Organometallics **1985,** *4,* 1565–1572

81133-02-0; $Cp(CO)_2FeCH_2Cl$, 12107-38-9; $(C_5H_5)(CO)_3Fe^+PF_6^-$, 38834-26-3; $Cp(CO)_2FeCH_2CH{=}CH_2$, 38960-10-0; $[Cp(CO)_2Fe]_2$, 12154-95-9; $Cp(CO)_2FeCH_3$, 12080-06-7; η^5-Cp(CO)Fe-(CH_2CHCH_2), 52326-25-7; $Cp(CO)_2FeFBF_3$, 76391-69-0; $(C_5H_5)(CO)_2FeCH_2CH_2CH{=}CH_2$, 34807-88-0; $Cp(CO)_2Fe^+PF_6^-$, 81141-37-9; $Cp(CO)_2FeI$, 12078-28-3; $Cp(CO)_3MoCH_2Cl$, 12244-83-6; $Cp(CO)_3MoI$, 12287-61-5; $Cp(CO)_3MoCH_3$, 12082-25-6; $Cp(CO)(pph_3)FeH$, 32660-22-3; $Cp(CO)_2FeCH{=}CH_2$, 12152-71-5; $Cp(CO)_2FeCH_2I$, 97011-69-3; $CpFe(CO)(PPh_3)(CH_3)OCH_2CH_3^+PF_6^-$, 97011-70-6; $CpMo(CO)_3CH_2OCH_3$, 12244-92-7; $CpMo(CO)_3(THF)^+PF_6^-$, 97011-71-7; $Ph_3PMe^+BH_3CN^-$, 97011-68-2.

Iron Complexes of Phosphinine[†] Derivatives

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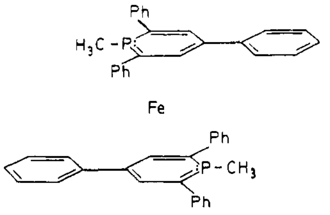
New bis(1,2,4,6-tetrasubstituted phosphinine)iron complexes were synthesized according to the procedure of Märkl and Martin.[1] Contrary to former interpretations[1,2] the compounds are very similar to the "open ferrocenes".[8] However, the ligands are closed by a 1,5-phosphorus bridge. The phosphorus with three carbon bonds can be alkylated to give phosphonium salts. No principal change of the (η^5-carbon)$_2$–Fe system occurs. A chair-like structure, phosphorus being outside of the nearly flat five-carbon unit, is claimed for the complexes (see the following paper[3]). Temperature-dependent ^1H and ^{13}C NMR spectra agree with a rotation around the z axis, vertical to the ring planes. The activation energies of the neutral complexes are strongly influenced by the substituent in position 4. $\Delta G^{\ddagger}$ of **10a**, **10b**, and **10c** are 52.3, 64.3, and 75.3 kJ/mol for R^4 = Me, Ph, and *t*-Bu, respectively. The temperature-dependent NMR spectra of the bis(phosphonium)iron tetrafluoroborates **12a** and **12c** also have been measured. Reduction potentials of the neutral and mono- and dication complexes **10a**, **11a**, and **12a** decrease with increasing charge at the phosphorus atom. Mössbauer spectra of the crystalline **10a**, **11a**, and **12a** are very similar, the isomeric shifts nearly the same as those of ferrocenes and the quadrupole splittings only ca. half of ferrocene, just as those of "open ferrocenes". XPE spectroscopy of **10a**, **11b**, and **12c** gave interesting results. The unsymmetrical mono(phosphonium)iron iodide complex **11a**, which, due to the short time scale of the XPE method, shows two signals of the iron, one at the neutral and one at the cationic phosphinine ring. The bis(phosphonium)iron complexes **12a** and **12c** are remarkable soluble in water in spite of their hydrophobic substituents.

Introduction

Bis(1-methyl-2,4,6-triphenyl-λ^4-phosphinine)iron, as well as its 1-phenyl derivative, was first synthesized by Märkl and Martin.[1] 2,4,6-Triphenylphosphinine was treated with methyl- (respectively phenyl-) lithium to give the phosphorus-substituted (λ^4-phosphinine)lithium compounds[4] which then were treated with iron(II) chloride in THF. Structure **1** of the black ferrocene-like compound was derived from the analytical data, the high-field shift in the ^{31}P NMR spectrum, δ −55 (which is quite different from those of λ^5-phosphinines ($\delta(^{31}P)$ 6–73)[5] or the P–Fe-substituted λ^5-phosphinine **4** (see below)), and the ^1H NMR data. A broad signal at δ 5.37 with a coupling constant, $^3J_{PH}$ = 8 Hz, was assigned for the protons at C-3 and C-5, and the high-field shift of the P–CH_3 doublet at 0.04 ppm was interpreted in terms of the "anti" conformation **1**, in which the phenyl substituent of the second phosphinine ring is situated over the P–CH_3 group. Later, Lehmkuhl et al.[2] measured the temperature-dependent ^1H NMR spectra of bis(1-ethyl-2,4,6-triphenylphosphinine)iron in THF-d_8. At 80 °C a sharp doublet at 5.45 ppm with a small $^3J_{PH}$ = 2.5 Hz was observed, which was assigned to all four protons of the two phosphinine rings at C-3,5 and C-3′,5′. At 40 °C only a broad signal at δ 5.43 is observed which at −20 °C splits into two sharp doublets at δ 5.53 (J = 2.4 Hz) and 5.37 (J = 2.1 Hz). These results were interpreted by fluxional structures **2** and **2′** in which the carbon atoms 3 and 5 of each ring are differently bonded to the iron according to an allyl–ene η^2,η^3 structure. At higher temperature **2** and **2′** equilibrate. From the coa-



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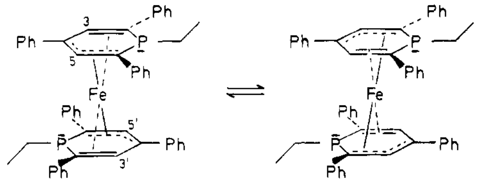

2 **2′**

[†] Earlier name phosphorin: Powell, W. H. *Pure Appl. Chem.* **1983**, *55*, 409.

[‡] Stipendiat of the Deutscher Akademischer Austauschdienst.

[§] Synthetic and spectroscopic part.

[∠] Results of temperature-dependent NMR spectra.

[‖] Results of cyclic voltammetric measurements.

[⊥] Results of Mössbauer spectroscopy.

[ʃ] Results of X-ray photoelectrospectroscopic measurements.

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Table I. ^1H NMR Spectra of 10a–c and ^{31}P NMR Shifts in CD_2Cl_2 at 25 °C

	$\delta(PCH_3)$ ($^2J_{P-H}$, Hz)	δ(H) at C-3,5 ($^3J_{P-H}$, Hz)	$\delta(R^4)$	$\delta(^{31}P)$
10a	−0.05 (5.9)	5.25, 5.45	6.94–7.68 (m)	−54.3
10b[a]	0.08 (5.6)	4.84 (s)[b] (5.3)	2.56 (s)	−57.5
10c	0.19 (6.0)	4.97 (2.1), 5.41 (1.2)	1.55 (s, Me of *t*-Bu)	−51.7

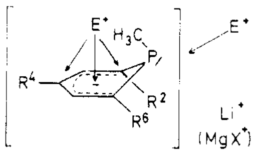
[a] In $CDCl_3$. [b] Only one signal corresponding to the low rotation energy $\Delta G^{\ddagger}$ = 52.3 kJ.

lescence temperature the free activation energy of the valence isomerism was evaluated to be in the order of 67 kJ. This interpretation **2** was accepted subsequently by Märkl in a review article.[6]

Ferrocene-like compounds of two six-membered, unsaturated heterocycles are nearly unknown. To our knowledge only 1-substituted borinine–ferrocene and -cobaltocene[7a–c] have been synthesized. The X-ray structure of the latter shows nearly flat borinine rings.[7d] Since we had some doubt about the interpretation of the above-mentioned bis(phosphinine) structures **1** and **2** ⇄ **2′** of the iron complexes, we studied them anew. In agreement with the earlier authors, we supposed that the iron is only bonded to the five unsaturated carbon atoms of the two phosphinine rings and not to the phosphorus atoms. In our opinion the phosphinine rings, however, have a chair-like conformation, the exo-methyl-substituted phosphorus atom being outside of the flat or nearly flat five-carbon atom portion of the rings. Therefore, the iron complexes of the phosphinine compounds can be regarded as C-2/C-6 bridged open ferrocenes. Indeed, the properties of the bis(phosphinine)iron complexes have many analogies with the "open ferrocenes", intensively studied by Ernst et al.[8] On the other hand, the (phosphinine)iron complexes should also have much in common with the (1,1-dimethyl-2,4,6-triphenyl(tri-*tert*-butyl)-λ^5-phosphinine)-tricarbonylchromium complexes[9] which according to X-ray analysis also show a chair-like conformation.[10] In these complexes the ^1H NMR shift of the exo PCH_3 group is also at relatively high field (δ 1.33 and 0.92, respectively) which is caused by its position over the π-electrons of the unsaturated carbon atoms of the (λ^5-phosphinine)tricarbonylchromium complex.[11] The PCH_3 ^1H shift of δ 0.04 alone, therefore, does not point to the anti conformation **1**. High-field PCH_3 ^1H NMR shifts also were found in the (phosphinine)iron complexes **10b** and **10c**, where the 4-phenyl group is exchanged for a 4-methyl or a 4-*tert*-butyl group (see Table I). The structures **2** ⇄ **2′** contradict the fact that we could not observe a C=C bond by IR as well as the equal distances of all C—C bonds of **10c** by X-ray analysis.[3]

Synthesis and Spectroscopic Results

1.1. λ^4-Phosphinine Anions. The anions of the lithium or magnesium salts of 1-methyl-2,4,6-triphenyl-λ^4-phosphinine (**3a**) or otherwise substituted λ^4-phosphinines are highly ambident.[12] The attack of the electrophiles E^+ depends on the substitution of the ring carbon atoms, the nature of the electrophile, and the reaction conditions, such as the polarity of the solvent. When **3a** is treated with methyl iodide in THF or benzene, only the P atom is attacked to give the 1,1-dimethyl-λ^5-phosphinine derivative. However, **3b** is attacked by methyl iodide at position 2 (6) to give 2,4,6-tri-*tert*-butyl-1,2-dimethyl-1,2-dihydrophosphinine.[13] Other electrophiles, however, such as a proton, trimethyloxonium tetrafluoroborate, and benzyl or alkyl bromide attack **3a** only at C-2 (6) to give the 1,2-dihydroxphosphinine derivatives.[12] (1,2,4,6-Tetraphenyl-λ^4-phosphinine)lithium in nonpolar solvents reacts with benzoyl chloride at position 4 to give 4-benzoyl-1,2,4,6-tetraphenyl-1,4-dihydrophosphinine.[12] Iron(II) chloride adds to the five delocalized π-electrons of the carbon atoms of two phosphinine rings. $CpFe(CO)_2I$, however, when allowed to react with **3a** in THF, adds to the phosphorus atom, to give the similar λ^5-phosphinine compound **4** with a P–Fe bond. This is a very sensitive crystalline compound. The ^{31}P shift of δ 26.3 is in the range of λ^5-phosphinines.[5] The protons of C-3,5 give a broad signal at δ 5.5. All spectral data are in accord with structure **4**. The phosphinine residue is a strongly electron-attracting ligand compared to iodine, shifting the C≡O IR frequencies of $CpFe(CO)_2I$ from 1982 and 2042 cm^{-1}[31] to 2020 and 2080 cm^{-1} in **4**. Corresponding with this fact, **4** readily reacts with nucleophiles at room temperature, such as MeOH or EtOH, by splitting the P–Fe bond to give the known 1-methyl-1-methoxy(1-ethoxy)-2,4,6-triphenyl-λ^5-phosphinines, **5a**[14a] (**5b**[14b]) in quantitative yield. [The mechanism of **4** → **5** was not studied in detail, as it seemed similar to the nucleophilic addition of alcohols to the 1,2,4,6-tetraphenylphosphinine cation (Dave, T.; Kaletsch, H.; Dimroth, K. *Angew. Chem.* **1984**, *96*, 984; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 989). One reviewer supposes first protonation of the $CpFe(CO)_2$ leaving group. We observed a higher reaction rate with alcohols (which is even catalyzed by acids) than with the sodium alcoholates. This supports the idea of the reviewer but does not



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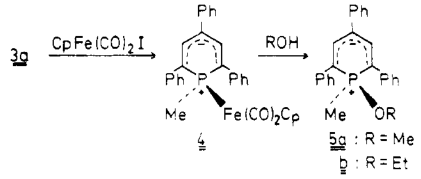
3a: $R^2 = R^4 = R^6 = Ph$
3b: $R^2 = R^4 = R^6 = Bu^t$



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[10] Debaerdemaeker, T. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *B35*, 1686; *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1982**, *C38*, 1209.

[11] See, e.g.: Khand, I. U.; Pauson, P. L.; Watts, W. E. *J. Chem. Soc.* **1969**, 2024. Awerbouch; D.; Kashman, Y. *Tetrahedron* **1975**, *31*, 33.

[12] Märkl, G.; Martin, C.; Weber, W. *Tetrahedron Lett.* **1981**, *22*, 1207. See also ref 6, p 96.

[13] Dimroth, K.; Kaletsch, H., unpublished; see also ref 9.

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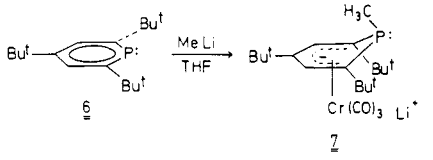
Table II. ^{13}C NMR Spectra of 10a, 10b, and 10c in CD_2Cl_2 at 25 °C

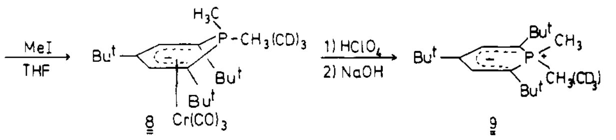
compd	$\delta(PCH_3)$ ($^1J_{P-C}$, Hz)	δ(C-2,6) ($^1J_{P-C}$, Hz)	δ(C-3,5) ($^2J_{P-C}$, Hz)	δ(C-4) ($^3J_{P-C}$, Hz)	$\delta(R^4)$
10a	18.0 (37.0)	51.1, 59.7	86.5, 93.2	91.5	127–143
10b (25 °C)	17.7 (36.2)	52.5^a	90.3^{a,b}	90.7	21.5 (4-Me)
10b (−60 °C)	17.2 (33.1)	46.8, 54.2	84.7, 94.9	90.7	21.7
10c	17.3 (39.0)	46.8 (6.1), 56.3 (4.4)	77.7 (7.9), 87.8 (7.6)	107.9	35.5 (q) 32.6 (Me of *t*-Bu)

^{a} See footnote *b* of Table I. ^{b} $^1J_{CH}$ = 158.1 Hz.

fully exclude the nucleophilic properties of the alcohols.]

On the other hand, when (2,4,6-tri-*tert*-butylphosphinine)tricarbonylchromium (**6**) is first treated with methyllithium to give **7** (^{1}H NMR of PCH_3 at δ 0.82) and then with methyl iodide, (2,4,6-tri-*tert*-butyl-1,1-dimethyl-λ^5-phosphinine)chromium tricarbonyl (**8**) is formed (^{1}H NMR of the exo PCH_3 at δ 0.92 and the endo PCH_3 at δ 2.36). When the tricarbonylchromium protecting group is removed, 2,4,6-tri-*tert*-butyl-1,1-dimethyl-λ^5-phosphinine, not available by other routes,[9] is formed.





Since no structure or NMR spectra of (λ^4-phosphinine)lithium compounds have been reported, we measured the ^{31}P and ^{1}H NMR spectra of **3a** and **3b** (Li salts) in THF-d_8. The ^{31}P shifts are at δ −73.8 (**3a**) and δ −78.6 (**3b**). The shift of the PCH_3 protons are at high field: δ 0.63 ($^2J_{PH}$ = 5 Hz) (**3a**) and δ 0.30 ($^2J_{PH}$ = 5 Hz) (**3b**). Whereas the ring protons at C-3,5 or **3a** cannot be observed under the multiplet of the aromatic ring protons, they are easily found in **3b** at 6.7 ppm with a relative small coupling constant, $^3J_{P-H}$ = 5.5 Hz (contrary to 20–50 Hz of $^3J_{P-H}$ of the λ^5-phosphinines with a flat ring[5]). The 6.7 ppm value for the protons at C-3,5 partly points to some delocalization of the negative charge in the ring system. These results support chair-like conformation of the 1-substituted phosphinine anions **3** with a dihedral angle of P–H (at C-3,5) smaller than 180° according to the Karplus equation. The spectroscopic data agree with the chemical fact that no anionic salts of tertiary phosphines are known. This holds for structures such as **3** or **7**, the PCH_3 group being over the π-electrons of the ring.

1.2. Bis(1,4-dimethyl-2,6-diphenylphosphinine)iron and Bis(4-*tert*-butyl-1-methyl-2,6-diphenylphosphinine)iron and Their Temperature-Dependent ^{1}H NMR Spectra. Unfortunately, bis(1-methyl-2,4,6-triphenylphosphinine)iron (**10a**) cannot be isolated as good crystals, suitable for an X-ray analysis. Since (2,4,6-tri-*tert*-butyl-1-methylphosphinine)lithium did not react with iron(II) chloride to give an iron complex (probably for steric reasons), we synthesized the iron complexes of bis(1,4-dimethyl-2,6-diphenylphosphinine)iron (**10b**) and bis(4-*tert*-butyl-1-methyl-2,6-diphenylphosphinine)iron (**10c**). The latter compound gives good crystals for X-ray analysis, the results of which confirm the chair conformation and the exo position of the PMe group as well as nearly equal C–C distances within the phosphinine rings, disproving the structures **1** and **2** ⇄ **2′**. Tables I and II summarize the ^{1}H, ^{13}C, and ^{31}P NMR spectra of **10a**, **10b**, and **10c** at 25 °C.

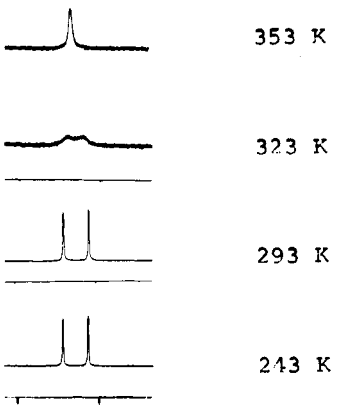


Figure 1. ^{1}H NMR of **10** in toluene-d_8.

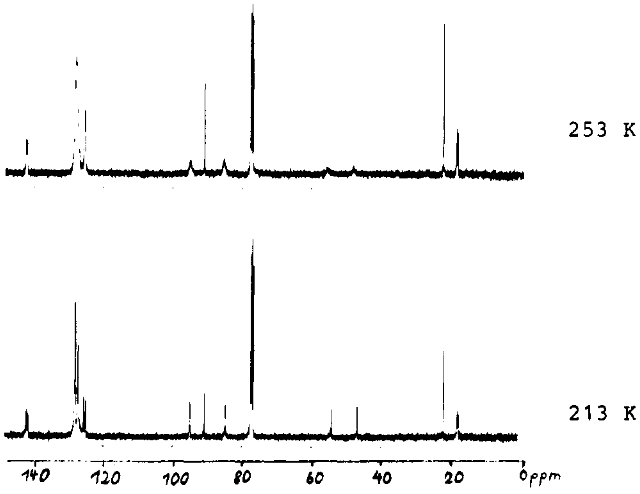


Figure 2. ^{13}C NMR of **10b** in $CDCl_3$.

Lehmkuhl et al.[2] have measured the temperature-dependent ^{1}H NMR spectra of bis(1-ethyl-2,4,6-triphenylphosphinine)iron at 80 MHz and found an activation barrier of 67 kJ/mol. The spectra were interpreted in terms of a valence isomerization within the π-systems according to **2** ⇄ **2′**. When we repeated their experiment at 400 MHz, the value of the activation barrier was exactly confirmed. Instead of the valence isomerization, however, a rotation of the phosphinine rings around the iron can also explain the temperature-dependent NMR spectra (Figures 1 and 2). An experiment which would distinguish between these two processes was carried out by the introduction of other substituents at C-4 of the phosphinine rings. These can influence both valence isomerism as well as bond rotation. One would expect, however, that electronically similar substituents such as a methyl or a *tert*-butyl group would not vary the activation barrier for a valence isomerization drastically. Our experimental findings of 52.3 kJ/mol for the 4-methyl compound **10b**, of 64.3 kJ/mol for the 4-phenyl compound **10a**, and of 75.3

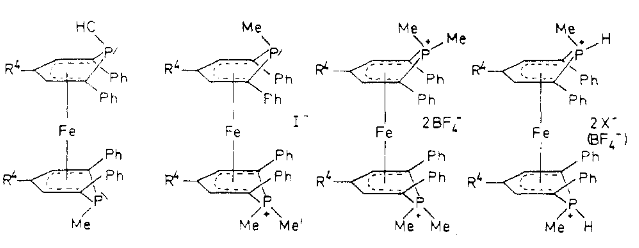
Table III. ^{1}H, ^{13}C, and ^{31}P NMR Spectra of 11a, 11c, 12a, 12c, and 13 in CD_2Cl_2 at 25 °C

	^{1}H NMR		^{13}C NMR				
compd	δ(PCH_3) ($^2J_{P-H}$, Hz)	δ(H) at C-3,5 and C-3′,5′ ($^3J_{P-H}$, Hz)	δ(P–CH_3) ($^1J_{P-C}$, Hz)	δ(C-2,6) ($^1J_{P-C}$, Hz)	δ(C-3,5) ($^2J_{P-C}$, Hz)	δ(C-4) ($^3J_{P-C}$, Hz)	^{31}P NMR[a] δ
11a	0.16 (Me exo, 5.2)	5.3, 5.9 (3,5)	18.3 (Me exo, 35.4)	61.0 (10.4), 62.1 (11.6)	85.1 (6.7), 94.3 (7.8)	94.7 (4.83)	−54.1
	1.27 (Me′ exo, 11.4)		20.3 (Me′ exo, 35.4)				
	1.87 (Me′ endo, 13.8)	5.2 (17.2), −5.4 (18.0) (3′,5′)	6.8 (Me′ endo, 65.9)	37.4 (78.7), 43.9 (75.1)	90.8, 96.8	92.5 (12.82)	+18.4
11c	0.26 (Me exo, 5.6)	5.5, 5.6 (3,5)					−50.6
	1.0 (Me′ exo, 10.2)						
	1.76 (Me′ endo, 13.1)	4.7 (17.3), 5.7 (18.0) (3′,5′)					+22.9
12a	1.00 (exo Me, 13.6)	5.7 (18.1)	18.4 (31.1)	47.1 (73.9)	96.8	95.0 (13.4)	+30.0
	2.48 (endo Me, 14.0)		9.2 (64.7)				
12c	0.94 (exo Me, 12.0)	6.07 (8.0), Me of *t*-Bu 1.42	18.1 (exo Me, 31.7)	40.7 (74.0)	85.3[b] (2.4)	111.8 (13.5), Me of *t*-Bu 36.6	+34.0
	2.25 (endo Me, 13.9)	6.25 (5.0)	9.1 (endo Me, 64.7)	48.8 (7.63)	97.8[b] (2.4)		
13a	1.21 (14.5)	6.1 (18.7)	15.2 (22.0)	43.5 (78.8)	92.8	96.4 (13.4)	−19.51 ($^1J_{PH}$ = 532 Hz)
	2.7[c] (532)						

[a] ^{31}P NMR in CD_3OD. [b] $^1J_{CH}$ = 172.4 Hz. [c] Bis(tetrafluoroborate) δ(PH) ($^1J_{PH}$).

kJ/mol for the 4-*tert*-butyl compound **10c** are very much in favor of hindered rotation of the ligands in these η^5-bound complexes. This interpretation is similar to the results of temperature-dependent ^{1}H NMR spectra of the open ferrocenes. As one reviewer suggests, an additional argument arises from a comparison of the ^{13}C NMR data. In compounds **10a–c** the 2,6-carbon atoms resonate at about 50 ppm, a value quite comparable with that of the terminal carbon atoms of the "open ferrocenes".[8]

1.3. Methylation and Protonation of the Phosphorus Atom of 10a and 10c. The phosphorus with three carbon bonds of the neutral bis(1-methyl-2,4,6-substituted phosphinine)iron complexes **10** can be alkylated or protonated at the phosphorus atom to give phosphonium salts. When **10a** is treated with methyl iodide, one phosphorus is methylated and an unsymmetrical brown iodide with three methyl groups, **11a**, is isolated. The stronger methylating reagent trimethyloxonium tetrafluoroborate in dichloromethane affords the red brown crystalline bis(tetrafluoroborate) **12a** in quantitative yield, the preliminary results of the X-ray analysis of which are mentioned in ref 3. (For similar results of (3,4-dimethyl-1-oxo-1,2-diphenylphosphinine)cyclopentadienyliron see ref 15).



10 11 12 13

a : R^4 = Ph
b : R^4 = Me
c : R^4 = Bu^t

Analogous methylation of **10c** with methyl iodide gave the iodide **11c** and of **10c** with trimethyloxonium tetrafluoroborate gave the bis(tetrafluoroborate) **12c**. The ^{1}H, ^{13}C, and ^{31}P NMR spectra at 25 °C are summarized in Table III. To establish the steric position of the methyl groups of **10a**, **11a**, and **12a**, [(1-trideuteriomethyl)-2,4,6-triphenyl-λ^4-phosphinine]lithium (**3a**, CD_3 instead of CH_3) was synthesized and reacted with iron(II) chloride to give **10a′** (Me = CD_3). After the addition of methyl iodide only one ^{1}H NMR signal of the endo *P*-methyl group of **11a′** at δ 1.89 could be observed. By a similar route, when **10a** was treated with trideuteriomethyl iodide, only the ^{1}H signals of the two exo *P*-methyl signals at δ 0.18 and 1.28 were found. Finally, when **10a′** was methylated with trimethyloxonium tetrafluoroborate, only the endo methyl groups at δ 2.48 of **12a′** were observed. The ^{1}H NMR spectra of the compounds **12** are again temperature dependent.

Since the protons at C-3,5 display a spin–spin coupling constant to the phosphorus atom, a simple treatment using the coalescence point method similar to the compounds **10a–c** gives no exact data. The temperature-dependent ^{1}H NMR spectra of **12a** (compare Figure 3) have, therefore, been simulated by using the DNMR3 program by Binsch,[16] yielding a $\Delta G^{\ddagger}$(298) value of 52.9 kJ/mol. This value is considerably smaller than that of the corresponding compound **10a** (64.3 kJ/mol). This could be interpreted to mean that the introduction of an additional methyl group at the phosphorus atom raises the ground state of the molecule, thus lowering the barrier for hindered rotation.

Indeed, a careful comparison between the X-ray studies of **10c** and **12a**[3] reveals that the mean distance between the rings in **12a** is 0.16 Å greater than in **10c** and the distance between the phosphorus atoms 0.56 Å greater. Thus, the introduction of the two additional methyl groups at the phosphorus atoms changes the structure of the complexes significantly which is seen also in the lower barrier for hindered rotation in the NMR spectra. Also, the positive charge of both phosphinine rings may diminish

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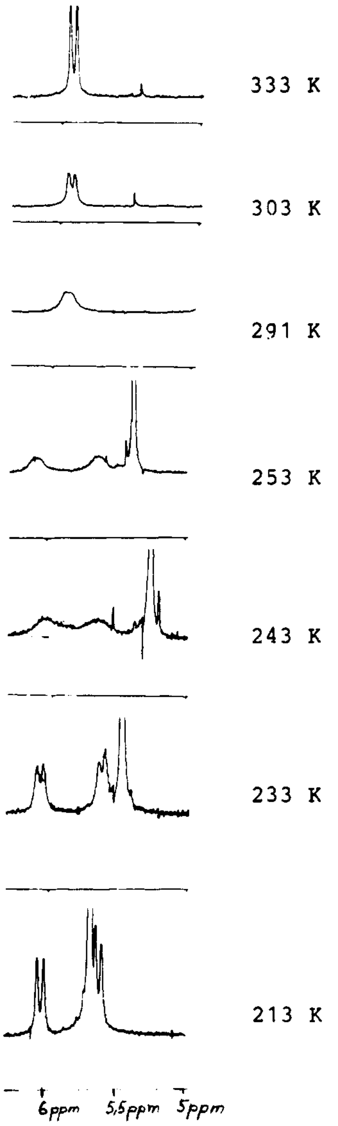

Figure 3. ^{1}H NMR of **12a** in CD_3OD.

the activation energy compared with the neutral complex **10a**.

In addition to the described hindered rotation we have found at very low temperature another type of dynamic behavior in the proton spectra affecting only the phenyl groups in **12a**. Due to the complicated spectral situation in the aromatic region and the low solubility of these compounds at −100 °C this was not investigated in detail.

Table III also includes the results of the protonation of **10a**. When the ^{31}P NMR signal of the solution of **10a** in dichloromethane was observed on adding small amounts of trifluoroacetic acid, the ^{31}P signal of **10a** at −54.3 ppm moves with increasing concentrations of the acid continuously to a lower field giving always one single signal. We interpret this observation in terms of a fast inter- or intramolecular exchange of the proton between the two phosphorus atoms of the iron complex. With an excess of acid or in a solution of the crystallized diprotonated bis(tetrafluoroborate) (see Experimental Section), however, the ^{31}P signal is at relatively high field (δ ~20), in contrast to the bis(tetramethyl) salts **12a–c**.

The phosphonium salts **12a** and **12c** are soluble in dichloromethane and only moderately soluble in tetrachloroethane but, in spite of the large hydrophobic substituents of the phosphinine ring, relatively well soluble in water. We suppose that the hydrophilic phosphonium salt and the hydrophobic bis(phosphinium) ion unit at higher concentrations in water have micelle structures, about which we will report in another account.

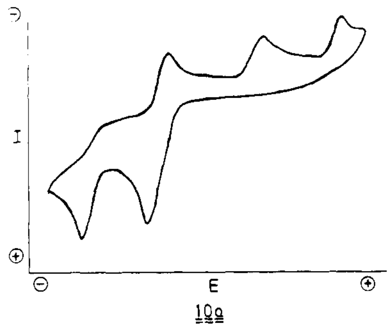

Figure 4.

Table IV. Reduction of 10a, 11a, and 12a by Cyclic Voltammetry vs. Saturated SCE (mV) in Dimethoxyethane[a]

	first step	second step
10a	−1160[b]	−2200[c]
11a	−840	−1640
12a	−390[d]	−840[d]

[a] Working electrode glassy carbon and supporting electrolyte tetra-*n*-butylammonium perchlorate. [b] Reversible. [c] Irreversible. [d] Quasireversible.

Table V. Mössbauer Data of Quadrupole Splitting (QS) and Isomer Shift (IS) with Respect to the Center of a Metallic Iron Spectrum at 4.2 and 100 K, Respectively

compd	temp, K	QS, mm/s	IS, mm/s
10a	100	1.05 (1)	0.518 (8)
11a	100	1.00 (1)	0.529 (8)
	4.2	1.01 (1)	0.525 (8)
12a	100	1.03 (1)	0.522 (8)
	4.2	1.05	0.520 (10)
$Fe(Cp)_2$	100	2.40 (1)	0.53 (1)

2. Electrochemical Reduction of the Iron Complexes 10a, 11a, and 12a. Whereas the oxidation of **10a**, iodide **11a**, and the tetrafluoroborates **12a** by cyclic voltammetry leads to an irreversible decomposition of the iron complexes, cyclic voltammetric reduction gives interesting results. These fully agree with the largely independent function of the phosphorus bridge in the open ferrocene-like complexes. As expected, the highest charged complex, the dication **12a**, is most easily reduced. There are two steps at $E°_1$ = −390 mV and $E°_2$ = −840 mV vs. SCE; both steps to some extent are reversible (Figure 4). The monocation **11a** also shows two reduction steps; both, however, are nearly irreversible at E_{pc_1} = −890 mV and E_{pc_2} = −1640 mV vs. SCE. The neutral complex **10a** can be reversibly reduced in the first step at $E°_1$ = −1660 mV, followed by a second irreversible reduction at a cathodic peak potential of E_{pc_2} = −2200 mV. After the reversal of the potential at −2.5 V some oxidation peaks can be observed on the anodic branch of the first reduction step. These are caused by unknown reaction products of the iron complexes after reduction (see Table IV).

All three compounds show characteristic differences between the first and the second reduction step: **10a**, Δ = ~1600 mV; **11a**, Δ = ~750 mV; **12a**, Δ = ~460 mV. These may possibly ascribed to the transfer of electron(s) to unoccupied orbitals of the phosphorus.

3. ^{57}Fe Mössbauer Spectroscopy. The results of the ^{57}Fe Mössbauer experiments are summarized in Table V, and a representative spectrum of **12a** compared to that of ferrocene is shown in Figure 5. Within statistical errors the quadrupole splittings and the isomer shifts show similar values in compounds **10a**, **11a**, and **12a**, illustrating that the electronic structure around the iron nucleus is very

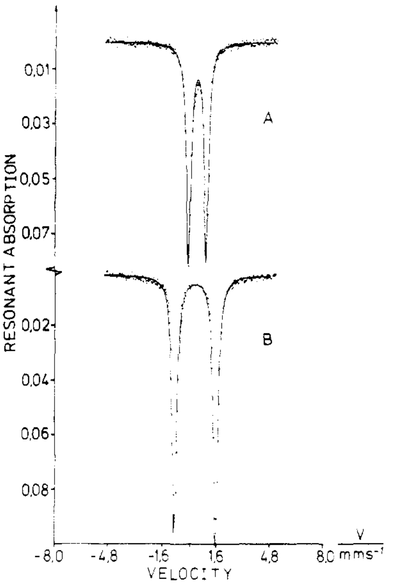

Figure 5. Mössbauer spectra of compound **12a** (A) and ferrocene (B) at 100 K. The isomer shift scale is with reference to the used ^{57}Co(Rh) source.

much the same. All of the spectra consist of two well-resolved resonance lines, each of which has a full-width at half-maximum of about 0.30 mm/s corresponding to a single iron site. From the temperature independence of the quadrupole splittings we can exclude a $3d^7$ electron configuration. Magnetic susceptibility measurements reveal diamagnetism for the three compounds and therefore a $3d^6$ electron configuration as in ferrocene. We have detected no evidence for an unresolved hyperfine interaction in any of the spectra or an indication of a Fe(II)/Fe(III) relaxation effect. The temperature dependence of the isomer shift values was found to be practically identical for the three compounds. As far as this parameter has been studied, it shows that the vibrational properties which involve the metal atom are very similar. From the data summarized in Table V the most significant difference between ferrocene and compounds **10a**, **11a**, and **12a** consists of the fact that the latter compounds show quadrupole splittings, which are more than a factor of 2 smaller than that of ferrocene. However, the corresponding isomer shift and, therefore, the electron density at the Fe nucleus are not altered as compared to ferrocene.

The MO treatment[18] explaining the quadrupole splitting in ferrocene is a rough approximation[17,19-21] for the iron orbitals at the iron site if the electronic structure is lower than that in ferrocene. In the D_{5d} geometry the π-orbitals of two parallel C_5H_5 ligands form three sets of nearly degenerate orbitals, a pair of low-lying filled orbitals of a_{1g} and a_{2u} symmetry, a set of filled e_{1g} and e_{1u} orbitals, and a high-lying set of antibonding orbitals of e_{2g} and e_{2u} symmetry. These interact with the orbitals of the metal. Of the metal 3d orbitals the a_{1g} (d_z) level is in all cases only very weakly involved in the bonding. The e_{1g} (d_{xz}, d_{yz}) and e_{2g} ($d_{x^2} - d_{yz}$, d_{xy}) orbitals both interact strongly with the ligand orbitals, generating and e_1 set which is predominantly ligand based and an e_2 set which is metal based. Since the corresponding electric field gradients have different signs,[19] the decrease in the quadrupole splitting can be interpreted as the result of mutually cancelling contributions, e.g., removal of the electron charge from the e_{2g} and/or addition of the electron charge via the e_{1g} orbitals. The chair-like conformation of the three (phosphinine)iron complexes has a symmetry lower than C_{2v} on the iron site. For "open ferrocenes" with C_2 symmetry MO calculations[8b] indicate a much higher degree of metal–ligand coupling compared to ferrocene. In the open ferrocenes this results in a depopulation of the e_{2g} orbitals while the e_{1g} orbital populations increase.

Table VI. Binding Energies of 10a, 11a, and 12a by XPE Spectroscopy in eV

compd	$E_b(2p_{3/2})$	$E_b(Fe_{2p_{3/2}})$	$E_b(C_{1s})^a$	$E_b(I_{3d_{5/2}})$	$E_b(F_{1s})$
10a	130.5	708.7	285.0		
11a	130.6, 132.7[b]	709.5,[c] 712.2	285.0	618.4	
12a	133.0	709.5	285.0		687.2

[a] For calibration of the XPE spectra the internal C_{1s} signal was set to $E_b(C_{1s})$ 285.0 eV. [b] The intensity of both phosphorus signals is 1:1. [c] s = shoulder.

Therefore, the lowered symmetry in ferrocene-like systems (D_{5d}), compared with "open ferrocene" (C_{2v})[8d] and the chair-like (phosphinine)ferrocenes with a symmetry lower than C_{2v}, leads to more nearly equal d orbital populations and to a more reduced quadrupole splitting in the (phosphinine)iron complexes. The observed decrease in the quadrupole splitting has to be considered as a consequence of the lower molecular symmetry.

4. X-ray Photoelectronic Spectra of 10a, 11a, and 12a. In Table VI the most intense signals of the core electrons of phosphorus, iron, carbon (for calibration), iodine, and fluorine are summarized. The binding energy, E_b, of the phosphorus 2p electrons of **10a** (an unresolved spin orbit $2p_{3/2-1/2}$) is low and similar to E_b of the phosphorus of triphenylphosphine (E_b = 130.6 eV) but higher than that of 2,4,6-triphenylphosphinine, E_b = 130.04 eV. This is the lowest E_b of the 2p electrons of phosphorus of all measured organophosphorus compounds.[22] **10a** therefore has a lower electron density at the phosphorus atom than 2,4,6-triphenylphosphinine. **11a** has two differently charged phosphorus atoms. A broad signal of the P_{2p} electrons was observed. Curve analysis gives two singlets at 130.6 and 132.7 eV. The line at 130.6 eV is ascribed to the phosphorus coordination number 3 and that of 132.7 eV to the positive phosphorus, coordination number 4. The assignment was possible by comparing the P signals of **10a** with that of **12a**, as well as from ref 22. **12a** shows a phosphorus signal at 133 eV which is similar to that of 1,1-dimethyl-2,4,6-triphenyl-λ^5-phosphinine (133.5 eV).[22] This proves that in the iron complex **12a** the two positively charged phosphinine rings have no significant influence on the E_b value. The E_b of the iron $2p_{3/2}$ electrons of **10a** is somewhat greater than that of the Fe(II) of the bis(ferrocene) Fe(II)/Fe(III) picrate.[23] That absolute value, however, is uncertain, as the XPE spectra have not been calibrated to eliminate the positive charge. The iron signal of **11a** shows a maximum at 712.2 eV with a distinct shoulder at 709.5 eV. According to ref 23 this corresponds to a "mixed" iron(II)/iron(III) valence with a smaller difference of 2.7 eV compared to 3.4 eV of ref 23. **11a**, however, has only one iron atom which according to the low time scale of the XPE spectroscopy between 3 × 10^{-18} s, the time of the passage of one wavelength of the soft

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X-rays, and 5 × 10^{-17} s, the Heisenberg half-life of the cadmium 4p ionization,[24] one observes two signals. One of these is ascribed to the iron nearer to the neutral phosphinine part, the other one to the iron nearer to the positive charged phosphinine ring. X-ray PE spectroscopy, therefore, registers an instantaneous situation in contrast to Mössbauer spectroscopy, which has a greater time scale. For this reason in X-ray PE spectroscopy a rapid fluctuation of the iron of compound **11a** can be observed, whereas Mössbauer spectroscopy records only one signal. Compound **12a** gives only one $Fe_{2p_{3/2}}$ band at 709.5 eV which corresponds to that of the π-bonded Fe(II) of ferrocene.[25,26] The E_b of iodine of **11a** is in the usual range of the iodide ion.[27] The same is true for the fluorine 1s electrons of BF_4^- of **12a**.[28]

Experimental Section

All reactions were carried out under purified argon. Nonaqueous solvents were dried over sodium/potassium benzophenone and distilled prior to use. CH_2Cl_2 was predried with alumina and distilled over calcium chloride. Anhydrous iron(II) chloride was purchased from Ventron GmbH and handled under argon. For column chromatography silica gel Woelm or alumina Woelm neutral was used, depending upon the reactivity of the compound. Melting points, determined by the Reichert microscope, are not corrected. Elemental analysis was performed by the microanalytical laboratory Beller, Göttingen, and the microanalytical laboratory of the Fachbereich Chemie, Marburg. ^1H and ^{13}C NMR spectra were recorded on JEOL FX-100 (90.55 MHz) or Bruker WH-400 (400 MHz) spectrometer and ^{31}P NMR on Varian XL-100 (40.5 MHz). ^1H and ^{13}C shifts are recorded in parts per million against internal Me_4Si standard and ^{31}P NMR in parts per million (positive values for downfield shifts) against external 85% phosphoric acid. IR spectra were measured in KBr, using Beckman IR 33, and UV/vis spectra in CH_2Cl_2, using Beckman Acta-3. In none of the compounds **10–c**, **11a,c**, and **12a,c** was an absorption band in the range of a carbon–carbon double bond (1635–1690 cm^{-1}) observed. Cyclic voltammetry was performed in ca. 10^{-3} M concentrations in dry 1,2-dimethoxyethane/tetra-*n*-butylammonium perchlorate in a special cell,[29] developed for extremely sensitive compounds. Potentiostat Amel 552 and multipurpose uni Amel 563 together with storage oscilloscope Nicolet 2090-1 and a X/Y recorder Kipp and Zonen BD 90 were used. Mössbauer spectra were obtained with a conventional velocity-scanning spectrometer, in conjunction with a multichannel analyzer according to the multicolor mode. The room-temperature source consisted of about 10 mCi of ^{57}Co diffused into metallic Rh. The spectra were measured in the velocity range about ±4.8 mm s^{-1} at temperatures between 4.2 and 295 K (± 2 K). Calibration was made with metallic iron. X-ray photoelectron spectra were recorded with ESCA 3 (Vacuum Generators, England) according to the multiple scan mode. Each spectrum was an accumulation of 10 scans. The spectra were calibrated with the internal C_{1s} signal of the phenyl substituents.

Bis(1-methyl-2,4,6-triphenylphosphinine)iron (10a) was synthesized according to ref 1: UV (CH_2Cl_2) λ_{max} 240 (ε 39 900), 275 nm (44 200); ^1H, ^{13}C, ^{31}P NMR, see Tables I and II.

Bis(1,4-dimethyl-2,6-diphenylphosphinine)iron (10b) was prepared from (1,4-dimethyl-2,6-diphenylphosphinine)lithium and iron(II) chloride in THF and was isolated after chromatography: mp >320 °C; 20% yield. MS, *m/e* (relative intensity) 610 (100), 611 (33.7); UV (CH_2Cl_2) λ_{max} 235 (ε 33 000), 336 (35 200). Anal. Calcd for $C_{38}H_{36}FeP_2$ (610.5): C, 74.8; H, 5.9. Found: C, 74.9; H, 6.1.

Bis(4-*tert*-butyl-1-methyl-2,6-diphenylphosphinine)iron (10c) was prepared from (4-*tert*-butyl-1-methyl-2,6-diphenylphosphinine)lithium and iron(II) chloride in THF and was isolated as brown-black needles (mp 174–176 °C in 60% yield) after chromatography on a short column containing Al_2O_3 (activity III) using benzene/hexane (1:1) as eluant. MS, *m/e* (relative intensity) 694 (100), 695 (38.7); UV (CH_2Cl_2) λ_{max} 240 (ε 28 000), 320 nm (22 500). Anal. Calcd for $C_{44}H_{48}FeP_2$ (694.6): C, 76.1; H, 7.0. Found: C, 76.0; H, 7.1.

(1-Methyl-2,4,6-triphenylphosphinine)(1,1-dimethyl-2,4,6-triphenylphosphinine)iron Iodide (11a). A 1.14-g (1.5-mmol) sample of **10a** was dissolved in 10 mL of CH_2Cl_2. A 0.22-g (1.5-mmol) sample of methyl iodide was added gradually with a syringe at room temperature into the stirred solution. After 1 h the solvent was removed in vacuo. After slow addition of diethyl ether, stable brown crystals were isolated, washed with diethyl ether, and dried in vacuo: 1.24 g (94% yield); mp 178–180 °C after recrystallization from ethanol; MS, *m/e* (relative intensity) 354 (100), 355 (44), 749 (49), 329 (30), 751 (7.8), 750 (27.8); UV (CH_2Cl_2) λ_{max} 247 (ε 40 700), 285 nm (33 200). Anal. Calcd for $C_{49}H_{43}FeIP_2$ (876.5): C, 67.1; H, 4.9. Found: C, 67.1; H, 4.9.

(4-*tert*-Butyl-1-methyl-2,6-diphenylphosphinine)(4-*tert*-butyl-1,1-dimethyl-2,6-diphenylphosphinine)iron Iodide (11c). A 0.2-g (0.29-mmol) sample of **10c** was dissolved in 2 mL of CH_2Cl_2. A 0.04-g (0.29-mmol) sample of methyl iodide was added with a micropipette at room temperature into the stirred solution. After 4 h the solvent was removed in vacuo. After slow addition of diethyl ether stable brown crystals were isolated, washed with diethyl ether, and dried in vacuo: 0.21 g (86% yield); mp 135–145 °C; FDMS, *m/e* (relative intensity) 710 (93), 709 (3), 695 (21), 334 (100); UV (CH_2Cl_2) λ_{max} 245 (ε 44 850), 310 nm (28 500). Anal. Calcd for $C_{45}H_{51}FeIP_2 \cdot 0.5CH_2Cl_2$ (879.03): C, 62.16; H, 5.96. Found: C, 62.0; H, 6.09.

Bis(1,1-dimethyl-2,4,6-triphenylphosphinine)iron Bis(tetrafluoroborate) (12a). To the solution of 1.14 g (1.5 mmol) of **10a** in 10 mL of CH_2Cl_2 was added 0.53 g (3.6 mmol) trimethyloxonium tetrafluoroborate.[30] The suspension was stirred for 70 h at room temperature. After the solvent was removed in vacuo, the compound was precipitated by slow addition of diethyl ether. The red air-stable crystals were recrystallized from ethanol and dried in vacuo: 0.95 g (66% yield); mp 182–183 °C; they are readily soluble in water; MS, *m/e* (relative intensity) 354 (100), 355 (41), 749 (0.5); UV (CH_2Cl_2) λ_{max} 240 (ε 57 900), 310 (33 300), 425 nm (9450). Anal. Calcd for $C_{50}H_{46}FeP_2 \cdot 2BF_4$ (938.3): C, 64.00; H, 4.9. Found: C, 63.9; H, 5.0.

Bis(4-*tert*-butyl-2,6-diphenylphosphinine)iron Bis(tetrafluoroborate) (12c). This was prepared according to the same procedure as **12a**: red crystals from CH_2Cl_2/MeOH (1:2) by slow addition of diethyl ether; 69% yield; mp 179–181 °C. MS, *m/e* (relative intensity) 334 (100), 335 (79.4); UV (CH_2Cl_2) λ_{max} 235 (ε 36 000), 305 (34 200), 405 nm (11 100). Anal. Calcd for $C_{46}H_{54}FeP_2 \cdot 2BF_4 \cdot CH_2Cl_2$ (983.3): C, 57.40; H, 5.74. Found: C, 57.46; H, 5.90.

Bis(1-methyl-2,4,6-triphenylphosphinium)iron Bis(tetrafluoroborate) (13a). A 0.4-g (0.54-mmol) sample of **10a** was dissolved in 5 mL of CH_2Cl_2 and stirred with a large excess of 50% etheric tetrafluoroboric acid. After 1 h the solvent was removed in vacuo and the solid salt isolated with diethyl ether and carefully washed with diethyl ether. Recrystallization from ethanol gave 0.47 g (96% yield) of **13a**: mp 182–183 °C; MS, *m/e* (relative intensity) 734 (100), 736 (33), 735 (59.5); UV (CH_2Cl_2) λ_{max} 235 nm. Anal. Calcd for $C_{48}H_{42}FeP_2 \cdot 2BF_4$ (910.3): C, 63.3, H, 4.7. Found: C, 61.9; H, 4.8.

(1-Methyl-2,4,6-triphenylphosphinine-*P*)dicarbonyl(η^5-cyclopentadienyl)iron (4). A solution of 0.91 g (3 mmol) of dicarbonyl(η^5-cyclopentadienyl)iron iodide[31] in 40 mL of THF was added to 3 mmol of (1-methyl-2,4,6-triphenylphosphinine)lithium using a transfer needle. The resulting blue mixture was stirred for 2 h at room temperature. After the solvent was removed in vacuo, the residue was extracted with benzene/hexane (1:1) to give highly air-sensitive crystals of **4** in nearly quantitative yield: mp 178 °C; ^{31}P NMR (CH_2Cl_2) δ 26.3; ^1H NMR (C_6D_6) δ 7.3–6.8 (17 H, m, aromatic H, and 2 H at $C_{3/5}$), 4.3 (J_{P-H} = 1.6 Hz, Cp), 4.3 (5 H, d, Cp), 2.02 ($^2J_{P-H}$ = 9.7 Hz, 3 H, PMe); FDMS, *m/e*

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(relative intensity) 516 (100), 517 (50), 304 (16), 356 (8). Anal. Calcd for $C_{31}H_{25}FeO_2P$ (516.4): C, 72.1; H, 4.9. Found: C, 71.7; H, 4.9.

1-Methyl-1-methoxy-2,4,6-triphenyl-λ^5-phosphinine (5a), identical by ^{1}H NMR with the known material,[14a] was isolated in quantitative yield by adding methanol to 4 and workup by chromatography.

1-Ethoxy-1-methyl-2,4,6-triphenyl-λ^5-phosphinine (5b) (mp 114–116 °C), identical by ^{1}H and ^{31}P NMR with the known material,[14b] was isolated in quantitative yield by adding ethanol to 4.

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Registry No. **3a**, 97011-51-3; **3b**, 96999-77-8; 4, 97011-50-2; **5a**, 36240-81-0; **5b**, 58159-59-4; **10a**, 96999-78-9; **10b**, 96999-79-0; **10c**, 96999-80-3; **11a**, 96999-81-4; **11c**, 96999-82-5; **12a**, 96999-84-7; **12c**, 97042-25-6; **13a**, 96999-86-9; (1,4-dimethyl-2,6-diphenylphosphinine)lithium, 96999-87-0; (4-*tert*-butyl-1-methyl-2,6-diphenylphosphinine)lithium, 96999-88-1; iron(II) chloride, 7758-94-3; dicarbonyl(η^5-cyclopentadienyl)iron iodide, 12078-28-3.

Iron Complexes of Phosphinine Derivatives: The Crystal Structure of [η^5-t-BuPh$_2$C$_5$H$_2$P(CH$_3$)]$_2$Fe

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The structure of the title compound was determined by single-crystal X-ray diffraction at $T = 22$ °C and refined to $R_w = 0.051$ for 1807 reflections. The space group is *Pbcn* ($Z = 8$) with $a = 19.277$ (5) Å, $b = 19.921$ (3) Å, and $c = 19.300$ (4) Å. The bis(phosphinine) sandwich complex has the gauche-eclipsed conformation, and iron is five-carbon η^5-bonded to both phosphinine rings (mean Fe–C distance = 2.16 Å, Fe–P = 2.91 Å). All the C–C distances in the almost planar C_5 part of the rings are very similar (mean 1.41 Å), and the "chair angles" between these C_5 planes and the C1–P–C5 planes are 33.3° and 37.4°. Thus a relationship to the "open ferrocenes" is obvious.

Introduction

Dimroth et al.[1] have synthesized a series of new substituted phosphinine sandwich complexes of iron. The neutral complexes as well as the corresponding biphosphonium dications reveal spectroscopic features similar to those of the "open ferrocenes" of Ernst et al.[2] To elucidate the interesting stereochemical properties, a single-crystal X-ray structure analysis has been performed on a typical representative of a neutral phosphinine complex: bis(4-*tert*-butyl-1-methyl-2,6-diphenylphosphinine)iron (1).

Experimental Section

The synthesis of 1 is reported in the preceding paper.[1] A dark brown, small needle-shaped crystal of 1 which has been obtained from benzene/hexane was investigated on a four-circle diffractometer (CAD4). The experimental details are summarized in Table I. The lattice parameters were refined from 25 machine-centered high-angle reflections.

Table I. Experimental Data for the Crystal Structure Determination of Bis(4-*tert*-butyl-1-methyl-2,6-diphenylphosphinine)iron (1)

	Crystal Data
formula	$C_{44}H_{48}P_2Fe$
M_r	694.7
dimens	approximately 0.35 × 0.1 × 0.08 mm^3
absorptn	$\mu = 4.8$ cm^{-1}, no correction
space group	*Pbcn*, $Z = 8$
lattice consts (Mo Kα)	$a = 19.277$ (5) Å, $b = 19.921$ (3) Å, $c = 19.300$ (4) Å
temp	295 K
density	$d_{\text{calcd}} = 1.245$ g cm^{-3}
	Data Collection
diffractometer	four-circle CAD4 (Enraf-Nonius)
radiation	Mo Kα, graphite monochromator
scan type	ω scan
scan width	$(1.2 + 0.35 \tan \theta)$° and 25% on the left and right side of a reflection for background determination
measuring range	$1° < \theta < 20°$, $+h,+k,+l$
reflctns	3478, 1807 independent, $>3\sigma(F_o)$
	Computing
computer	Telefunken TR440 and Sperry 1100/62 at the Rechenzentrum der Universität Marburg
programs	system STRUX[3] with programs SHELX[4] and ORTEP[5]
	atomic scattering factors for neutral atoms[6]
	anomalous scattering corrected[7]

Structure Determination of 1. The systematic absences $0kl$, $k \neq 2n$, $h0l$, $l \neq 2n$, and $hk0$, $h + k \neq 2n$, are consistent with the space group *Pbcn*. The structure was solved by the heavy-

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