixture was warmed to room temperature for 0.5 h and subsequently cooled to −78 °C again. A cooled (−78 °C) solution of Fc′(PCl$_2$)$_2$ (0.30 g, 0.78 mmol) in diethyl ether (5 mL) was added to the reaction mixture. After stirring at the same temperature for 1 h, the mixture was allowed to warm to room temperature for 1 h, upon which it turned orange. DBU (0.24 g, 1.58 mmol) was added to the solution at room temperature, and the mixture immediately turned red-violet. After continued stirring for 30 min the solvent is removed. The residue is extracted with *n*-hexane and filtered. Evaporation of the filtrate under reduced pressure afforded diphosphene **3b** (1.00 g, 0.71 mmol, 91%) as a dark red solid (mp: 259.5 °C (dec)). ^{31}P (C$_6$D$_6$): 500.0 (d, $^1J_{PP} =$ 555 Hz), 492.5 (d, $^1J_{PP} =$ 555 Hz). ^{1}H (C$_6$D$_6$): 0.11 (s, 36 H), 0.20 (s, 36 H), 0.26 (s, 36 H), 2.66 (s, 4 H), 2.83 (s, 2 H), 4.30−4.80 (brd m, 8 H), 6.53 (s, 2 H), 6.64 (s, 2 H). ^{13}C (C$_6$D$_6$): 0.72 (CH_3), 0.80 (CH_3), 1.66 (CH_3), 29.23 (CH), 30.38 (CH), 30.59 (CH), 69.82−76.51 (m, brd, C_5H_4), 122.80 (s, *m*-C_6H_2), 124.88 (s, *p*-C_6H_2), 127.82 (d, $^3J_{CP} =$ 33 Hz, *m*-C_6H_2), 144.13 (dd, $^1J_{PP} =$ 64 Hz, $^2J_{PP} =$ 44 Hz, *ipso*-C_6H_2), 150.16−152.43 (m, brd, *o*-C_6H_2). Anal. (%) Calcd for C$_{64}$H$_{126}$FeP$_4$Si$_{12}$ (1412.45): C 54.42, H 8.99. Found: C 54.14, H 9.27. UV−vis (toluene): 545 nm, 380 nm. MS (FAB, *m*-NBA): 1412.3 (24%, M + H$^+$), 1166.4 (10%, Tbt$_2$P$_2$H$_2^+$), 828.2 (25%, M$^+$ − TbtP), 583.3 (98%, TbtPH$^+$), 552.3 (60%, TbtH$^+$), 246 (2%, M$^+$ − 2TbtP), 73.1 (100%, TMS$^+$).

Bis-1,3-dihydrotriphosphane (6). A solution of Tbt-PH$_2$ (1.17 g, 2 mmol) in benzene was added to a solution of **3b** (1.41 g, 1 mmol) in benzene at room temperature while stirring. The resulting solution is stored at room temperature without stirring in the dark. After several days platelike orange crystals of **6** formed, which were separated from the supernatant mother liquor and dried in a vacuum (1.16 g, 0.45 mmol, 45%). On heating, liquescent samples of neat **6** turned dark orange at 92 °C and intensive dark red at 98 °C. ^{31}P (C$_6$D$_6$): −18 to −85 (broad multiplets of the various spin systems of the isomeric mixture). Anal. (%) Calcd for C$_{118}$H$_{248}$FeP$_6$Si$_{24}$ (2582.97): C 54.87, H 9.68. Found: C 54.49, H 9.77.

Crystallographic Details for 6. A yellow plate-shaped crystal of **6** with dimensions 0.25 × 0.10 × 0.05 mm was used. The measurements were performed on a Nonius Kappa CCD diffractometer using graphite-monochromatized Mo Kα radiation at 123 K. A total of 65 722 reflections were collected ($\theta_{max} =$ 25.02°), from which 27 445 were unique ($R_{int} =$ 0.0640), with 13 425 having $I > 2\sigma(I)$. The structure was solved by direct methods and refined by full-matrix least-squares techniques against F^2 with SHELXL-97. The non-hydrogen atoms were refined with anisotropic displacement parameters. Also the H(P) were localized by electron density determination, and the coordinates were refined free with $U(H) = 1.2\ U_{eq}(P)$. The absolute structure of **6** has been determined by refinement of Flack's x parameter ($x = -0.01(2)$). For 1366 parameters (31 restraints) final R indices of $R = 0.0558$ (for $I > 2\sigma(I)$) and wR2 = 0.1049 (for all data) (GOF = 0.849) were obtained.

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Computational Details. Ab initio quantum chemical calculations were performed for compounds **4** and **5** using the program package Gaussian 03[31] at the Hartree−Fock and DFT(B3LYP) levels, employing a Dunning/Huzinaga full double-ζ basis set on first-row elements[32] and Los Alamos ECP plus DZ on Na−Bi.[33−35] Harmonic vibrational frequencies and their infrared intensities for all of the optimized structures have been evaluated by the B3LYP method to determine if a structure is a genuine minimum. Representations of the molecular orbitals are shown at a contour value of 0.04.

Supporting Information Available: Complete crystallographic details of the X-ray structure of **6** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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