Heterolytic Cleavage of Dihydrogen by Frustrated Lewis Pairs Derived from α-(Dimesitylphosphino)ferrocenes and $B(C_6F_5)_3$†

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Received April 16, 2008

Treatment of the α-dimethylamino[3]ferrocenophane system **3** with methyl iodide followed by dimesitylphosphine (Mes_2PH) gave the α-(dimesitylphosphino)[3]ferrocenophane **5**. This forms a frustrated Lewis pair [**5/8**] with $B(C_6F_5)_3$ (**8**) that rapidly reacts with dihydrogen under ambient conditions to probably give the phosphonium cation/hydrido borate anion salt [**5**-H^+/H-**8**$^-$]. This, however, is unstable under the applied reaction conditions with regard to replacement of the newly formed phosphonium leaving group at the ferrocenophane α-position for hydride from the [$HB(C_6F_5)_3^-$] counteranion to eventually yield the unfunctionalized [3]ferrocenophane product (**10**) and $Mes_2PH \cdot B(C_6F_5)_3$ (**11**)—both characterized by independent syntheses. Analogously, Ugi's amine (**6**) was converted to (1-(dimesitylphosphino)-ethyl)ferrocene (**7**). The frustrated pair [**7/8**] consumes dihydrogen under similar conditions to yield the reduction products ethylferrocene (**14**) and $Mes_2PH \cdot B(C_6F_5)_3$ (**11**).

Introduction

Until recently catalytic dihydrogen activation had been a domain of transition-metal chemistry. Homolytic or heterolytic H_2 cleavage and activation has been achieved by a variety of bulk metals and/or by a great variety of molecular transition-metal complexes.[1−3] Even the natural H_2-converting enzymes, the hydrogenases, make use of the unique features of transition metals (Fe−Fe, Fe−Ni) in special chemical environments to utilize the reductive power of dihydrogen ($H_2 \rightarrow 2H^+ + 2e^-$).[4,5] Quite recently, Stephan et al. discovered metal-free systems that were able to split H_2 by a non-self-quenching combination of a bulky phosphine and a very electrophilic borane to give the corresponding phosphonium/hydrido borate products (see Scheme 1, eq 1).[6−9] It was later shown that some such "frustrated Lewis pairs" were able to serve as catalysts for the hydrogenation of bulky imines. Even some combinations of bulky imines or nitriles with $B(C_6F_5)_3$ showed H_2-activation properties and led to hydrogenation of these unsaturated organic products.[6,7] We had recently described the weakly internally coordinated

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† Dedicated to Professor Klaus Kühlein on the occasion of his 70th birthday.

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§ NMR experiments.

⊥ X-ray crystal structure analyses.

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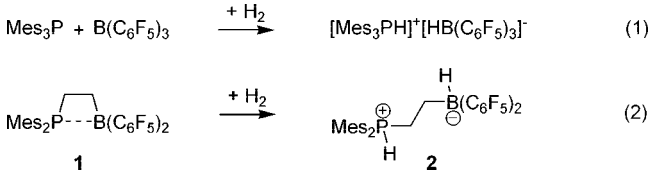
10.1021/om800339c CCC: $40.75
Publication on Web 09/26/2008

Scheme 1



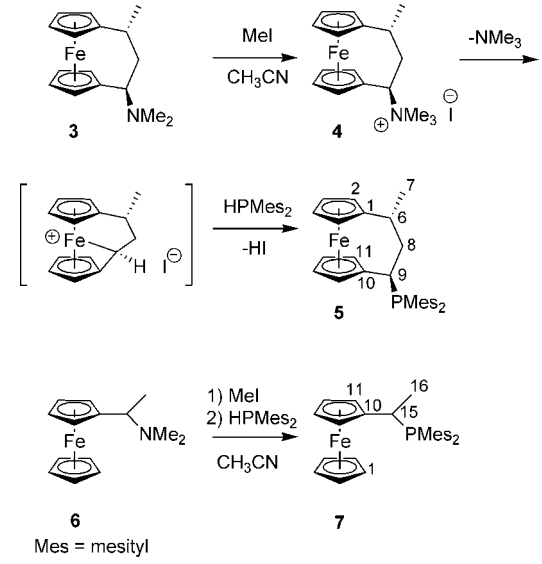
frustrated phosphine/borane pair **1** and shown that it represents one of the most active metal-free H_2-activation systems reported so far. The **1/2** system is an active hydrogenation catalyst for enamines and bulky imines at room temperature[10] (Scheme 1, eq 1).

The ferrocene backbone has served as a very useful framework for ligand design and synthesis in, for example, hydrogenation catalysis.[3] Therefore, it was tempting to synthesize and investigate P/B pairs that involve these metallocene backbones at the bulky phosphorus, the borane component, or both. We here wish to report the syntheses of the (to our knowledge) first examples of active frustrated pairs based on phosphine-substituted ferrocenes and ferrocenophanes. These showed some remarkable chemical behavior subsequent to fast heterolytic dihydrogen activation and splitting. This noticeable reactivity pattern of these new systems will be described below for two examples.

Results and Discussion

The first synthesis was started from the α-(dimethylamino)[3]-ferrocenophane system **3**. This, in turn, was prepared by a sequence starting from 1,1′-diacetylferrocene via a Mannich reaction followed by catalytic hydrogenation, as previously described by us in the literature.[11] For this synthesis we only employed the *rac* series. We started from a sample of **3** that was highly enriched in the *trans* isomer (ca. 20:1). The tertiary amine **3** was quaternized by treatment with methyl iodide (to give **4**) and then treated with dimesitylphosphine. The exchange reaction apparently proceeded by means of the typical two-step reaction mechanism, involving anchimeric assistance of the iron center [12,13] to eventually yield the α-dimesitylphosphino-substituted [3]ferrocenophane derivate **5** (ca. 55%) (see Scheme 2).

Scheme 2



Single crystals of **5** suitable for X-ray crystal structure analysis were obtained from cold pentane. Complex **5** features a typical [3]ferrocenophane framework in the crystal. The Cp planes are almost parallel to each other, with Fe−C(Cp) distances ranging from 2.000(3) to 2.047(4) Å. The C_3 bridge shows a typical cycloalkane-like folded geometry with a strong structural differentiation of pseudo-axial and -equatorial substituent positions. The (small) CH_3 substituent at the bridge position C6 thus features a pseudo-axial arrangement, with the C6−C7 vector (1.515(4) Å) being almost oriented coplanar with the C1 to C5 Cp ring plane (see Figure 1). Consequently, the bulky *trans*-Mes_2P substituent at C9 is found in a pseudo-equatorial orientation at the bridge (dihedral angles: C6−C8−C9−P1 = 174.5(2)°, C14−C10−C9−P1 = −119.2(3)°). The coordination geometry of the phosphorus center in **5** strongly deviates from planarity, as expected. It features C−P−C bond angles of 102.0(1)° (C9−P1−C24), 114.1(1)° (C9−P1−C15), and 100.9(1)° (C15−P1−C24).

In solution, compound **5** exhibits a set of a total of eight ^{13}C NMR *C*H signals of the pair of C_5H_4 groups plus two corresponding *ipso*-C resonances (δ 90.8 (s, C1), δ 89.6 (d, $^2J_{PC}$ = 21.5 Hz, C10) and the typical ^{13}C NMR resonances of the disubstituted [3]ferrocenophane bridge (δ 18.6 (6-CH_3), 26.8 ($^3J_{PC}$ = 12.9 Hz, C-6), 48.4 ($^2J_{PC}$ = 28.6 Hz, C-8), and 27.9 ($^1J_{PC}$ = 19.1 Hz, C-9)). As expected, the mesityl groups at the stereogenic phosphorus center are diastereotopic, featuring pairs of well-separated ^1H NMR *o*- and *p*-methyl resonances and *m*-H signals (for details see the Experimental Section). The ^{31}P NMR resonance of **5** is at δ −10.0 (in d_6-benzene).

Analogously, we have converted (racemic) "Ugi's amine" (**6**)[14] to the corresponding (1-(dimesitylphosphino)ethyl)ferrocene (**7**) by quaternization with MeI followed by the substitution reaction by treatment with dimesitylphosphine (Mes_2PH) in acetonitrile (see Scheme 2). Compound **7** was also characterized by X-ray diffraction (single crystals from pentane).

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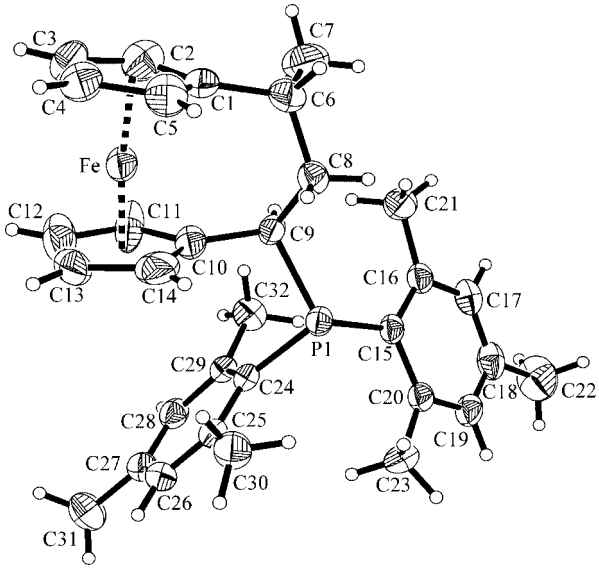


Figure 1. View of the molecular geometry of **5**. Selected bond lengths (Å) and angles (deg) for **5**: Fe−C_{Cp} = 2.000(3)−2.047(4), C1−C6 = 1.535(4), C6−C7 = 1.515(4), C6−C8 = 1.549(4), C8−C9 = 1.546(4), C9−C10 = 1.498(4), C9−P1 = 1.899(3), P1−C15 = 1.862(3), P1−C24 = 1.856(3); C1−C6−C7 = 112.6(3), C1−C6−C8 = 113.5(2), C7−C6−C8 = 112.2(3), C6−C8−C9 = 117.3(2), C8−C9−C10 = 112.0(2), C8−C9−P1 = 108.8(2), C10−C9−P1 = 106.2(2), C9−P1−C15 = 114.1(1), C9−P1−C24 = 102.0(1), C15−P1−C24 = 100.9(1).

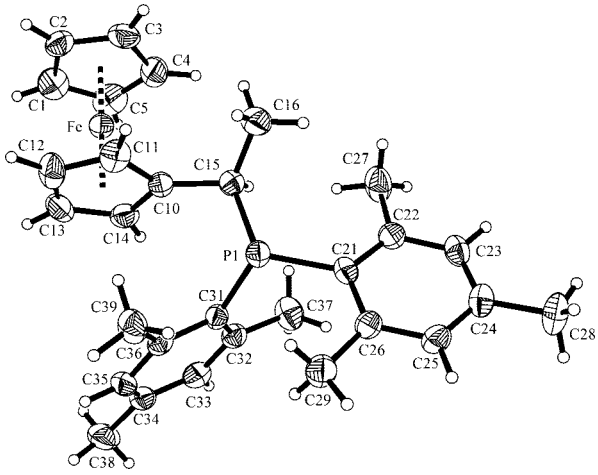
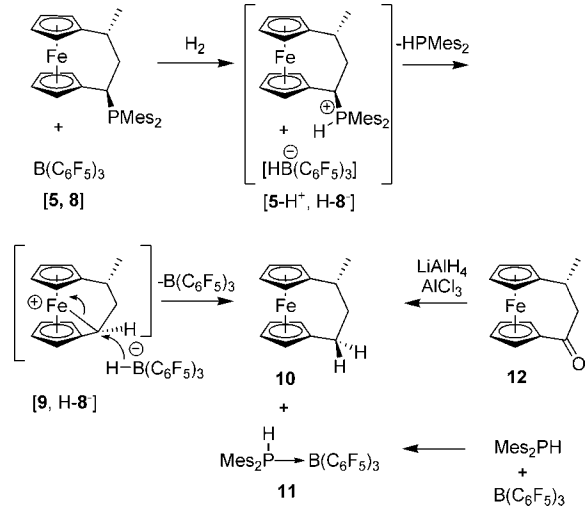


Figure 2. Molecular structure of **7**. Selected bond lengths (Å) and angles (deg): Fe−C_{Cp} = 2.029(3)−2.061(3), C16−C15 = 1.544(4), C15−C10 = 1.499(4), C15−P1 = 1.887(3), P1−C21 = 1.858(3), P1−C31 = 1.851(3); C16−C15−C10 = 110.5(3), C16−C15−P1 = 108.7(2), C10−C15−P1 = 105.7(2), C15−P1−C21 = 113.3(2), C15−P1−C31 = 101.0(1), C21−P1−C31 = 106.1(1).

In the crystal complex **7** exhibits the typical ferrocene framework, with Fe−C(Cp) bond lengths in a range between 2.029(3) and 2.061(3) Å (Figure 2). The 1-phosphinoethyl substituent at a Cp ring features a conformation that has the C−CH_3 vector rotated ca. 30° out of the adjacent Cp ring plane (dihedral angle C11−C10−C15−C16 = −29.6(5)°). The very bulky −$PMes_2$ group is rotated away from the ferrocene core. This *anti* substituent orientation is characterized by the dihedral angles C11−C10−C15−P1 = 87.8(3)° and C14−C10−C15−P1 = −89.5(3)°. The C10−C15−P1 angle amounts to 105.7(2)° (C10−C15−C16 = 110.5(3)°). The coordination geometry at P1 is nonplanar (bond angles: C15−P1−C31 = 101.0(1)°, C15−P1−C21 = 113.3(2)°, C21−P1−C31 = 106.1(1)°). The angle between the planes of the pair of mesityl substituents at P1 (i.e., C31 to C36 vs C21 to C26) was found at 98.1°.

Scheme 3



Mixing of the α-(dimesitylphosphino)[3]ferrocenophane (**5**) with the strong boron Lewis acid $B(C_6F_5)_3$[15] (**8**) in d_6-benzene did not result in any observed adduct formation.[16] The absence of any appreciable change of the NMR features of the components in the ca. 1:1 mixture rendered **5**/$B(C_6F_5)_3$ (**8**) a frustrated Lewis pair [**5/8**] (see Scheme 3). Consequently, the **5**/$B(C_6F_5)_3$ (**8**) mixture reacted rapidly with dihydrogen (1.8 bar) at room temperature. After specific workup of the reaction mixture (for details see the Experimental Section) we isolated the [3]ferrocenophane derivate **10** in >70% yield. This specific ferrocenophane product derived from the hydrogenation reaction mixture was characterized by spectroscopy and by comparison with a reference sample independently synthesized by $LiAlH_4$/$AlCl_3$ reduction of the [3]ferrocenophanone **12**,[17] including an X-ray crystal structure analysis. The product **10** features a very typical set of NMR data (^{1}H NMR: δ 2.09, 1.61 (9-H,H′), 1.76, 1.63 (8-H,H′), 1.87 (6-H), 1.12 (6-CH_3)), including a set of 10 separate ^{13}C(Cp) NMR resonances.

In the crystal, compound **10** shows a typical [3]ferrocenophane geometry (see Figure 3) with Fe−C(Cp) bond lengths in the range 2.013(4)−2.050(4) Å. The C_3 bridge is again strongly folded. However, in contrast to the structure of the corresponding phosphino[3]ferrocenophane derivative **5** (see above and Figure 1), the monosubstituted compound **10** shows a conformational arrangement of the bridge that features the CH_3 substituent at C6 in a pseudo-equatorial orientation (dihedral angles: C2−C1−C6−C7 = 70.5(6)°, C2−C1−C6−C8 = −63.5(6)°, C1−C6−C8−C9 = −56.7(7)°).

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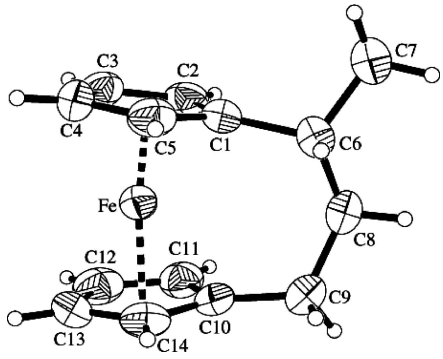


Figure 3. Molecular structure of **10**. Selected bond lengths (Å) and angles (deg): Fe−C_{Cp} = 2.013(4)−2.050(4), C1−C6 = 1.524(6), C6−C7 = 1.498(6), C6−C8 = 1.468(6), C8−C9 = 1.476(5), C9−C10 = 1.505(6); C1−C6−C7 = 111.5(4), C1−C6−C8 = 115.4(4), C7−C6−C8 = 115.3(4), C6−C8−C9 = 122.7(4), C8−C9−C10 = 116.7(4).

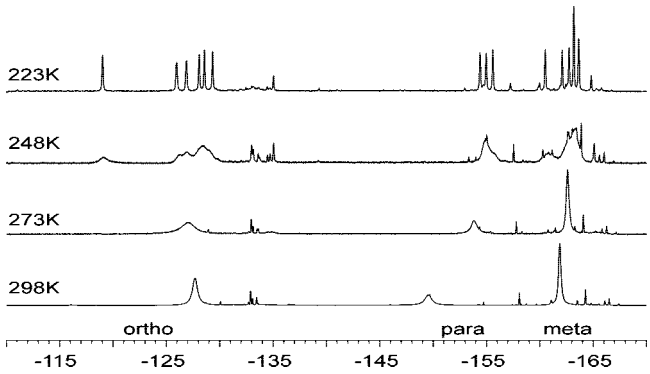
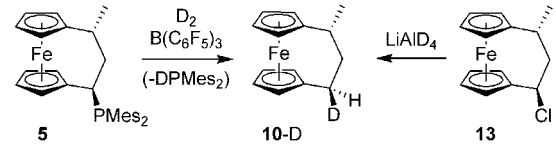


Figure 4. Dynamic ^{19}F NMR spectra of the $Mes_2PH \cdot B(C_6F_5)_3$ adduct **11** (in d_8-toluene).

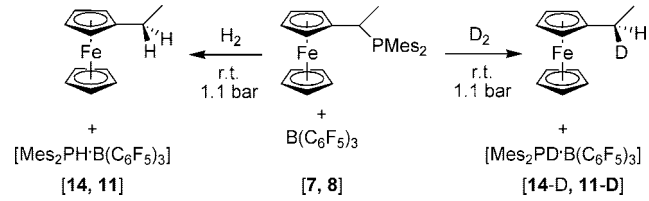
Since the product **10** was free of phosphorus and was isolated in high yield, we needed to identify the phosphorus-containing coproduct. This was identified from the reaction mixture as the $Mes_2PH \cdot B(C_6F_5)_3$ adduct **11**. The product **11** was characterized by its very typical temperature-dependent NMR spectra (see above) and by comparison with an authentic reference sample independently prepared from Mes_2PH and $B(C_6F_5)_3$ (**8**). In one experiment, the reference was actually added to the reaction mixture to show its identity by NMR.

Product **11** shows rather uncharacteristic NMR spectra at ambient temperature, featuring, for example, three broad ^{19}F NMR signals. Decreasing the monitoring temperature leads to a rapid decoalescence, eventually resulting in a very characteristic low-temperature ^{19}F NMR spectrum that exhibits a total of 14 separate resonances, namely six *o*-F, three *p*-F, and five signals corresponding to six *m*-F atoms (one signal of double intensity) of the three C_6F_5 groups at boron in the adduct **11** (see Figure 4). This indicates freezing of the conformational equilibration of the L−$B(C_6F_5)_3$ part of **11**, probably due to a chiral conformation.[18] Consequently, the prochiral Mes_2PH part of the $Mes_2PH \cdot B(C_6F_5)_3$ adduct **11** features dynamic ^{1}H NMR spectra: upon decreasing the monitoring temperature, we here observe decoalescence of, for example, the mesityl *m*-H singlet to eventually give a set of four separate ^{1}H NMR resonances at the limiting low-temperature situation.

Scheme 4



Scheme 5



We then reacted the [**5**/**8**] frustrated pair with D_2. After the usual workup the corresponding monodeuterated [3]ferrocenophane derivative **10**-D was isolated (90% yield). Again, the composition of the product was characterized by spectroscopy and by direct comparison with a reference sample (for details see the Supporting Information), which in this case was prepared by $LiAlD_4$ reduction of the corresponding *trans*-α-chloro[3]ferrocenophane derivative **13**.[19] From these combined experiments it is likely that treatment of the [**5**/**8**] pair with dideuterium has selectively resulted in the formation of the *trans*-disubstituted [3]ferrocenophane derivative **10**-D (see Scheme 4).

The (1-(dimesitylphosphino)ethyl)ferrocene/$B(C_6F_5)_3$ mixture [**7**/**8**] was also treated with H_2 (Scheme 5). It reacted at room temperature and 1.1 bar of dihydrogen pressure. From the NMR spectroscopic characterization of a reaction mixture in d_8-toluene formation of $Mes_2PH \cdot B(C_6F_5)_3$ (**11**) was found. Workup of a reaction mixture involving chromatography gave the product ethylferrocene (**14**) in 57% yield (^{1}H NMR δ 2.19 (q, 2H), 1.08 (t, $^2J_{HH}$ = 7.5 Hz, 3H, CH_2CH_3); ^{13}C NMR δ 69.2 (Cp), 91.6, 68.2, 67.9 (C_5H_4), 23.1, 15.5 (C_2H_5)). For comparison, compound **14** was independently synthesized by reduction of the corresponding ferrocenyl ethanol with $Me_2S \cdot BH_3$.[20] The frustrated pair [**7**/**8**] also reacts cleanly with D_2 (12 h, 1.1 bar, room temperature) under analogous conditions to give the monodeuterium-substituted ethylferrocene product **14**-D, isolated in 51% yield after chromatographic workup. It features a 1:1:1 triplet at δ 22.7 of the Fe−*C*HD−CH_3 carbon atom in the ^{13}C NMR spectrum in d_6-benzene.

Conclusions

This study shows that ferrocene and ferrocenophane derivatives that bear very bulky dimesitylphosphino substituents at the position α to the metallocene nuclei can readily be prepared. These very bulky phosphines form frustrated Lewis pairs with $B(C_6F_5)_3$ (**8**). The systems [**5**/**8**] and [**7**/**8**] both cleave dihydrogen heterolytically under ambient conditions. It is likely that the phosphonium cation/hydrido borate anion pairs [**5**-H^+/H-**8**$^-$] and [**7**-H^+/H-**8**$^-$] are initially formed (see Scheme 3). It appears that the α-Mes_2PH^+ substituent in these special cases is a sufficiently good leaving group to make the systems kinetically labile. Cleavage of the Mes_2PH moiety from [**5**-H^+],

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(20) Kim, D.-H.; Ryu, E.-S.; Cho, C. S.; Shim, S. C.; Kim, H.-S.; Kim, T.-J. *Organometallics* **2000**, *19*, 5784. Routaboul, L.; Chiffre, J.; Balavoine, G. G. A.; Daran, J.-C.; Manoury, E. *J. Organomet. Chem.* **2001**, *637*−*639*, 364.

probably assisted by the iron neighboring group followed by nucleophilic hydride attachment from the [H-**8**$^-$] counteranion, is likely to be the favored pathway of a subsequent reaction in this system following the initial H_2 activation process. The observed regio- and stereochemical outcome[12,13] of the respective experiments employing D_2 instead of the H_2 supports this description of reaction sequence observed here. A similar reaction mode was observed starting from the [**7/8**] frustrated Lewis pair. We conclude that these specific ferrocene or ferrocenophane moieties at a bulky phosphine are compatible with rapid heterolytic dihydrogen activation and cleavage by frustrated Lewis pairs. We have seen that the positioning of the phosphine substituent at a substitution-sensitive position of the metallocene framework might lead to specific subsequent reactivities. Electronic or steric stabilization of this situation must be considered in order to produce sufficiently persistent systems which might be of interest to allow for a subsequent intermolecular utilization of the H_2-derived reduction equivalents.

Experimental Section

General Procedures. All manipulations involving air-sensitive materials were carried out using standard Schlenk type glassware (or a glovebox) under an atmosphere of argon. Solvents were dried with the procedure reported by Grubbs[21] or were distilled from appropriate drying agents. The amines **3** and **6** and the borane **8** were prepared as reported.[11,13,15] NMR spectra were recorded on AC 200, AV 300, DPX300, and AV400 spectrometers from Bruker, INOVA 500 and UnityPlus 600 spectrometers from Varian, and JNM-ECP500 and ECA600 spectrometers from JEOL. NMR assignments were made by various 2D NMR measurements. For the X-ray crystal structure analyses, data sets were collected with a Nonius KappaCCD diffractometer, equipped with a rotating anode generator. Programs used are as follows: data collection, COLLECT (Nonius BV, 1998); data reduction, Denzo-SMN;[22] absorption correction, SORTAV[23] and Denzo;[24] structure solution, SHELXS-97;[25] structure refinement, SHELXL-97 (G. M. Sheldrick, Universität Göttingen, 1997); graphics, XP (BrukerAXS, 2000).

Preparation of the *rac*-α-(Dimesitylphosphino)[3]ferrocenophane System (5). Amine **3** (0.70 g, 2.47 mmol, *trans*:*cis* = 20:1) was dissolved in acetonitrile (20 mL) and cooled (0 °C) before MeI (1.5 mL, 0.024 mol) was added dropwise. After 10 min, the reaction mixture was warmed to room temperature and stirred (2 h). Removal of the solvent and drying (0.5 h, high vacuum) gave the ammonium iodide **4.** Dimesitylphosphine (0.60 g, 2.20 mmol) and acetonitrile (20 mL) were added, and the mixture was kept overnight at 65 °C. Diethyl ether was added at room temperature. After filtration, the solvent was evaporated from the filtrate. Chloroform was added, a precipitate was filtered off, the solvent was removed in vacuo, and the residue was chromatographed (cyclohexane) to give product **5**. The product was then crystallized from pentane and obtained in pure form with a *trans*:*cis* ratio of about 15:1 (0.67 g, 54% yield). Crystals suitable for the X-ray crystal structure analysis were obtained from cold pentane. ^{1}H NMR (C_6D_6, 600 MHz, 298 K): δ 6.76 (d, J_{HP} = 1.9 Hz, 2H, $H^{Mes'}$), 6.61 (d, J_{HP} = 2.0 Hz, 2H, H^{Mes}), 4.42 (α), 3.93 (β), 3.89 (β), 3.80 (α), (each m, each 1H, H-11 to H-14), 4.00 (2H, β), 3.98 (1H, α), 3.97 (1H, α) (each m, H-2 to H-5), 3.95 (m, 1H, H-9), 2.61 (s, 6H, *o*-$CH_3^{Mes'}$), 2.56 (m, 1H, H-6), 2.52 (s, 6H, *o*-CH_3^{Mes}), 2.21, 2.03 (each m, each 1H, H-8), 2.10 (s, 3H, *p*-$CH_3^{Mes'}$), 1.98 (s, 3H, *p*-CH_3^{Mes}), 1.03 (d, J_{HH} = 7.2 Hz, 3H, H-7). ^{13}C{^{1}H} NMR (C_6D_6, 151 MHz, 298 K): δ 143.3 (broad, d, J_{CP} = 15.6 Hz, *o*-Mes′), 143.0 (d, J_{CP} = 14.4 Hz, *o*-Mes), 137.9 (*p*-Mes′), 137.4 (*p*-Mes), 133.1 (broad, d, J_{CP} = 30.5 Hz, *i*-Mes′), 132.7 (d, J_{CP} = 25.7 Hz, *i*-Mes), 130.5 (d, J_{CP} = 2.8 Hz, *m*-Mes′), 130.3 (d, J_{CP} = 2.8 Hz, *m*-Mes), 90.8 (C-1), 89.6 (broad, d, J_{CP} = 21.5 Hz, C-10), 70.4 (d, J_{CP} = 3.4 Hz, α), 68.6 (α), 68.6 (β), 68.3 (β) (C-11 to C-14), 69.5 (β), 69.2 (β), 68.5 (α), 67.8 (α) (C-2 to C-5), 48.4 (d, J_{CP} = 28.6 Hz, C-8), 27.9 (d, J_{CP} = 19.1 Hz, C-9), 26.8 (d, J_{CP} = 12.9 Hz, C-6), 23.5 (d, J_{CP} = 13.8 Hz, *o*-CH_3^{Mes}), 23.1 (d, J_{CP} = 14.4 Hz, *o*-$CH_3^{Mes'}$), 20.9 (*p*-$CH_3^{Mes'}$), 20.8 (*p*-CH_3^{Mes}), 18.6 (broad, C-7). ^{31}P{^{1}H} NMR (C_6D_6, 162 MHz, 298 K): δ −10.0 ($\nu_{1/2}$ = 3 Hz, ca. 4% probably *cis* isomer). Anal. Calcd for $C_{32}H_{37}FeP$: C, 75.59; H, 7.33. Found: C, 75.63; H, 7.27. X-ray crystal structure analysis of **5**: formula $C_{32}H_{37}FeP$, M_r = 508.44, yellow crystal 0.35 × 0.10 × 0.10 mm, a = 15.4990(2) Å, b = 15.2570(2) Å, c = 22.8414(3) Å, V = 5401.27(12) Å^3, ρ_{calcd} = 1.250 g cm^{-3}, μ = 0.636 mm^{-1}, empirical absorption correction (0.808 ≤ T ≤ 0.939), Z = 8, orthorhombic, space group *Pbca* (No. 61), λ = 0.710 73 Å, T = 223 K, ω and φ scans, 40 084 reflections collected (±h, ±k, ±l), (sin θ)/λ = 0.66 Å^{-1}, 6424 independent (R_{int} = 0.090) and 3895 observed reflections ($I \geq 2\sigma(I)$), 314 refined parameters, R1 = 0.053, wR2 = 0.146, maximum (minimum) residual electron density 0.68 (−0.45) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of *rac*-(1-(Dimesitylphosphino)ethyl)ferrocene (7). Methyl iodide (2.60 mL, 41.8 mmol) was added at 0 °C to a solution of (1-(dimethylamino)ethyl)ferrocene (**6**; 1.54 g, 5.99 mmol) in acetonitrile (30 mL). After stirring (2 h, 0−5 °C), the volatiles were removed in vacuo. The resulting yellow solid was dissolved in acetonitrile (50 mL), and dimesitylphosphine (1.62 g, 5.99 mmol) was added. After the mixture was stirred (24 h, 60 °C), the volatiles were removed in vacuo and the crude product was recrystallized from pentane. Phosphine **7** was isolated as orange crystals (0.97 g, 33% yield). Crystals suitable for X-ray analysis were obtained from cold pentane. ^{1}H NMR (C_6D_6, 600 MHz, 298 K): δ 6.72 (d, J_{HP} = 2.1 Hz, 2H, Mes), 6.65 (d, J_{HP} = 2.2 Hz, 2H, Mes′), 4.17 (qd, J_{HH} = 7.1, J_{HP} = 4.4 Hz, 1H, CH), 4.13, 3.87, 3.71, 3.57 (each m, each 1H, C_5H_4), 4.00 (s, 5H, Cp), 2.48 (s, 6H, *o*-CH_3^{Mes}), 2.38 (s, 6H, *o*-$CH_3^{Mes'}$), 2.09 (s, 3H, *p*-$CH_3^{Mes'}$), 2.04 (s, 3H, *p*-CH_3^{Mes}), 1.65 (dd, J_{HP} = 17.3 Hz, J_{HH} = 6.8 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (C_6D_6, 151 MHz, 298 K): δ 144.6 (d, J_{CP} = 14.5 Hz, *o*-Mes′), 143.0 (d, J_{CP} = 14.5 Hz, *o*-Mes), 138.5 (s, *p*-Mes′), 137.7 (s, *p*-Mes), 133.3 (d, J_{CP} = 33.9 Hz, *i*-Mes), 133.0 (d, J_{CP} = 25.3 Hz, *i*-Mes′), 131.3 (d, J_{CP} = 1.6 Hz, *m*-Mes), 130.4 (d, J_{CP} = 3.2 Hz, *m*-Mes′), 92.8 (d, J_{CP} = 18.6 Hz, C-10), 70.0 (d, J_{CP} = 3.2 Hz, α), 68.0 (d, J_{CP} = 5.7 Hz, α), 67.8 (s, β), 67.5 (s, β) (C-11 to C14), 69.2 (s, C-1 to C-5), 30.1 (d, J_{CP} = 17.6 Hz, CH), 23.6 (d, J_{CP} = 14.6 Hz), 23.5 (d, J_{CP} = 14.6 Hz) (*o*-CH_3^{Mes}, *o*-$CH_3^{Mes'}$), 21.4 (s, *p*-$CH_3^{Mes'}$), 21.2 (s, *p*-CH_3^{Mes}), 20.4 (d, J_{CP} = 29.9 Hz, CH_3). ^{31}P{^{1}H} NMR (C_6D_6, 243 MHz, 298 K): δ −3.7 (q, broad, J_{PH} = 15.8 Hz). Anal. Calcd for $C_{30}H_{35}FeP$: C, 74.69; H, 7.31. Found: C, 74.71; H, 7.39. X-ray crystal structure analysis of **7**: formula $C_{30}H_{35}FeP$, M_r = 482.40, yellow crystal 0.35 × 0.20 × 0.10 mm, a = 7.4493(2) Å, b = 12.5125(3) Å, c = 14.4119(4) Å, α = 71.541(2)°, β = 85.738(1)°, γ = 77.417(1)°, V = 1243.59(6) Å^3, ρ_{calcd} = 1.288 g cm^{-3}, μ = 0.686 mm^{-1}, empirical absorption correction (0.795 ≤ T ≤ 0.935), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.710 73 Å, T = 223 K, ω and φ scans, 10 460 reflections collected (±h, ±k, ±l), (sin θ)/λ = 0.66 Å^{-1}, 5746 independent (R_{int} = 0.055) and 3323 observed reflections ($I \geq 2\sigma(I)$), 296 refined parameters, R1 = 0.059, wR2 = 0.149, maximum (minimum) residual electron density 0.65 (−0.59) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

1,1′-[Butane-1,3-diyl]ferrocene (10). From 5. Phosphine derivative **5** (27.0 mg, 0.053 mmol) was dissolved in C_6D_6 (1.5 mL) in

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(24) Otwinowski, Z.; Borek, D.; Majewski, W.; Minor, W. *Acta Crystallogr.* **2003**, *A59*, 228.
(25) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

the glovebox before borane **8** (30.0 mg, 0.059 mmol) was added. After short evacuation, dihydrogen pressure (1.8 bar) was applied (4 h) and the reaction mixture was stirred overnight. Residual **5** was oxidized by treatment with sulfur (2 h) to allow a convenient subsequent chromatographic separation. Chromatography (silica gel, pentane) gave **10** (9.30 mg, 73% yield). ^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ 4.05 (2H), 4.00 (2H), 3.92 (1H), 3.89 (2H), 3.86 (1H) (each m, C_5H_4), 2.08 (1H), 1.86 (1H), 1.73 (1H), 1.62 (2H) (each m, CH_2CH_2CH), 1.12 (d, J_{HH} = 7.0 Hz, 3H, Me). ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz, 298 K): δ 90.3 (C-1), 86.9 (C-10), 70.9, 70.2, 69.0, 68.9, 68.5, 68.1, 67.9, 66.2 (C_5H_4), 44.2, 30.6, 24.0 (CH_2CH_2CH), 21.3 (Me).

From Ketone 12. Ketone **12** (248 mg, 0.98 mmol) was added to $LiAlH_4$ (214 mg, 6.50 mmol) in Et_2O (50 mL). $AlCl_3$ (1.56 g, 1.17 mmol) was added before the reaction mixture was refluxed (40 °C, 5 h). After addition of ethyl acetate (wet), MeOH (wet), and H_2O, extraction (THF), drying ($MgSO_4$), filtration, evaporation, and chromatography (pentane), product **10** was obtained (0.22 g, 94%). ^{1}H NMR (C_6D_6, 600 MHz, 298 K): δ 4.04, 3.99, 3.88, 3.88 (each m, each 1H, H-2 to H-5), 4.03, 3.98, 3.92, 3.85 (each m, each 1H, H-11 to H-14), 2.09 (m, 1H, H-9), 1.87 (m, 1H, H-6), 1.76 (m, 1H, H-8), 1.63 (dm, J_{HH} = 11.2 Hz, 1H, H8′), 1.61 (dm, J_{HH} = 11.2 Hz, 1H, H-9′), 1.12 (d, J_{HH} = 7.0 Hz, 3H, H-7). ^{13}C{^{1}H} NMR (C_6D_6, 151 MHz, 298 K): δ 90.5 (C-1), 86.8 (C-10), 71.0, 69.1, 68.5, 68.0 (C-11 to C-14), 70.2, 69.0, 68.1, 66.2 (C-2 to C-5), 44.2 (C-8), 30.6 (C-6), 24.1 (C-9), 21.3 (C-7). Anal. Calcd for $C_{14}H_{16}Fe$: C, 70.03; H, 6.72. Found: C, 69.93; H, 6.68. X-ray crystal structure analysis of **10**: formula $C_{14}H_{16}Fe$, M_r = 240.12, yellow crystal 0.30 × 0.20 × 0.02 mm, a = 9.8523(4) Å, b = 7.6564(3), Å, c = 15.4974(7) Å, β = 106.337(2)°, V = 1121.82(8) Å^3, ρ_{calcd} = 1.422 g cm^{-3}, μ = 1.305 mm^{-1}, empirical absorption correction ($0.696 \le T \le 0.974$), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.710 73 Å, T = 223 K, ω and φ scans, 6062 reflections collected ($\pm h$, $\pm k$, $\pm l$), (sin θ)/λ = 0.62 Å^{-1}, 2282 independent (R_{int} = 0.072) and 1268 observed reflections ($I \ge 2\sigma(I)$), 137 refined parameters, R1 = 0.049, wR2 = 0.115, maximum (minimum) residual electron density 0.58 (−0.35) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

1,1′-[1-Deuteriobutane-1,3-diyl]ferrocene (10-D). From 5. Phosphine **5** (47.8 mg, 0.094 mmol) was dissolved in C_6D_6 (2 mL) before borane **8** (50.0 mg, 0.098 mmol) was added. After short evacuation, dideuterium pressure (1.8 bar) was applied (10 min), the vessel was closed, and the mixture was stirred overnight. After the reaction mixture was treated with excess S_8, stirred overnight, and chromatographed (pentane), the product **10-D** (18 mg, 96% yield) was obtained. ^{1}H NMR (C_6D_6, 600 MHz, 298 K): δ 4.04, 3.99, 3.88, 3.88 (each m, each 1H, H-2 to H-5), 4.03, 3.98, 3.92, 3.86 (each m, each 1H, H-11 to H14), 2.07 (dm, J_{HH} = 6.3 Hz, 1H, H-9), 1.86 (dqd, J_{HH} = 9.9, 7.0, 2.8 Hz, 1H, H-6), 1.75 (ddd, J_{HH} = 13.5, 6.3, 2.8 Hz, 1H, H-8), 1.62 (dm, J_{HH} = 13.5 Hz, 1H, H-8), 1.11 (d, J_{HH} = 7.0 Hz, 3H, H-7). ^{13}C{^{1}H} NMR (C_6D_6, 151 MHz, 298 K): δ 90.4 (C-1), 86.9 (C-10), 70.9, 69.0, 68.5, 67.9 (C-11 to C-14), 70.2, 68.9, 68.0, 66.2 (C-2 to C-5), 44.1 (C-8), 30.5 (C-6), 23.7 (t(1:1:1), J_{CD} = 19.5 Hz, C-9), 21.3 (C-7). ^{2}H NMR (C_6H_6, 77 MHz, 298 K): δ 1.55 (broad, D-9).

From Chloride 13. A suspension of $LiAlD_4$ (86 mg, 2.05 mmol) in Et_2O (5 mL) was added to a solution of **13** (224 mg, 0.82 mmol) in Et_2O (10 mL) at 0 °C. After stirring of the mixture overnight at room temperature, addition of H_2O and $NaHCO_3$ (saturated aqueous), extraction with Et_2O, drying ($MgSO_4$), filtration, evaporation, and chromatography (pentane), the product **10-D** was obtained (162 mg, 82% yield). Anal. Calcd for $C_{14}H_{15}DFe$: C, 69.73; H, 7.11. Found: C, 70.52; H, 6.96.

Dimesitylphosphine−Tris(pentafluorophenyl)borane Adduct (11). Tris(pentafluorophenyl)borane (**8**; 479 mg, 0.94 mmol) was suspended in pentane (40 mL), and dimesitylphosphine (254 mg, 0.94 mmol) was dissolved in pentane (6 mL). The phosphine solution was then added to the borane solution at room temperature via cannula, which resulted in the formation of a white suspension. Stirring at room temperature (2 h) gave an almost clear solution, which was filtered and reduced to about 25% of the original volume. Cooling overnight (−20 °C) resulted in the precipitation of the white solid **11**, which was then stored at −20 °C (0.70 g, 92% yield). ^{1}H NMR (d_8-toluene, 600 MHz, 233 K): δ 7.50 (d, broad, J_{HP} = 404 Hz, 1H, PH), 6.33, 6.23, 6.13, 5.92 (each broad, each 1H, *m*-Mes), 2.18 (3H), 1.81 (9H), 1.60 (3H), 0.81 (3H) (each s, each broad, *o*-CH_3^{Mes}, *p*-CH_3^{Mes}). ^{31}P NMR (d_8-toluene, 243 MHz, 233 K): δ −44.7 ($\nu_{1/2}$ = 120 Hz). ^{19}F NMR (d_8-toluene, 564 MHz, 233 K): δ −119.0, −129.4 (each 1F, *o*-F), −155.0 (1F, *p*-F), −162.1, 163.7 (each 1F, *m*-F) (each broad, C_6F_5), −126.0[a], −128.1 (each 1F, *o*-F), −154.4 (1F, *p*-F), −160.5, −163.2 (each 1F, *m*-F) (each broad, C_6F_5), −126.9[a], −128.6 (each 1F, *o*-F), −155.6 (1F, *p*-F), −162.8, −163.2 (each 1F, *m*-F) (each broad, C_6F_5) (the superscript "a" indicates that there is no relative assignment).

1-Ethylferrocene (14). From 7. Phosphine **7** (68 mg, 0.14 mmol) and tris(pentafluorophenyl)borane (**8**; 71 mg, 0.14 mmol) were dissolved in C_6D_6 (1.0 mL), and the mixture was stirred under a hydrogen atmosphere (1.1 bar) for 12 h. The resulting reaction mixture was analyzed by NMR. Isolation of product **14** (17 mg, 57% yield) as a yellow oil was achieved by chromatography of the reaction mixture (pentane). ^{1}H NMR (C_6D_6, 600 MHz, 298 K): δ 3.99 (s, 5H, Cp), 3.95 (s, 4H, C_5H_4), 2.19 (q, J_{HH} = 7.5 Hz, 2H, CH_2CH_3), 1.08 (t, J_{HH} = 7.5 Hz, 3H, CH_2CH_3). ^{13}C{^{1}H} NMR (C_6D_6, 151 MHz, 298 K): δ 91.6 (C-1), 69.2 (Cp), 68.2, 67.9 (C_5H_4), 23.0 (CH_2), 15.5 (CH_3).

From Alcohol. Borane−dimethyl sulfide complex (0.10 mL, 0.98 mmol) was added to a solution of 1-(1-hydroxyethyl)ferrocene (200 mg, 0.87 mmol) in THF (10 mL). The solution was stirred at 50 °C for 1 h. After removal of the volatiles in vacuo, the crude product was purified by chromatography (pentane). Ethylferrocene (**14**) was obtained as an orange oil (113 mg, 61%).

1-Deuterioethylferrocene (14-D). Phosphine **7** (100 mg, 0.21 mmol) and borane **8** (105 mg, 0.21 mmol) were dissolved in C_6D_6 (1.0 mL) and stirred under a dideuterium atmosphere (12 h, ca. 1.1 bar). The resulting solution was analyzed by NMR. Chromatography (pentane) gave the product **14-D** (22 mg, 51% yield) as a yellow oil. Reaction mixture at room temperature: ^{1}H NMR (C_6D_6, 600 MHz, 298 K) δ 3.99 (s, 5H, Cp), 3.95 (s, 4H, C_5H_4), 2.18 (qt (1:1:1), J_{HH} = 7.6 Hz, J_{HD} = 2.2 Hz, 1H, CHD), 1.07 (dt (1:1:1), J_{HH} = 7.6 Hz, J_{HD} = 1.0 Hz, 3H, CH_3); ^{2}H NMR (C_6D_6, 92 MHz, 298 K) δ 2.15 (dq, J_{HD} = 2.2 Hz, 1.1 Hz, 1D, CH*D*CH_3); ^{13}C{^{1}H} NMR (C_6D_6, 151 MHz, 298 K) δ 91.5 (C-1), 69.2 (Cp), 68.2, 67.9 (C_5H_4), 22.7 (CDH), 15.4 (CH_3).

Acknowledgment. Financial support from the Deutsche Forschungsgemeinschaft (IRTG Münster-Nagoya "Complex Functional Systems in Chemistry") and the Fonds der Chemischen Industrie is gratefully acknowledged. We thank the BASF AG for a gift of solvents.

Supporting Information Available: Text and figures giving details of the characterization of the compounds, including comparison with the separately prepared reference systems, and CIF files giving crystal data for **5**, **7**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM800339C