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Synthesis of Racemic Aminoalkylferrocenyldichlorophosphanes and -dialkylphosphonites and Their Conversion to Primary Phosphanes†

Carolin Limburg,† Peter Lönnecke,† Santiago Gómez-Ruiz,†,‡ and Evamarie Hey-Hawkins*,†

†*Institut für Anorganische Chemie der Universität Leipzig, Johannisallee 29, D-04103 Leipzig, Germany, and* ‡*Departamento de Química Inorgánica y Analítica, ESCET, Universidad Rey Juan Carlos, 28933 Móstoles, Madrid, Spain*

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The dichlorophosphanyl-substituted ferrocene complexes 1-dichlorophosphanyl-2-*N*,*N*-dimethylaminomethyl-3-diphenylphosphanylferrocene (**2a**) and 1-dichlorophosphanyl-2-*N*,*N*-dimethylaminomethyl-3,1′-bis(diphenylphosphanyl)ferrocene (**2b**) have been prepared by the reaction of phosphorus trichloride with the corresponding lithiated aminoalkylferrocene precursors. The crystal structure of **2a** reveals a short N···P distance, which is suggestive of a weak N→P dative bond. Using diethyl chlorophosphite instead of phosphorus trichloride as electrophile gave 1-diethoxyphosphanyl-2-*N*,*N*-dimethylaminomethyl-3-diphenylphosphanylferrocene (**3a**) and 1-diethoxyphosphanyl-2-*N*,*N*-dimethylaminomethyl-3,1′-bis(diphenylphosphanyl)ferrocene (**3b**), respectively. The latter was converted to the corresponding dimethoxy compound **4b** by reaction with methanol. Crystal structures of **3** and **4b** have been determined. Reduction of **2**, **3**, and **4b** with $LiAlH_4$ or $LiAlH_4/SiMe_3Cl$ yielded the primary phosphanes 1-diphenylphosphanyl-2-*N*,*N*-dimethylaminomethyl-3-phosphanylferrocene (**5a**) and 1,1′-bis(diphenylphosphanyl)-2-*N*,*N*-dimethylaminomethyl-3-phosphanylferrocene (**5b**). The latter was also structurally characterized by X-ray diffraction.

Introduction

Since the first synthesis of 1,1′-bis(diphenylphosphanyl)-ferrocene (DPPF),[1] ferrocene has proved to be a versatile substituent for phosphanes because of its rich chemistry, stability, and redox properties.[2] Ferrocenylphosphanes attract constant attention for their coordination chemistry, with significant recent emphasis on the application of chiral ferrocenylphosphane metal complexes in asymmetric homogeneous catalysis. The first chiral phosphanylferrocene complex, (*R*)-*N*,*N*-dimethyl-1-[(*S*)-2-(diphenylphosphanyl)ferrocenyl]ethylamine ((*R*,*S*)-PPFA), was prepared by Hayashi et al. in 1974[3] and was successfully applied in homogeneous catalysis only two years later.[4] Henceforward, 1,2-disubstituted phosphanylferrocenes have been of special interest in organometallic and coordination chemistry because of their planar chirality, for which racemization is virtually impossible.[5] The number of such planar-chiral phosphanylferrocenes has been growing ever since,[6] as has the number of applications of these complexes as ligands in asymmetric reactions such as hydrogenation, Grignard reactions, hydrosilylations, and aldol reactions.[2−4,7] Considering the large amount of information published concerning the chemistry of phosphane ligands containing ferrocenyl moieties, it is surprising that only very little is known about primary ferrocenyl-substituted phosphanes.

Primary phosphanes have generally a very rich chemistry accessible through the reactivity of the P−H bonds.[8] Reactions with unsaturated systems, carbonyl groups, Michael acceptors, alkyl and aryl halides, halogens, alkali metals, and Lewis acids are well known and provide many possibilities to produce functionalized secondary or tertiary phosphanes, which may even contain chiral phosphorus centers.[9] Owing to the reactive character of the P−H bonds, preparation of primary phosphanes with ferrocenyl groups incorporated into the molecule would provide a useful means for further

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*To whom correspondence should be addressed. E-mail: hey@rz.uni-leipzig.de.

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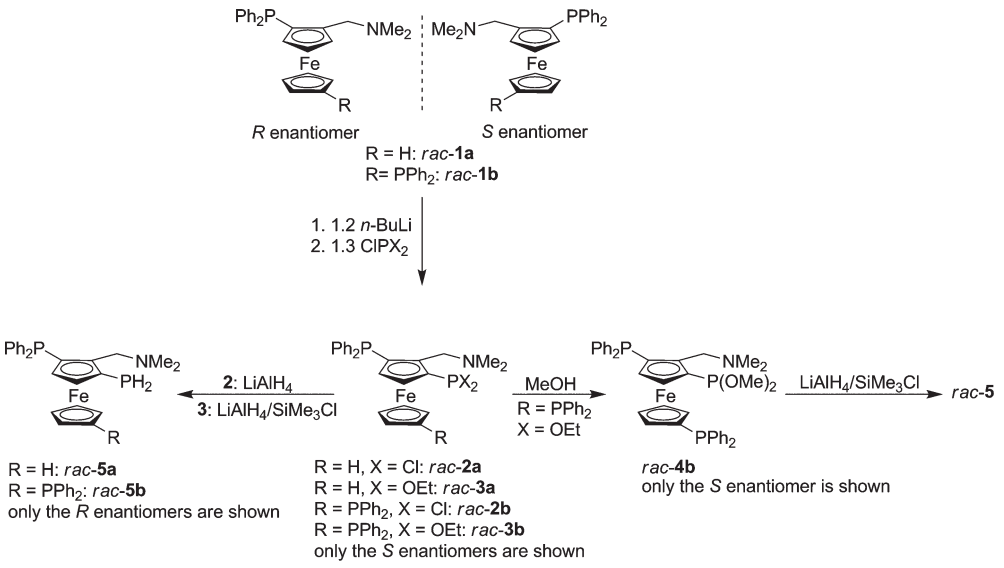
Scheme 1



formation of other ferrocene-containing compounds. However, primary phosphanes in which a ferrocene unit is directly attached to the phosphorus atom are not well investigated, possibly because in most reported cases the compounds were highly air sensitive and could only be handled in an inert atmosphere. In addition to the known phosphanylferrocene[10] and 1,1′-bis(phosphanyl)ferrocene,[11] we recently reported the synthesis of planar-chiral primary aminoalkylphosphanylferrocenes by reduction of the corresponding ferrocenylphosphonates[12] or ferrocenyldichlorophosphanes.[13]

With regard to the numerous applications of compounds such as *N*,*N*-dimethyl-1-[2-(diphenylphosphanyl)ferrocenyl]-ethylamine (PPFA)[3] and *N*,*N*-dimethyl-1-[1′,2-bis(diphenylphosphanyl)ferrocenyl]ethylamine (BPPFA),[14] as well as the versatile synthetic possibilities offered by reactivity of P−H bonds, we were interested in including a primary phosphanyl group in well-known planar-chiral ferrocenylphosphanes for the following preparation of alkali-metal ferrocenylphosphanides, which may be suitable precursors for the synthesis of novel phosphines[15,16] or transition-metal phosphanides, which are known to exhibit versatile reactivity.[17]

As a first step in the attainment of this goal, we herein report the facile and convenient synthesis of the novel racemic primary phosphanes 1-diphenylphosphanyl-2-*N*,*N*-dimethylaminomethyl-3-phosphanylferrocene (**5a**) and 1,1′-bis(diphenylphosphanyl)-2-*N*,*N*-dimethylaminomethyl-3-phosphanylferrocene (**5b**). The preparation of the corresponding ferrocenyldichlorophosphanes (**2**) and -dialkylphosphonites (**3** and **4b**), which are the key intermediates in the synthesis of the primary phosphanes, is also described.

Results and Discussion

Readily available aminoalkylferrocenyldiphenylphosphanes (**1**)[13,18] were used as starting materials for the synthesis of the desired primary ferrocenylphosphanes **5**. Suitable precursors containing a PX_2 group, which can be converted into a PH_2 group, needed to be prepared first. As shown in Scheme 1,

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racemic 1-diphenylphosphanyl-2-*N*,*N*-dimethylaminomethylferrocene (**1a**) and racemic 1,1′-bis(diphenylphosphanyl)-2-*N*,*N*-dimethylaminomethylferrocene (**1b**) were further functionalized by *ortho*-selective lithiation and subsequent treatment with an electrophile.

Synthesis of Dichlorophosphanes 2a and 2b. The dichlorophosphanes **2** were prepared by reaction of the monolithiated species with a slight excess of PCl_3 at low temperature. The resulting compounds are stable in the solid state, but decompose in solution. In general, aminoalkylferrocenyldichlorophosphanes decompose in all common solvents. They are slightly more stable in chlorinated or aromatic solvents, whereas in nonpolar solvents such as *n*-hexane decomposition occurs rapidly.[13] Despite intense efforts, we were not able to purify **2b** by crystallization due to its fast decomposition even in CH_2Cl_2. Therefore, **2b** could be verified only as a crude product by $^{31}P\{^1H\}$ NMR spectroscopy ($\delta_P = -21.2$, -24.1, and 137.7 ppm). However, racemic **2a** was isolated by crystallization in a 66% yield and was consequently characterized by common analytical techniques. The $^{31}P\{^1H\}$ NMR spectra exhibit resonances of the diphenylphosphanyl and the dichlorophosphanyl group in the expected range ($\delta_P = -23.0$ and 138.3 ppm). A significant feature that is well known for ferrocenyldichlorophosphane complexes[13,19] is the exceptionally large $^1J_{CPCl_2}$ coupling constant, in this case 66.9 Hz, which can be observed in the $^{13}C\{^1H\}$ NMR spectrum. It is caused by the electronegativity of the chlorine substituents and the resultant enhanced s character of the hybrid orbitals of the phosphorus atom directed toward the cyclopentadienyl ring.[20]

The molecular structure of **2a** is depicted in Figure 1. The geometrical environment of both phosphorus atoms is distorted tetrahedral. Bending of the dimethylaminomethyl group toward the PCl_2 group indicates a weak N→P dative bond, similar to that observed for 1-dichlorophosphanyl-2-*N*,*N*-dimethylaminomethylferrocene.[13] The N···P1 distance of 2.680(2) Å, which is a little longer than that reported for the above example, but rather short in comparison to those reported for tertiary aminomethylarylphosphanes,[21] verifies the existence of such an interaction. The P−Cl bonds [P1−Cl1 2.1224(9), P1−Cl2 2.0922(8) Å] are longer than in structurally characterized aryldichlorophosphanes[22] and 1,1′-bis(dichlorophosphanyl)ferrocene,[19,23] which in general lie between 2.05 and 2.08 Å. The unusually long P1−Cl1 bond (*trans* to the weak N→P dative bond) is also indicative of a dative interaction between P and N and in accordance with comparable compounds.[13,24] The weak dative bond is not retained in solution, as ^1H NMR measurements at room temperature show only one singlet for the two methyl groups attached to the nitrogen atom.

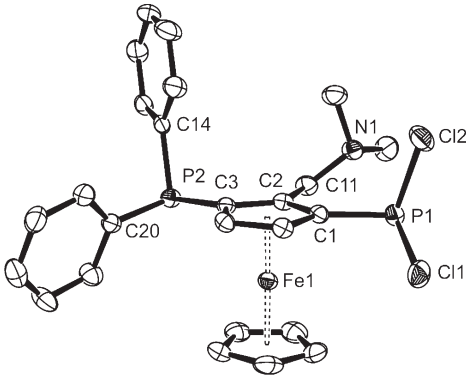

Figure 1. Molecular structure of **2a** (only the *S* enantiomer is shown) with thermal ellipsoids at the 50% probability level. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): P1−Cl1 2.1224(9), P1−Cl2 2.0922(8), P1−C1 1.799(2), P2−C3 1.818(2), P1···N1 2.680(2), C1−P1−Cl1 96.76(7), C1−P1−Cl2 100.94(8), Cl1−P1−Cl2 95.68(4).

Synthesis of Diethylphosphonites 3 and Dimethylphosphonite 4b. In a similar procedure to the synthesis of **2**, diethylphosphonites **3** can be prepared by treatment of the monolithiated ferrocenyl species with diethyl chlorophosphite. The resulting diethylphosphonites are stable in solution and in the solid state, which makes them much more convenient to handle than the dichloro-substituted compounds. Hence, racemic **3** could be isolated with better yields than the corresponding dichlorophosphanes (**3a**: 82%; **3b**: 68%). Treating **3b** with an excess of methanol leads to quantitative exchange of the ethoxyl groups and formation of racemic compound **4b**.

In the $^{31}P\{^1H\}$ NMR spectra the resonances of the diphenylphosphanyl groups [$\delta_P = -23.9$ (**3a**); -24.4 and -18.7 (**3b**); -24.5 and -18.8 ppm (**4b**)] and of the dialkylphosphonite groups [$\delta_P = 158.4$ (**3a**); 157.2 (**3b**); 162.9 ppm (**4b**)] appear in the expected range. Due to the less electronegative character of the alkoxyl substituents compared to the chloro substituents, the $^1J_{CP(OR)_2}$ coupling constant [23.4 (**3a**), 23.8 (**3b**), and 25.4 Hz (**4b**)] is significantly smaller than $^1J_{CPCl_2}$ observed for **2b**.

The molecular structures of the dialkylphosphonites are shown in Figure 2; selected bond lengths and angles are given in Table 1. As for the dichlorophosphanyl compound, the geometrical environment of all phosphorus atoms is distorted tetrahedral. The dimethylaminomethyl group faces toward the phosphonite group in **3a**, whereas in the 1,1′-bis(diphenyl)phosphanyl-substituted compounds it faces toward the diphenylphosphanyl group. Even though the N···P1 distance of **3a** of 3.158(1) Å is significantly longer than that of **2a**, it is still smaller than the sum of the van der Waals radii of 3.40 Å.[25] Hence, the presence of a weak N→P dative bond can be assumed. For the cyclic amino phosphonite PhP(μ-OC_6H_2-2,4-Me_2-6-CH_2)$_2$NMe such an interaction is described for a N···P1 distance of 3.152(3) Å.[26] However, the P−O bond lengths are in the same range as in other reported aromatic phosphonites and do not verify the presence of a N→P dative interaction.[26,27] Steric

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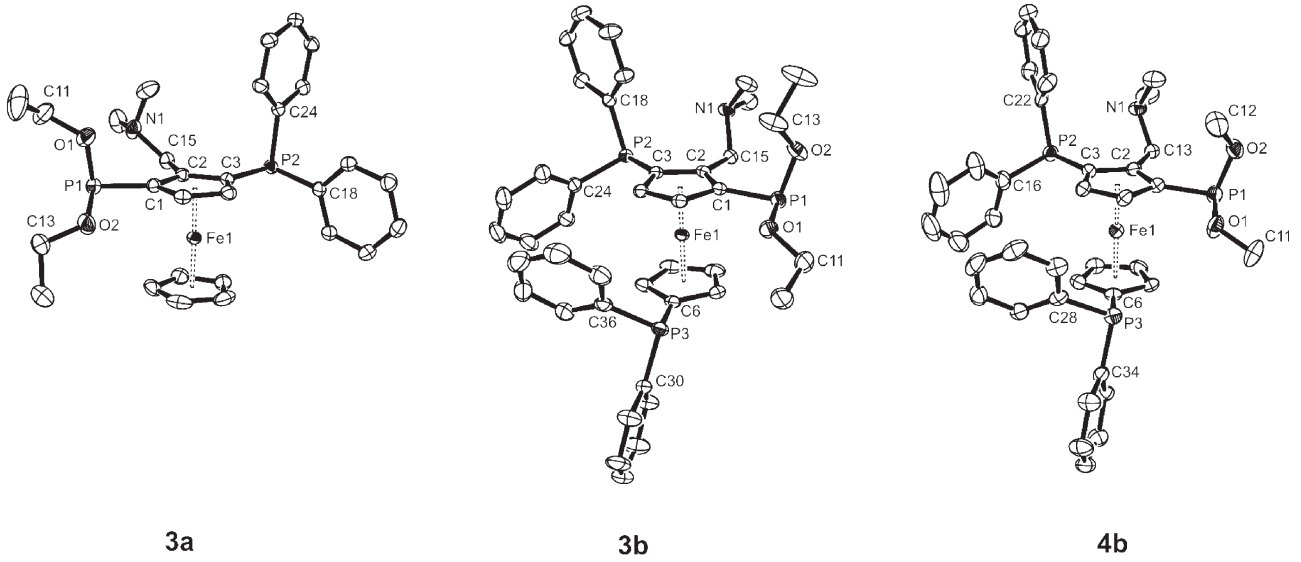

Figure 2. Molecular structures of **3a** (only the *R* enantiomer is shown), **3b** (only the *S* enantiomer is shown), and **4b** (only the *S* enantiomer is shown) with thermal ellipsoids at the 50% probability level. H atoms have been omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 3a, 3b, and 4b

	3a	3b	4b
P1−O1	1.639(1)	1.630(2)	1.632(2)
P1−O2	1.645(1)	1.619(2)	1.619(2)
P1−C1	1.804(1)	1.810(2)	1.803(2)
P2−C3	1.815(1)	1.816(2)	1.815(2)
P3−C6		1.810(2)	1.817(2)
O1−C11	1.432(2)	1.437(3)	1.415(3)
O2−C13	1.438(2)	1.442(3)	
O2−C12			1.433(3)
P1···N1	3.158(1)	4.365(2)	4.480(2)
P2···N1	4.541(1)	3.422(2)	3.187(2)
C1−P1−O1	95.55(6)	95.27(8)	95.0(1)
C1−P1−O2	94.99(5)	103.23(8)	103.3(1)
O1−P1−O2	102.34(6)	103.60(8)	102.99(9)

interactions might be the reason for the comparably short N···P distance found in **3a** and also in **4b**, in which the N···P2 distance is only 3.187(2) Å.

Synthesis of Primary Phosphanes 5a and 5b. According to Scheme 1, all compounds described above are suitable starting materials for the synthesis of the corresponding primary phosphanes **5**. Due to the higher reactivity of the P−Cl bonds, the dichlorophosphanyl ferrocene complexes can be reduced to the primary phosphanes by treatment with $LiAlH_4$ at room temperature, whereas the dialkylphosphonites can only be converted quantitatively by using a mixture of $LiAlH_4$ and $SiMe_3Cl$. Even though the dialkylphosphonites are stable in solution and therefore easier to handle, the most convenient and high-yielding method for preparing the primary phosphanes is via the dichlorophosphanes. While diethyl ether can be used as solvent for the reduction with $LiAlH_4$,[10] THF is required for the reaction with $LiAlH_4$/$SiMe_3Cl$.[11,28] The variation in the reaction procedure seems to be marginal but leads to a tremendous and yield-influencing difference in the workup procedure. Therefore, the primary phosphanes can be obtained only in poor yields of 45−49% from the dialkylphosphonites. As purification of the dichlorophosphanes is also a low-yield procedure, the best-yield synthetic method for the preparation of primary phosphanes is the procedure that was already described for the synthesis of 1-phosphanyl-2-*N*,*N*-dimethylaminomethylferrocene.[13] Thus, crude **2a** or **2b** was used without any further purification to give racemic **5a** in 66% yield and racemic **5b** in 70% yield.

Formation of the primary phosphanes can be shown by ^{31}P NMR spectroscopy. The resonances of the PPh_2 groups are very similar to those of the dichlorophosphane or the dialkyl phosphonite derivatives [δ_P = −23.2 (**5a**); −23.7 and −18.8 ppm (**5b**)]. The signal assigned to the PH_2 group appears as a triplet at lower frequencies [δ_P = −150.1 ppm, $^1J_{PH}$ = 199.6 Hz (**5a**); −150.3 ppm, $^1J_{PH}$ = 199.9 Hz (**5b**)]. The electronegative or electropositive character of the substituents on the phosphorus atom has a strong influence on the direct carbon−phosphorus coupling constant, as was already observed for **2**, **3**, and **4b**. In the case of the primary phosphanes, the lower electronegativity of the hydrogen atoms results in a rather small direct carbon−phosphorus coupling, $^1J_{CPH_2}$, of 9.5 Hz (**5a**) and 10.6 Hz (**5b**).

The primary phosphanes **5** are crystalline solids that are air-stable in the solid state and stable in solution toward oxygen over a prolonged period of time (at least 5 days). They are thus two rare examples of air-stable primary phosphanes.[13,29] Despite intense efforts, no crystals of **5a** suitable for X-ray diffraction were obtained. However, the molecular structure of **5b**, which is depicted in Figure 3, could be determined. It represents, to the best of our knowledge, the second structurally characterized primary phosphanylferrocene without a spacer between the phosphanyl group and the ferrocene moiety. The hydrogen atoms at P1 could be located, whereas all other hydrogen atoms were included in a riding mode. The P1−C1 bond length is within the same range as in other reported aromatic primary

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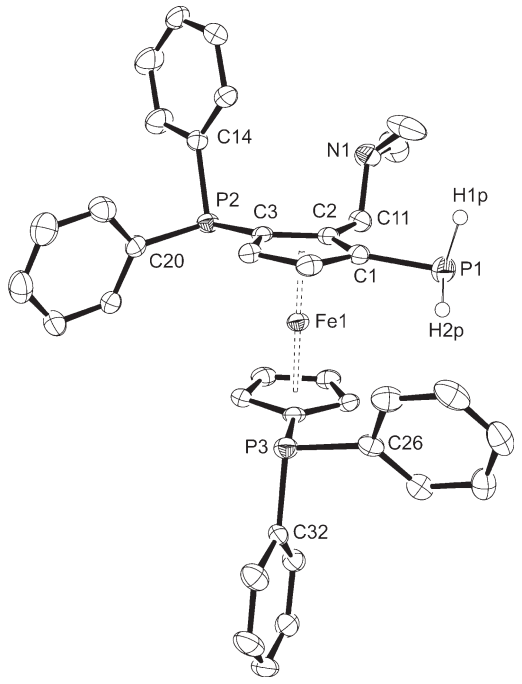

Figure 3. Molecular structure of **5b** (only the *R* enantiomer is shown) with thermal ellipsoids at the 50% probability level. H atoms except at P have been omitted for clarity. Selected bond lengths (Å) and angles (deg): P1−H1p 1.38(2), P1−H2p 1.38(2), P1−C1 1.821(2), P2−C3 1.814(2), C1−P1−H1p 97.7(8), C1−P1−H2p 97.3(9), H1p−P1−H2p 90(1).

phosphanes.[13,30] Also, within the standard deviation, the P1−H distances and the H−P1−H angle are in similar ranges to those observed in other structurally characterized primary phosphanes for which the protons were located.[13,30b,31] In contrast to **2a** or **3b** the dimethylaminomethyl group is bent out of the plane of the cyclopentadienyl ring, so that no N→P dative bond is present.

Conclusion

The introduction of a primary phosphanyl group into diphenylphosphanyl-substituted aminoalkylferrocene complexes can be achieved by *ortho*-selective lithiation and subsequent reaction with an electrophile. By this simple reaction pathway we have synthesized the dichlorophosphanyl ferrocene complexes 1-dichlorophosphanyl-2-*N*,*N*-dimethylaminomethyl-3-diphenylphosphanylferrocene (**2a**) and 1-dichlorophosphanyl-2-*N*,*N*-dimethylaminomethyl-3,1′-bis(diphenylphosphanyl)ferrocene (**2b**) and the ferrocenylphosphonites 1-diethoxyphosphanyl-2-*N*,*N*-dimethylaminomethyl-3-diphenylphosphanylferrocene (**3a**) and 1-diethoxyphosphanyl-2-*N*,*N*-dimethylaminomethyl-3,1′-bis(diphenylphosphanyl)ferrocene (**3b**). We further prepared dimethylferrocenylphosphonite **4b** by reaction of **3b** with methanol. Compound **2b** could not be isolated but was detected by $^{31}P\{^1H\}$ NMR spectroscopy, whereas all other compounds were fully characterized by common analytical techniques and X-ray diffraction. Finally, we have presented the synthesis of the corresponding primary phosphanes from compounds **2**, **3**, and **4b**. A facile method is the use of crude **2** and $LiAlH_4$. The primary phosphanes 1-diphenylphosphanyl-2-*N*,*N*-dimethylaminomethyl-3-phosphanylferrocene (**5a**) and 1,1′-bis-(diphenylphosphanyl)-2-*N*,*N*-dimethylaminomethyl-3-phosphanylferrocene (**5b**) are rare examples of air-stable primary phosphanes and could also be characterized by common analytical techniques. **5b** could further be structurally characterized by X-ray diffraction.

Experimental Section

General Considerations. All manipulations were carried out by standard Schlenk techniques under an atmosphere of dry, high-purity nitrogen. Diethyl ether, toluene, and *n*-hexane were taken from an MBRAUN solvent purification system MB SPS-800; *n*-pentane was distilled from sodium. All these solvents were nitrogen-saturated and stored over potassium mirror. EtOH and MeOH were dried over sodium and distilled. H_2O was degassed in a nitrogen stream in an ultrasonic bath. 2-(*N*,*N*-Dimethylaminomethyl)-1-diphenylphosphanylferrocene (**1a**)[18] and 2-(*N*,*N*-dimethylaminomethyl)-1,1′-bis(diphenylphosphanyl)-ferrocene (**1b**)[14] were synthesized according to literature procedures. Other chemicals were obtained from commercial sources and used as supplied, except PCl_3, which was distilled and degassed with nitrogen prior to use. ^1H (400.13 MHz), ^{13}C (100.16 MHz), and ^{31}P (161.98 MHz) NMR spectra were recorded on a Bruker Avance DRX 400 spectrometer at +20 °C in C_6D_6 and referenced to tetramethylsilane (TMS).[32] The signals of the ^1H, ^{13}C, and ^{31}P NMR spectra were assigned by $^1H\{^{31}P\}$, $^1H-^1H$ COSY, APT, $^1H-^{13}C$ HMQC, $^1H-^{13}C$ HMBC, and $^{13}C\{^{31}P\}$ experiments. EI mass spectra were recorded on a ZAB-HSQ-VG12-520 Analytical Manchester spectrometer or a MASPEC II spectrometer; ESI mass spectra were recorded on a Bruker-Daltonics FT-ICR-MS APEX II. FTIR spectra were recorded on a Perkin-Elmer Spectrum 2000 spectrometer. Melting points were determined in sealed glass capillaries under nitrogen and are uncorrected.

1-Dichlorophosphanyl-2-*N*,*N*-dimethylaminomethyl-3-diphenylphosphanylferrocene (*rac*-2a). A solution of *n*-BuLi (5.10 mL, 12.08 mmol, 2.37 M in *n*-hexane) was slowly added to a solution of **1a** (4.69 g, 10.98 mmol) in diethyl ether (50 mL). The mixture was stirred for 8 h and slowly added to a solution of PCl_3 (1.81 g, 13.17 mmol) in diethyl ether (10 mL) at −80 °C. The mixture was warmed to room temperature overnight and filtered. The solvent was evaporated and the residue dried *in vacuo*. Recrystallization from a mixture of toluene and *n*-hexane (1:10) at −18 °C gave pure **2a** as orange crystals. Yield: 3.83 g (66%). Mp: 131 °C (dec). ^1H NMR: δ 1.91 (s, 6H, $N(CH_3)_2$), 3.03 (d, $^2J_{HH}$ = 14.4 Hz, 1H, CH_2N), 3.70 (d, $^2J_{HH}$ = 14.4 Hz, 1H, CH_2N), 3.90 (s, 1H, C_5H_2 *o* to PPh_2), 4.04 (s, 5H, C_5H_5), 4.97 (s, 1H, C_5H_2 *o* to PCl_2), 7.01 (br s, 3H, C_6H_5), 7.10 (br s, 3H, C_6H_5), 7.27 (br s, 2H, C_6H_5 *o* to P), and 7.50 (br s, 2H, C_6H_5 *o* to P) ppm. $^{13}C\{^1H\}$ NMR: δ 45.2 (s, $N(CH_3)_2$), 56.9 (dd, $^3J_{CPCl_2}$ = 4.4 Hz, $^3J_{CPPh_2}$ = 7.2 Hz, CH_2N), 71.8 (s, C_5H_5), 72.0 (d, $^2J_{CPCl_2}$ = 1.4 Hz, C_5H_2 *o* to PCl_2), 73.5 (d, $^2J_{CPPh_2}$ = 1.6 Hz, C_5H_2 *o* to PPh_2), 77.9 (d, $^1J_{CPPh_2}$ = 11.6 Hz, $C_{Fc}PPh_2$), 85.1 (dd, $^1J_{CPCl_2}$ = 66.9 Hz, $^3J_{CPPh_2}$ = 3.1 Hz, $C_{Fc}PCl_2$), 97.1 (dd, $^2J_{CPCl_2}$ = 9.2 Hz, $^2J_{CPPh_2}$ = 22.8 Hz, $C_{Fc}CH_2N$), 128.3−128.4 (3 signals overlapping with C_6D_6, C_6H_5), 129.3 (s, C_6H_5), 132.7 (d, $^2J_{CPPh_2}$ = 19.1 Hz, C_6H_5 *o* to P), 134.8 (d, $^2J_{CPPh_2}$ = 21.2 Hz, C_6H_5 *o* to P), 136.7 (d, $^1J_{CPPh_2}$ = 10.7 Hz, $C_{Ph}P$), and 138.8 (d, $^1J_{CPPh_2}$ = 10.7 Hz, $C_{Ph}P$) ppm. $^{31}P\{^1H\}$ NMR: δ −23.0 (PPh_2) and 138.3 (PCl_2) ppm. FT-IR (KBr; cm^{-1}): 3069 (w), 3050 (w), 2945 (m), 2863 (s), 2828 (s), 2785 (s), 1962 (w), 1895 (w), 1823 (w), 1776 (w), 1728 (w), 1667 (w), 1585 (w), 1477 (m), 1457 (s), 1434 (s), 1410 (m), 1373 (m),

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1337 (w), 1310 (w), 1253 (m), 1226 (m), 1173 (m), 1131 (s), 1091 (s), 1024 (s), 1001 (s), 925 (w), 837 (s), 746 (s), 698 (s), 616 (w), 501 (s), 460 (s), 442 (s), and 416 (s). MS (EI pos. 14 eV; *m*/*z*): 527 [M^+] (99.6%), 500 (9.1%), 491 [$(M - Cl)^+$] (9.3%), 477 (10.5%), 455 (42.2%), 448 [$(M - HN(CH_3)_2 - Cl)^+$] (13.3%), 441 (11.1%), 427 [$(HM - PCl_2)^+$] (100%), and 414 (20.3%). Anal. Calcd for $C_{25}H_{25}Cl_2FeNP_2$: C, 56.85; H, 4.77; N, 2.65. Found: C, 56.96; H, 4.79; N, 2.69.

1-Dichlorophosphanyl-2-*N*,*N*-dimethylaminomethyl-3,1′-bis-(diphenylphosphanyl)ferrocene (*rac*-2b). The procedure for the preparation of **2a** was followed using **1b** (1.93 g, 3.15 mmol), *n*-BuLi (1.54 mL, 3.78 mmol, 2.45 M in *n*-hexane), and PCl_3 (0.56 g, 4.10 mmol). Pure **2b** could not be obtained due to its very fast decomposition in solution. $^{31}P\{^1H\}$ NMR: δ −21.2 (PPh_2), −24.1 (PPh_2), and 137.7 (PCl_2) ppm.

1-Diethoxyphosphanyl-2-*N*,*N*-dimethylaminomethyl-3-diphenylphosphanylferrocene (*rac*-3a). A solution of *n*-BuLi (4.94 mL, 12.36 mmol, 2.50 M in *n*-hexane) was slowly added to a solution of **1a** (4.40 g, 10.30 mmol) in diethyl ether (50 mL). After stirring for 8 h, the reaction mixture was cooled to −80 °C and diethylchlorophosphite (2.10 g, 13.39 mmol) was added slowly. The reaction mixture was warmed to room temperature overnight and filtered. The solvent was then evaporated and the residue dried *in vacuo* for 1 h at 50 °C. Recrystallization from *n*-pentane and storage at −64 °C gave **3a** as an orange solid. Crystals suitable for X-ray diffraction were obtained after recrystallizing twice from *n*-pentane at −18 °C. Yield: 4.62 g (82%). Mp: 88 °C. ^1H NMR: δ 1.13 (t, $^3J_{HH}$ = 7.0 Hz, 3H, OCH_2CH_3), 1.18 (t, $^3J_{HH}$ = 7.0 Hz, 3H, OCH_2CH_3), 2.06 (s, 6H, $N(CH_3)_2$), 3.75 (br m, 2H, OCH_2CH_3), 3.76 (d, $^2J_{HH}$ = 13.3 Hz, 1H, CH_2N), 3.91 (br m, 2H, OCH_2CH_3), 3.99 (d, $^2J_{HH}$ = 13.3 Hz, 1H, CH_2N), 4.07 (s, 5H, C_5H_5), 4.11 (s, 1H, C_5H_2 *o* to PPh_2), 4.76 (s, 1H, C_5H_2 *o* to $P(OEt)_2$), 7.09 (br m, 6H, C_6H_5), 7.41 (br m, 2H, C_6H_5 *o* to P), and 7.69 (br s, 2H, C_6H_5 *o* to P) ppm. $^{13}C\{^1H\}$ NMR: δ 16.8 (d, $^3J_{CP(OEt)_2}$ = 4.2 Hz, OCH_2CH_3), 17.3 (d, $^3J_{CP(OEt)_2}$ = 6.4 Hz, OCH_2CH_3), 44.6 (s, $N(CH_3)_2$), 56.8 (pt, $^3J_{CP(OEt)_2}$ = 6.3 Hz, $^3J_{CPPh_2}$ = 7.9 Hz, CH_2N), 60.3 (d, $^2J_{CP(OEt)_2}$ = 3.7 Hz, OCH_2CH_3), 63.7 (d, $^2J_{CP(OEt)_2}$ = 22.2 Hz, OCH_2CH_3), 70.6 (s, C_5H_5), 71.2 (s, C_5H_2 *o* to $P(OEt)_2$), 72.7 (d, $^2J_{CPPh_2}$ = 4.3 Hz, C_5H_2 *o* to PPh_2), 80.7 (dd, $^3J_{CP(OEt)2}$ = 2.0 Hz, $^1J_{CPPh_2}$ = 12.7 Hz, $C_{Fc}PPh_2$), 83.1 (dd, $^1J_{CP(OEt)_2}$ = 23.4 Hz, $^3J_{CPPh_2}$ = 2.6 Hz, $C_{Fc}P(OEt)_2$), 95.4 (dd, $^2J_{CP(OEt)_2}$ = 21.7 Hz, $^2J_{CPPh_2}$ = 24.5 Hz, $C_{Fc}CH_2N$), 127.4 (s, C_6H_5), 127.5−127.9 (2 signals, obscured by C_6D_6, C_6H_5), 128.7 (s, C_6H_5), 132.5 (d, $^2J_{CPPh_2}$ = 18.4 Hz, C_6H_5 *o* to P), 135.4 (d, $^2J_{CPPh_2}$ = 22.0 Hz, C_6H_5 *o* to P), 139.0 (d, $^1J_{CPPh_2}$ = 10.9 Hz, $C_{Ph}P$), and 141.1 (d, $^1J_{CPPh_2}$ = 9.9 Hz, $C_{Ph}P$) ppm. $^{31}P\{^1H\}$ NMR: δ −23.9 (PPh_2) and 158.4 ($P(OEt)_2$). FT-IR (KBr; cm^{-1}): 3054 (m), 2974 (s), 2941 (s), 2863 (s), 2812 (s), 2768 (s), 1585 (w), 1475 (m), 1453 (m), 1434 (s), 1382 (s), 1343 (w), 1249 (m), 1226 (m), 1178 (m), 1160 (m), 1128 (s), 1093 (s), 1044 (s), 1000 (m), 911 (s), 843 (m), 816 (m), 748 (s), 723 (s), 698 (s), 623 (w), 526 (m), and 498 (s). MS (EI pos. 14 eV; *m*/*z*): 547 [M^+] (100%), 518 [$(M - CH_2CH_3)^+$] (3.8%), and 504 [$(M - N(CH_3)_2)^+$] (4.0%). Anal. Calcd for $C_{29}H_{35}FeNO_2P_2$: C, 63.63; H, 6.44; N, 2.56. Found: C, 63.65; H, 6.51; N, 2.57.

1-Diethoxyphosphanyl-2-*N*,*N*-dimethylaminomethyl-3,1′-bis-(diphenylphosphanyl)ferrocene (*rac*-3b). The procedure for the preparation of **3a** was followed using **1b** (2.89 g, 4.73 mmol), *n*-BuLi (2.31 mL, 5.67 mmol, 2.45 M in *n*-hexane), and diethylchlorophosphite (1.03 g, 6.62 mmol). Pure **3b** was obtained as an orange solid by recrystallization from EtOH at −64 °C followed by a second recrystallization from *n*-hexane at −64 °C. Crystals suitable for X-ray diffraction were obtained after a third recrystallization from *n*-pentane at −18 °C. Yield: 2.35 g (68%). Mp: 55 °C. ^1H NMR: δ 1.14 (t, $^3J_{HH}$ = 7.0 Hz, 3H, OCH_2CH_3), 1.27 (t, $^3J_{HH}$ = 7.0 Hz, 3H, OCH_2CH_3), 2.05 (s, 6H, $N(CH_3)_2$), 3.46 (s, 1H, C_5H_4), 3.76 (br m, 3H, OCH_2CH_3 and CH_2N), 3.95 (br m, 4H, OCH_2CH_3, CH_2N and C_5H_2), 4.31 (s, 1H, C_5H_4), 4.50 (s, 1H, C_5H_4), 4.52 (s, 1H, C_5H_4), 4.91 (s, 1H, C_5H_2), 6.99 (br m, 12H, C_6H_5), 7.34 (br m, 6H, C_6H_5 *o* to P), and 7.54 (br m, 2H, C_6H_5 *o* to P) ppm. $^{13}C\{^1H\}$ NMR: δ 16.9 (d, $^3J_{CP(OEt)_2}$ = 4.2 Hz, OCH_2CH_3), 17.5 (d, $^3J_{CP(OEt)_2}$ = 7.1 Hz, OCH_2CH_3), 44.6 (s, $N(CH_3)_2$), 56.6 (pt, $^3J_{CP(OEt)_2}$ = $^3J_{CPPh_2}$ = 7.0 Hz, CH_2N), 60.4 (d, $^2J_{CP(OEt)_2}$ = 3.7 Hz, OCH_2CH_3), 64.1 (d, $^2J_{CP(OEt)_2}$ = 22.6 Hz, OCH_2CH_3), 73.8 (s, C_5H_4), 73.9 (s, C_5H_2), 74.0 (s, C_5H_2), 74.2 (s, C_5H_4), 74.3 (s, C_5H_4), 76.8 (d, $^2J_{CPPh_2}$ = 24.3 Hz, C_5H_4 *o* to PPh_2), 78.3 (d, $^1J_{CPPh_2}$ = 10.7 Hz, $C_{Fc}PPh_2$ of C_5H_4), 81.7 (d, $^1J_{CPPh_2}$ = 14.0 Hz, $C_{Fc}PPh_2$ of C_5H_2), 84.4 (dd, $^1J_{CP(OEt)_2}$ = 23.8 Hz, $^3J_{CPPh_2}$ = 2.3 Hz, $C_{Fc}P(OEt)_2$ of C_5H_2), 95.7 (dd, $^2J_{CP(OEt)_2}$ = 21.1 Hz, $^2J_{CPPh_2}$ = 24.5 Hz, $C_{Fc}CH_2N$), 127.4−128.1(6 signals overlapping with C_6D_6, C_6H_5), 128.5 (s, C_6H_5), 128.7 (s, C_6H_5), 132.5 (d, $^2J_{CPPh_2}$ = 18.3 Hz, C_6H_5 *o* to P), 132.8 (d, $^2J_{CPPh_2}$ = 18.9 Hz, C_6H_5 *o* to P), 134.1 (d, $^2J_{CPPh_2}$ = 20.7 Hz, C_6H_5 *o* to P), 135.1 (d, $^2J_{CPPh_2}$ = 22.1 Hz, C_6H_5 *o* to P), 138.4 (d, $^1J_{CPPh_2}$ = 10.6 Hz, $C_{Ph}P$), 138.6 (d, $^1J_{CPPh_2}$ = 11.5 Hz, $C_{Ph}P$), 140.4 (d, $^1J_{CPPh_2}$ = 11.9 Hz, $C_{Ph}P$), and 141.0 (d, $^1J_{CPPh_2}$ = 9.6 Hz, $C_{Ph}P$) ppm. $^{31}P\{^1H\}$ NMR: δ −24.4 (PPh_2 at C_5H_2), −18.7 (PPh_2 at C_5H_4), and 157.2 ($P(OEt)_2$). FT-IR (KBr; cm^{-1}): 3068 (m), 3052 (m), 2973 (s), 2935 (m), 2876 (m), 2815 (m), 2768 (m), 1953 (w), 1815 (w), 1585 (w), 1477 (m), 1453 (m), 1434 (s), 1385 (m), 1344 (w), 1326 (w), 1307 (w), 1260 (m), 1225 (m), 1180 (m), 1160 (m), 1131 (m), 1095 (m), 1028 (s), 921 (s), 841 (m), 742 (s), 697 (s), 631 (w), 503 (m), 472 (m), and 415 (w). MS (EI pos. 14 eV; *m*/*z*): 731 [M^+] (100%), 687 [$(M - N(CH_3)_2)^+$] (3.1%), 610 [$(M - Ph - HN(CH_3)_2)^+$] and [$(M - P(OEt)_2)^+$] (4.2%), 546 [$(M - PPh_2)^+$] (11.9%). Anal. Calcd for $C_{41}H_{44}FeNO_2P_3$: C, 67.31; H, 6.06; N, 1.91. Found: C, 67.32; H, 6.19; N, 1.88.

1-Dimethoxyphosphanyl-2-*N*,*N*-dimethylaminomethyl-3,1′-bis-(diphenylphosphanyl)ferrocene (*rac*-4b). Crude **3b** can be used directly without further purification. Crude **3b** obtained from **1b** (3.00 g, 4.91 mmol) was dissolved in methanol and refluxed for 10 min. The mixture was filtered and stored at 4 °C. Pure **4b** precipitated overnight as an orange powder. Crystals suitable for X-ray diffraction were grown after recrystallization from *n*-hexane at room temperature. Yield: 2.35 g (69%). Mp: 142 °C. ^1H NMR: δ 2.05 (s, 6H, $N(CH_3)_2$), 3.39 (d, $^3J_{PH}$ = 9.2 Hz, 3H, OCH_3), 3.47 (br s, 1H, C_5H_4), 3.60 (s, 3H, $^3J_{PH}$ = 9.2 Hz, OCH_3), 3.71 (d, 1H, $^2J_{HH}$ = 12.6 Hz, CH_2N), 3.80 (br s, 1H, C_5H_2), 3.95 (d, 1H, $^2J_{HH}$ = 12.6 Hz, CH_2N), 4.28 (br s, 1H, C_5H_4), 4.47 (s, 2H, C_5H_4 and C_5H_2), 4.88 (br s, 1H, C_5H_4), 7.00 (br m, 12H, C_6H_5), 7.34 (br m, 6H, C_6H_5 *o* to P), and 7.53 (br m, 2H, C_6H_5 *o* to P) ppm. $^{13}C\{^1H\}$ NMR: δ 44.5 (s, $N(CH_3)_2$), 50.8 (s, OCH_3), 55.1 (d, $^2J_{CP(OMe)_2}$ = 22.5 Hz, OCH_3), 56.6 (pt, $^3J_{CP(OMe)_2}$ = $^3J_{CPPh_2}$ = 7.0 Hz, CH_2N), 73.7 (s, C_5H_4), 73.9 (s, C_5H_4 and C_5H_2 *o* to $P(OMe)_2$), 74.1 (d, $^2J_{CPPh_2}$ = 4.5 Hz, C_5H_4 *o* to PPh_2), 74.2 (s, C_5H_4), 76.5 (dd, $^3J_{CP(OMe)_2}$ = 3.9 Hz, $^2J_{CPPh_2}$ = 23.8 Hz, C_5H_2 *o* to PPh_2), 78.5 (d, $^1J_{CPPh_2}$ = 10.7 Hz, $C_{Fc}PPh_2$ of C_5H_4), 81.8 (dd, $^3J_{CP(OMe)_2}$ = 1.9 Hz, $^1J_{CPPh_2}$ = 13.9 Hz, $C_{Fc}PPh_2$ of C_5H_2), 83.3 (dd, $^1J_{CP(OMe)_2}$ = 25.4 Hz, $^3J_{CPPh_2}$ = 2.7 Hz, $C_{Fc}P(OMe)_2$ of C_5H_2), 95.9 (dd, $^2J_{CP(OMe)_2}$ = 21.3 Hz, $^2J_{CPPh_2}$ = 24.5 Hz, $C_{Fc}CH_2N$), 127.2−128.2 (6 signals overlapping with C_6D_6, C_6H_5), 128.5 (s, C_6H_5), 128.8 (s, C_6H_5), 132.5 (d, $^2J_{CPPh_2}$ = 18.3 Hz, C_6H_5 *o* to P), 132.9 (d, $^2J_{CPPh_2}$ = 19.0 Hz, C_6H_5 *o* to P), 134.1 (d, $^2J_{CPPh_2}$ = 20.6 Hz, C_6H_5 *o* to P), 135.1 (d, $^2J_{CPPh_2}$ = 22.1 Hz, C_6H_5 *o* to P), 138.3 (d, $^1J_{CPPh_2}$ = 10.5 Hz, $C_{Ph}P$), 138.5 (d, $^1J_{CPPh_2}$ = 11.5 Hz, $C_{Ph}P$), 140.3 (d, $^1J_{CPPh_2}$ = 12.0 Hz, $C_{Ph}P$), and 141.0 (d, $^1J_{CPPh_2}$ = 9.6 Hz, $C_{Ph}P$) ppm. $^{31}P\{^1H\}$ NMR: δ −24.5 (PPh_2 at C_5H_2), −18.8 (PPh_2 at C_5H_4), and 162.9 ($P(OMe)_2$) ppm. FT-IR (KBr; cm^{-1}): 3421 (bw), 3069 (w), 3051 (w), 2969 (m), 2934 (m), 2856 (w), 2813 (m), 2768 (m), 2363 (w), 2346 (w), 1774 (w), 1702 (w), 1655 (w), 1586 (w), 1570 (w), 1560 (w), 1508 (w), 1478 (m), 1452 (m), 1434 (s), 1392 (w), 1340 (w), 1308 (w), 1261 (m), 1226 (m), 1196 (m), 1178 (m), 1162 (m), 1131 (s), 1091 (m), 1027 (s), 1017 (s), 841 (m), 818 (m), 741 (s), 698 (s), 673 (w), 630 (w), 539 (m), 520 (m), 502 (m), 489 (m), 478 (m), 468 (m), 453 (m), and 419 (w). MS (ESI pos., CH_2Cl_2/CH_3CN): 734 [$(M + O + CH_3)^+$] (13.7%), 718 [$(M + CH_3)^+$] (59.4%), 704 [$(M + H)^+$] (100%), 672 [$(M - OCH_3)^+$] (16.9%), 659 [$(M - N(CH_3)_2)^+$] (48.7%), 626 [$(M - C_6H_5)^+$] (13.3%), 567

Table 2. Crystal Data and Structure Refinement for Compounds 2−5

	2a	3a	3b	4b	5b
formula	$C_{25}H_{25}Cl_2FeNP_2$	$C_{29}H_{35}FeNO_2P_2$	$C_{41}H_{44}FeNO_2P_3 \cdot C_5H_{12}$	$C_{39}H_{40}FeNO_2P_3$	$C_{37}H_{36}FeNP_3$
fw (g/mol)	528.15	547.37	803.68	703.48	643.43
T (K)	130(2)	130(2)	130(2)	130(2)	130(2)
cryst syst	monoclinic	triclinic	triclinic	orthorhombic	triclinic
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_12_12_1$	$P\bar{1}$
a (Å)	8.8526(3)	9.9909(2)	10.0395(2)	12.8067(3)	10.2115(4)
b (Å)	9.7236(3)	10.5284(2)	10.9011(3)	16.4070(5)	11.4581(4)
c (Å)	28.5180(7)	13.2106(2)	22.0156(5)	17.0077(4)	14.7424(6)
α (deg)	90	92.110(1)	93.855(2)	90	99.385(3)
β (deg)	97.079(3)	93.214(1)	102.631(2)	90	97.342(3)
γ (deg)	90	103.366(1)	111.892(3)	90	108.169(3)
V (Å^3)	2436.1(1)	1348.06(4)	2151.92(9)	3573.7(2)	1587.4(1)
Z	4	2	2	4	2
D_c (g/cm^{-3})	1.440	1.349	1.240	1.308	1.346
μ (mm^{-1})	0.983	0.705	0.499	0.591	0.654
F(000)	1088	576	852	1472	672
cryst size (mm)	0.4 × 0.15 × 0.05	0.5 × 0.4 × 0.3	0.3 × 0.3 × 0.2	0.4 × 0.3 × 0.05	0.2 × 0.1 × 0.1
θ range data collection (deg)	2.88−30.51	2.69−30.51	2.56−30.51	2.95−26.37	2.62−26.37
ranges of h,k,l	$-12 \le h \le 12$ $-13 \le k \le 13$ $-40 \le l \le 40$	$-14 \le h \le 14$ $-15 \le k \le 15$ $-18 \le l \le 18$	$-14 \le h \le 14$ $-15 \le k \le 15$ $-28 \le l \le 31$	$-11 \le h \le 16$ $-10 \le k \le 20$ $-20 \le l \le 21$	$-12 \le h \le 12$ $-14 \le k \le 14$ $-18 \le l \le 18$
no. of reflns collected	27 233	47 842	36 205	14 020	29 482
no. of indept reflns and (R_{int})	7435 (0.0554)	8220 (0.0260)	13 085 (0.0299)	7294 (0.0385)	6500 (0.0593)
GOF (F^2)	0.903	1.089	1.008	0.788	0.872
final R_1 (all data)	0.1005	0.0385	0.0743	0.0566	0.0681
wR_2 (all data)	0.0856	0.0927	0.1284	0.0500	0.0679
Flack param x				0.004(11)	

[$(M - C_6H_5 - N(CH_3)_2)^+$] (17.2%). Anal. Calcd for $C_{39}H_{40}FeNO_2P_3$: C, 66.58; H, 5.73; N, 1.99. Found: C, 66.01; H, 5.81; N, 1.97.

General Procedure for the Reduction of Phosphonites 3 and 4b to Primary Phosphanes 5. The reducing agent was prepared by adding a solution of $SiMe_3Cl$ (2 equiv) in thf to a suspension of an equimolar amount of $LiAlH_4$ in thf at 0 °C. The resulting suspension was stirred for 2 h at room temperature. The phosphonite (1 equiv) was dissolved in thf and slowly added to the reducing agent at 0 °C. After stirring overnight at room temperature, the resulting suspension was hydrolyzed by slowly adding an excess of methanol at 0 °C. The reaction mixture was stirred for 1 h at 0 °C and then warmed to room temperature. The solvent was evaporated *in vacuo* and the orange residue extracted with *n*-hexane for 5 h. After removal of the solvent the remaining orange powder was purified as described below starting from **2a**.

1-Diphenylphosphanyl-2-*N*,*N*-dimethylaminomethyl-3-phosphanylferrocene (5a). 3a (2.42 g, 4.42 mmol), $SiMe_3Cl$ (0.96 g, 8.84 mmol), $LiAlH_4$ (0.34 g, 8.96 mmol). Yield: 0.91 g (45% based on **3a**).

1,1′-Bis(diphenylphosphanyl)-2-*N*,*N*-dimethylaminomethyl-3-phosphanylferrocene (5b). 3b (2.35 g, 3.21 mmol), $SiMe_3Cl$ (0.70 g, 6.44 mmol), $LiAlH_4$ (0.25 g, 6.59 mmol). Yield: 0.95 g (46% based on **3b**).

4b (1.88 g, 2.67 mmol), $SiMe_3Cl$ (0.58 g, 5.34 mmol), $LiAlH_4$ (0.21 g, 5.53 mmol). Yield: 0.84 g (49% based on **4b**).

1-Diphenylphosphanyl-2-*N*,*N*-dimethylaminomethyl-3-phosphanylferrocene (5a) Starting from 2a. Crude **2a** can be used directly without further purification. Crude **2a** obtained from **1a** (2.91 g, 6.81 mmol) was dissolved in diethyl ether (50 mL) (solution became slowly turbid due to decomposition of **2a**) and was added to a slurry of $LiAlH_4$ (0.52 g, 13.62 mmol) in diethyl ether (10 mL) at room temperature. The mixture was stirred overnight, filtered, and carefully hydrolyzed with slightly basic (one KOH pellet) water (50 mL) at 0 °C. After stirring for 1 h at room temperature the organic layer was separated and dried over $MgSO_4$. After filtration the solvent was removed and the oily residue dried *in vacuo*. Recrystallization from ethanol at −18 °C gave **5a** as an orange powder. Yield: 2.06 g (66% based on **1a**). Mp: 68.5 °C. ^{1}H NMR: δ 2.00 (s, 6H, $N(CH_3)_2$), 3.54 (d, $^2J_{HH}$ = 12.8 Hz, 1H, CH_2N), 3.75 (dd, $^2J_{HH}$ = 12.4 Hz, $^1J_{PH}$ = 199.9 Hz, 1H, PH_2), 3.82 (s, 5H, C_5H_5), 3.89 (dd, $^2J_{HH}$ = 12.4 Hz, $^1J_{PH}$ = 199.4 Hz, 1H, PH_2), 3.91 (d, $^2J_{HH}$ = 12.8 Hz, 1H, CH_2N), 3.97 (br s, 1H, C_5H_2 *o* to PPh_2), 4.24 (br s, 1H, C_5H_2 *o* to PH_2), 7.04 (br m, 6H, C_6H_5), 7.36 (br m, 2H, C_6H_5 *o* to P), and 7.64 (br m, 2H, C_6H_5 *o* to P) ppm. $^{13}C\{^1H\}$ NMR: δ 44.5 (s, $N(CH_3)_2$), 56.8 (dd, $^3J_{CPH_2}$ = 1.5 Hz, $^3J_{CPPh_2}$ = 8.6 Hz, CH_2N), 69.6 (dd, $^1J_{CPH_2}$ = 9.5 Hz, $^3J_{CPPh_2}$ = 3.0 Hz, $C_{Fc}PH_2$), 70.9 (s, C_5H_5), 72.7 (dd, $^3J_{CPH_2}$ = 3.2 Hz, $^2J_{CPPh_2}$ = 4.4 Hz, C_5H_2 *o* to PPh_2), 77.1 (d, $^2J_{CPH_2}$ = 9.3 Hz, C_5H_2 *o* to PH_2), 80.3 (dd, $^3J_{CPH_2}$ = 1.5 Hz, $^1J_{CPPh_2}$ = 13.0 Hz, $C_{Fc}PPh_2$), 96.0 (dd, $^2J_{CPH_2}$ = 11.1 Hz, $^2J_{CPPh_2}$ = 25.2 Hz, $C_{Fc}CH_2N$), 127.0−128.0 (3 signals overlapping with C_6D_6, C_6H_5), 128.8 (s, C_6H_5), 132.5 (d, $^2J_{CPPh_2}$ = 18.2 Hz, C_6H_5 *o* to P), 135.4 (d, $^2J_{CPPh_2}$ = 22.0 Hz, C_6H_5 *o* to P), 138.8 (d, $^1J_{CPPh_2}$ = 10.4 Hz, $C_{Ph}P$), and 140.8 (d, $^1J_{CPPh_2}$ = 9.9 Hz, $C_{Ph}P$) ppm. ^{31}P NMR: δ −150.1 (t, $^1J_{PH}$ = 199.6 Hz, PH_2), −23.2 (s, PPh_2). FT-IR (KBr; cm^{-1}): 3069 (m), 3053 (m), 2972 (m), 2939 (s), 2857 (m), 2812 (s), 2763 (s), 2299 (s), 2266 (s), 1957 (w), 1891 (w), 1776 (w), 1723 (w), 1662 (w), 1586 (w), 1476 (m), 1455 (m), 1434 (s), 1403 (m), 1343 (w), 1326 (w), 1308 (w), 1256 (m), 1228 (m) 1179 (m), 1153 (w), 1132 (m), 1092 (s), 1025 (s), 1002 (s), 843 (s), 818 (s), 745 (s), 698 (s), 649 (w), 504 (s), and 470 (s). MS (EI pos. 14 eV; m/z): 459 [M^+] (42.6%) and 414 [$(M - HN(CH_3)_2)^+$] (100%). Anal. Calcd for $C_{25}H_{27}FeNP_2$: C, 65.38; H, 5.93; N, 3.05. Found: C, 65.27; H, 5.91; N, 3.01.

1,1′-Bis(diphenylphosphanyl)-2-*N*,*N*-dimethylaminomethyl-3-phosphanylferrocene (5b) Starting from 2b. The procedure for the preparation of **5a** was followed starting from crude **2b** obtained *in situ* from **1b** (1.93 g, 3.15 mmol) and $LiAlH_4$ (0.12 g, 3.16 mmol). The yellow-orange solid was recrystallized from ethanol at −64 °C. Crystals suitable for X-ray diffraction were obtained after a second recrystallization from refluxing ethanol by slowly cooling to room temperature. Yield: 1.41 g (70% based on **1b**). Mp: 134 °C. ^{1}H NMR: δ 1.98 (s, 6H, $N(CH_3)_2$), 3.37 (s, 1H, C_5H_4), 3.53 (d, $^2J_{HH}$ = 12.6 Hz, 1H, CH_2N), 3.69 (dd, $^2J_{HH}$ = 12.2 Hz, $^1J_{PH}$ = 202.7 Hz, 1H, PH_2), 3.83 (s, 1H, C_5H_4), 3.85 (d, $^2J_{HH}$ = 12.6 Hz, 1H, CH_2N), 3.88 (dd, $^2J_{HH}$ = 12.2 Hz, $^1J_{PH}$ = 198.8 Hz, 1H, PH_2), 4.03 (s, 2H, C_5H_2 *o* to PPh_2 and C_5H_4), 4.35 (s, 1H, C_5H_4), 4.48 (s, 1H, C_5H_2 *o* to PH_2), 6.99 (br m, 12H, C_6H_5), 7.37 (br m, 6H, C_6H_5 *o* to P), and 7.52 (br m, 2H, C_6H_5 *o* to P) ppm. $^{13}C\{^1H\}$ NMR: 44.5 (s, $N(CH_3)_2$), 56.6

(d, $^3J_{CPPh_2}$ = 7.5 Hz, CH_2N), 71.1 (dd, $^1J_{CPH_2}$ = 10.6 Hz, $^3J_{CPPh_2}$ = 2.9 Hz, $C_{Fc}PH_2$), 73.5 (d, J_{CPPh_2} = 9.2 Hz, C_5H_4), 73.6 (d, J_{CPPh_2} = 5.0 Hz, C_5H_4), 73.9 (s, C_5H_4), 74.6 (d, J_{CPPh_2} = 4.4 Hz, C_5H_4), 77.7 (dd, $^3J_{CPH_2}$ = 2.8 Hz, $^2J_{CPPh_2}$ = 19.7 Hz, C_5H_2 *o* to PPh_2), 78.6 (d, $^1J_{CPPh_2}$ = 10.1 Hz, $C_{Fc}PPh_2$ of C_5H_4), 79.8 (dd, $^2J_{CPH_2}$ = 6.2 Hz, $^3J_{CPPh_2}$ = 3.3 Hz, C_5H_2 *o* to PH_2), 81.1 (dd, $^3J_{CPH_2}$ = 1.3 Hz, $^1J_{CPPh_2}$ = 13.9 Hz, $C_{Fc}PPh_2$ of C_5H_2), 96.4 (dd, $^2J_{CPH_2}$ = 12.4 Hz, $^2J_{CPPh_2}$ = 25.2 Hz, $C_{Fc}CH_2N$), 127.7−128.1 (4 signals overlapping with C_6D_6, C_6H_5), 128.2 (s, C_6H_5), 128.3 (s, C_6H_5), 128.4 (s, C_6H_5), 128.9 (s, C_6H_5), 132.5 (d, $^2J_{CPPh_2}$ = 18.5 Hz, C_6H_5 *o* to P), 133.4 (d, $^2J_{CPPh_2}$ = 19.5 Hz, C_6H_5 *o* to P), 133.8 (d, $^2J_{CPPh_2}$ = 20.1 Hz, C_6H_5 *o* to P), 135.1 (d, $^2J_{CPPh_2}$ = 22.1 Hz, C_6H_5 *o* to P), 138.2 (d, $^1J_{CPPh_2}$ = 10.1 Hz, $C_{Ph}P$), 138.7 (d, $^1J_{CPPh_2}$ = 11.3 Hz, $C_{Ph}P$), 139.7 (d, $^1J_{CPPh_2}$ = 11.7 Hz, $C_{Ph}P$), and 140.8 (d, $^1J_{CPPh_2}$ = 9.7 Hz, $C_{Ph}P$) ppm. ^{31}P NMR: δ −150.3 (t, $^1J_{PH}$ = 199.9 Hz, PH_2), −23.7 (PPh_2 at C_5H_2), and −18.8 (PPh_2 at C_5H_4). FT-IR (KBr; cm^{-1}): 3423 (bm), 3052 (w), 2964 (s), 2764 (w), 2271 (m), 1584 (w), 1508 (s), 1477 (m), 1433 (s), 1262 (s), 1173 (m), 1130 (w), 1090 (m), 1024 (s), 878 (w), 836 (m), 815 (m), 745 (s), 697 (s), 560 (w), 519 (w), 500 (m), and 468 (m). MS (EI pos. 14 eV; *m*/*z*): 643 [M^+] (35.2%), 611 [$(M - PH)^+$] (10.7%), 598 [$(M - HN(CH_3)_2)^+$] (100%), 568 (6.6%), 333 (8.7%), and 250 (8.2%). Anal. Calcd for $C_{37}H_{36}FeNP_3$: C, 69.06; H, 5.64; N, 2.18. Found: C, 68.72; H, 5.64; N, 2.15.

X-ray Structure Determinations. Suitable crystals were mounted on a glass needle with perfluoropolyalkyl ether and cooled in a nitrogen stream. Crystallographic measurements were made using an Oxford Diffraction Xcalibur S diffractometer. Data were collected by using monochromatic Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods[33] and refined on F^2 by full-matrix least-squares techniques (SHELX97).[34] All non-hydrogen atoms were refined anisotropically; hydrogen atoms were calculated on idealized positions as a riding model and refined isotropically with the exception of **3a**, for which all H atoms were located on difference Fourier maps calculated at the final stage of the structure refinement, and the PH_2 fragment for **5b**. Figures show ORTEP depictions.[35] Crystal data and details of data collection and refinement are given in Table 2. Further details are included in the Supporting Information.

CCDC 775092 (*rac*-**2a**), 775093 (*rac*-**3a**), 775094 (*rac*-**3b**), 775095 (*rac*-**4b**), and 775096 (*rac*-**5b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.uk).

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Supporting Information Available: Crystallographic data for *rac*-**2a**, *rac*-**3a**, *rac*-**3b**, *rac*-**4b**, and *rac*-**5b** as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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