DOI: 10.1021/om100378y

ORGANOMETALLICS
Article

Frustrated Lewis Pair Reactions at the [3]Ferrocenophane Framework†

Kerstin Unverhau, Gerrit Lübbe, Birgit Wibbeling,‡ Roland Fröhlich,‡ Gerald Kehr, and Gerhard Erker*

Organisch-Chemisches Institut der Universität Münster, Corrensstrasse 40, 48149 Münster, Germany.
‡X-ray crystal structure analysis.

Received April 30, 2010

Condensation of the *o*-NH_2-/α-NMe_2-substituted [3]ferrocenophane **5** with aromatic aldehydes or ketones (PhC(R)═O) yields the corresponding organometallic Schiff bases **6** (R = H) and **7** (**a**, R = CH_3; **b**, R = CF_3). The *o*-imino/α-P(mesityl)$_2$ derivative **8** (R = CH_3) was obtained by exchange with H−P(mesityl)$_2$. Its treatment with $B(C_6F_5)_3$ generated a frustrated Lewis pair that reacted with dihydrogen by replacement of the phosphine and reduction of the imine to give the *o*-PhCHMeNH-substituted [3]ferrocenophane **12**. The ketimino functional group in **7a** is cleanly reduced with H_2 in the presence of 10 mol % of the Lewis acid hexyl$B(C_6F_5)_2$ to give the corresponding amine **14**. The analogous reaction reaction of **7b** yielded a 5:1 mixture of the amine diastereoisomers **13a**,**b**. The imine **6** reacts with $B(C_6F_5)_3$ by intramolecular hydride abstraction and transfer from the NMe_2 group to give the stabilized cyclic [3]ferrocenophane iminium salt **19**. Treatment of the related *o*-PPh_2/α-NMe_2 [3]ferrocenophane system **20** with $B(C_6F_5)_3$ proceeded in a related way to yield the annelated heterocyclic phosphonium salt **22**. The complexes **6**·HCl, **7b** (R = CF_3), **12**, **13a**, **14**, **19**, and **22** were characterized by X-ray diffraction.

Introduction

Lewis acids usually form strong adducts with Lewis bases.[1] Consequently, there is no residual reactivity seen from the individual components of the adduct. Using very bulky substituents at the Lewis acid and base hinders or even completely stops this quenching reaction. Therefore, such "frustrated Lewis pairs" show the typical reactivities of both the Lewis acid and the Lewis base[2,3] and often allow for new reaction pathways that originate from cooperativity between these two antagonistic components.[4]

Frustrated Lewis pairs have been shown to react with a variety of substrates; they undergo addition reactions to, for example, alkenes and alkynes,[5,6] to a variety of carbonyl compounds and even to carbon dioxide.[7] Some Lewis pairs activate dihydrogen and can be used as metal-free catalysts for the hydrogenation of specific substrates, such as bulky imines, enamines, and silyl enol ethers.[8,9] There have been a few applications of such catalytic reactions, especially in organometallic chemistry.[10]

We have now studied a variety of typical Lewis pair reactions that take place at [3]ferrocenophane substrates[11]

† Part of the Dietmar Seyferth Festschrift. Dedicated to Professor Dietmar Seyferth on the occasion of his retirement as the Organometallics Editor in Chief.

*To whom correspondence should be addressed. E-mail: erker@uni-muenster.de.

(1) Lewis, G. N. *Valence and the Structure of Atoms and Molecules*; Chemical Catalogue Company: New York, 1923.

(2) Stephan, D. W. *Dalton Trans.* **2009**, 3129–3136.

(3) Review: Stephan, D. W.; Erker, G. *Angew. Chem.* **2010**, *122*, 50−81; *Angew. Chem., Int. Ed.* **2010**, *49*, 46−76.

(4) (a) Tochtermann, W. *Angew. Chem.* **1966**, *78*, 355−375; *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 351−371. (b) Wittig, G.; Benz, E. *Chem. Ber.* **1959**, *92*, 1999–2013.

(5) (a) McCahill, J. S. J.; Welch, G. C.; Stephan, D. W. *Angew. Chem.* **2007**, *119*, 5056−5059; *Angew. Chem., Int. Ed.* **2007**, *46*, 4968−4971. (b) Sortais, J.-B.; Voss, T.; Kehr, G.; Fröhlich, R.; Erker, G. *Chem. Commun.* **2009**, 7417–7418. (c) Voss, T.; Chen, C.; Kehr, G.; Nauha, E.; Erker, G.; Stephan, D. W. *Chem. Eur. J.* **2010**, *16*, 3005–3008.

(6) (a) Mömming, C. M.; Kehr, G.; Wibbeling, B.; Fröhlich, R.; Schirmer, B.; Grimme, S.; Erker, G. *Angew. Chem.* **2010**, *122*, 2464−2467; *Angew. Chem., Int. Ed.*, **2010**, *49*, 2414-2417. (b) Mömming, C. M.; Frömel, S.; Kehr, G.; Fröhlich, R.; Grimme, S.; Erker, G. *J. Am. Chem. Soc.* **2009**, *131*, 12280–12289.

(7) Mömming, C. M.; Otten, E.; Kehr, G.; Fröhlich, R.; Grimme, S.; Stephan, D. W.; Erker, G. *Angew. Chem.* **2009**, *121*, 6770−6773; *Angew. Chem., Int. Ed.* **2009**, *48*, 6643-6646.

(8) (a) Spies, P.; Kehr, G.; Bergander, K.; Wibbeling, B.; Fröhlich, R.; Erker, G. *Dalton Trans.* **2009**, 1534–1541. (b) Welch, G. C.; Stephan, D. W. *J. Am. Chem. Soc.* **2007**, *129*, 1880–1881. (c) Spies, P.; Erker, G.; Kehr, G.; Bergander, K.; Fröhlich, R.; Grimme, S.; Stephan, D. W. *Chem. Commun.* **2007**, 5072–5074. (d) Welch, G. C.; San Juan, R. R.; Masuda, J. D.; Stephan, D. W. *Science* **2006**, *314*, 1124–1126. See also: (e) Rokob, T. A.; Hamza, A.; Stirling, A.; Papai, I. *J. Am. Chem. Soc.* **2009**, *131*, 2029–2036.

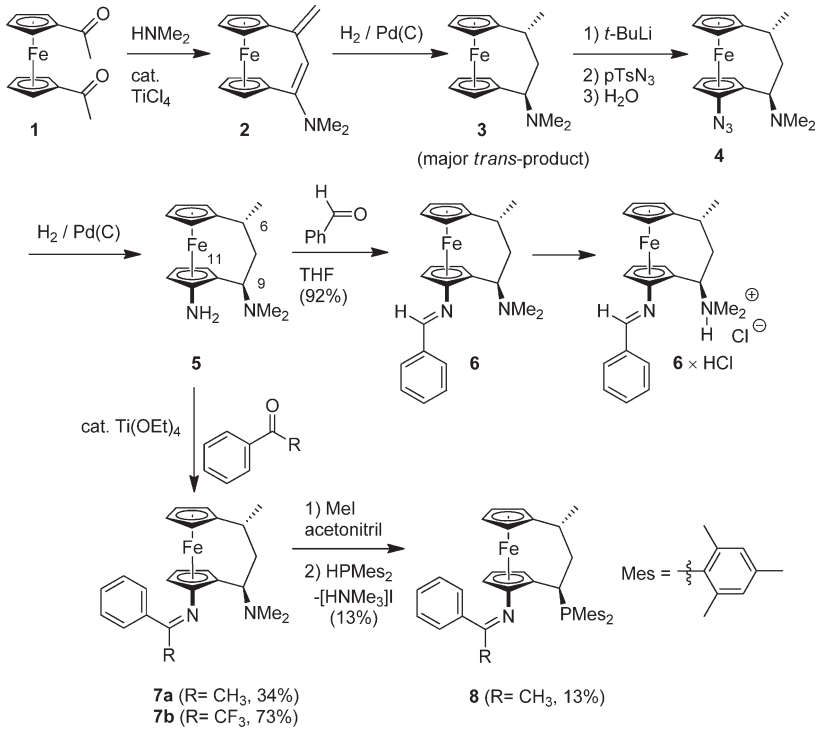
(9) (a) Chase, P. A.; Jurca, T.; Stephan, D. W. *Chem. Commun.* **2008**, 1701–1703. (b) Chen, D.; Klankermayer, J. *Chem. Commun.* **2008**, 2130–2131. (c) Spies, P.; Schwendemann, S.; Lange, S.; Kehr, G.; Fröhlich, R.; Erker, G. *Angew. Chem.* **2008**, *120*, 7654−7657; *Angew. Chem., Int. Ed.* **2008**, *47*, 7543−7546. (d) Wang, H.; Fröhlich, R.; Kehr, G.; Erker, G. *Chem. Commun.* **2008**, *45*, 5966–5968. (e) Chase, P. A.; Welch, G. C.; Jurca, T.; Stephan, D. W. *Angew. Chem.* **2007**, *119*, 8196−8199; *Angew. Chem., Int. Ed.* **2007**, *46*, 8050−8053.

(10) (a) Schwendemann, S.; Tumay, T. A.; Axenov, K. V.; Peuser, I.; Kehr, G.; Fröhlich, R.; Erker, G. *Organometallics* **2010**, *29*, 1067–1069. (b) Axenov, K.; Kehr, G.; Fröhlich, R.; Erker, G. *Organometallics* **2009**, *28*, 5148–5158. (c) Axenov, K.; Kehr, G.; Fröhlich, R.; Erker, G. *J. Am. Chem, Soc.* **2009**, *131*, 3454–3455.

(11) (a) Chen, C.; Fröhlich, R.; Kehr, G.; Erker, G. *Organometallics* **2008**, *27*, 3248–3253. (b) Liptau, P.; Tebben, L.; Kehr, G.; Fröhlich, R.; Erker, G.; Hollmann, F.; Rieger, B. *Eur. J. Org. Chem.* **2005**, 1909–1918. (c) Liptau, P.; Carmona, D.; Oro, L. A.; Lahoz, F. J.; Kehr, G.; Erker, G. *Eur. J. Inorg. Chem.* **2004**, 4586–4590.

 Published on Web 08/11/2010

Scheme 1



that carry an imine substituent in addition to other functional groups at their framework. These combinations of functional groups have resulted in a number of remarkable coupled reaction pathways that each have pairs of substituents involved. The examples of the disclosed reaction pathways have demonstrated to us the great variability that frustrated Lewis pair reactivity can offer with suitable substrates.

Results and Discussion

Preparation and Characterization of the [3]Ferrocenophane−Imine Substrates. Our study made use of an easy synthetic access to the "ortho"-amino-/α-dimethylamino-disubstituted [3]ferrocenophane system **5**, which we had recently developed and described (see Scheme 1).[12] The sequence starts with an intramolecular Mannich reaction of 1,1′-diacetylferrocene (**1**),[13,14] followed by catalytic hydrogenation of both C=C double bonds of the resulting conjugated dienamine functionality. This gives a ca. 7:1 mixture of *trans*- and *cis*-**3**. The major trans product was then subjected to a directed ortho metalation[15] to eventually introduce the $-NH_2$ group via a tosyl azide addition/reduction sequence.

Condensation of the amino group of complex **5** with benzaldehyde takes place readily in THF at room temperature to give the dark red aldimine **6** in >90% yield. The system features a set of seven ^{1}H NMR Cp signals of the trisubstituted ferrocene unit between δ 3.76 and 4.26. It shows a typical ^{1}H NMR aldimine −CH=N− resonance at δ 8.53 ($\delta(^{13}C)$ 156.8). Single crystals of the corresponding dimethylamine hydrochloride (**6**·HCl) were obtained by slow diffusion of pentane vapor into a solution of **6** in dichloromethane (see Figure 1). The X-ray crystal structure analysis shows the presence of a central [3]ferrocenophane unit with a typical "chair-like" folded geometry of the annelated C_3 bridge. The bulky $-NMe_2H^+$ substituent at the α-position C9 attains a pseudoequatorial orientation, whereas the *trans*-methyl substituent at C6 is pseudoaxially oriented. This brings the imino substituent at the "ortho"-Cp position C14 at the "lower" Cp ring of the ferrocene (C10 to C14) close to perpendicular with the C9−N1 vector (dihedral angle θ(N2−C14−C10−C9) = −5.5(4)°, θ(C14−C10−C9−N1) = 79.8(3)°). The aldimine is in an *E* configuration, as usual (θ(C10−C14−N2−C17) = 167.8(2)°, C14−N2 = 1.411(3) Å, C14−N2−C17 = 118.7(2)°), with the N2−C17 vector being oriented away from the adjacent NMe_2H^+ moiety. The phenyl substituent is coplanar with the imine

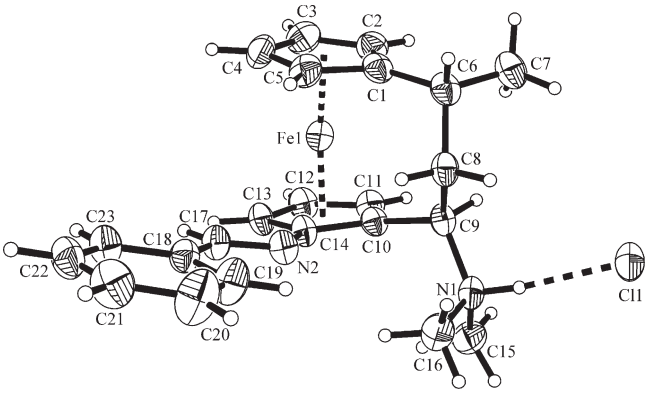


Figure 1. Projection of the molecular geometry of the aldimino [3]ferrocenophane ammonium salt **6**·HCl.

(12) Nilewski, C.; Neumann, M.; Tebben, L.; Fröhlich, R.; Kehr, G.; Erker, G. *Synthesis* **2006**, *13*, 2191–2200.
(13) Liptau, P.; Knüppel, S.; Kehr, G.; Kataeva, O.; Fröhlich, R.; Erker, G. *J. Organomet. Chem.* **2001**, *637−639*, 621–630.
(14) See for a comparison: (a) Knüppel, S.; Erker, G.; Fröhlich, R. *Angew. Chem.* **1999**, *111*, 2048−2051; *Angew. Chem., Int. Ed.*, **1999**, *38*, 1923−1926. (b) Bai, S.-D.; Wei, X.-H.; Guo, J.-P.; Liu, D.-S.; Zhou, Z.-Y. *Angew. Chem.* **1999**, *111*, 2051−2054; *Angew. Chem., Int. Ed.*, **1999**, *38*, 1926−-1928.
(15) Tebben, L.; Kehr, G.; Fröhlich, R.; Erker, G. *Eur. J. Inorg. Chem.* **2008**, 2654–2658.

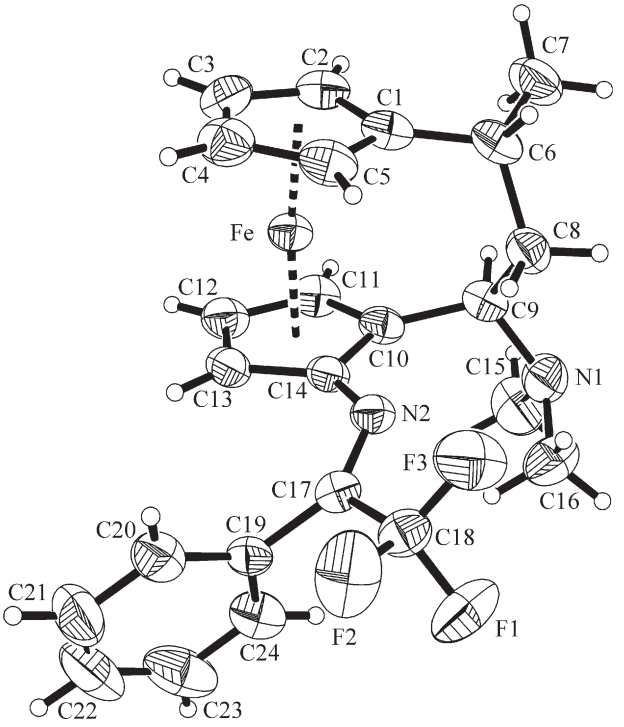


Figure 2. Molecular structure of complex **7b**.

−C(17)=N(2) double bond. Both lie approximately in the plane of the adjacent Cp ring (θ(C13−C14−N2−C17) = −9.4(4)°, θ(C14−N2−C17−C18) = −176.8(2)°, θ(N2−C17−C18−C19) = −4.3(4)°).

The formation of the related ketemines **7a**,**b** from **5** required Lewis acid catalysis.[16] Treatment of **5** with acetophenone under these conditions gave the ketimine **7a** (R = CH_3), which was eventually isolated in ca. 30% yield after chromatographic purification. The analogous reaction with the more reactive trifluoracetophenone was easier and gave the product **7b** (R = CF_3) in 71% yield. Both compounds were characterized by CHN elemental analysis and by spectroscopy (^{13}C NMR (−CR=N−) δ 165.5 (**7a**), δ 151.5 (q, $^2J_{FC} \sim 33$ Hz, **7b**)). Complex **7b** features a ^{19}F NMR signal at δ −69.3 (see Scheme 1).

Single crystals of compound **7b** suitable for an X-ray crystal structure analysis were obtained by slow solvent evaporation from a solution in pentane. In the crystal complex **7b** features the typical [3]ferrocenophane geometry with a pseudo-equatorially oriented $-NMe_2$ substituent at C9 (Figure 2). The rather bulky imino group is markedly rotated out of the plane of the adjacent ferrocenophane Cp ring (dihedral angle θ(C13−C14−N2−C17) = 34.1(5)°, N2−C17 = 1.269(4) Å, C14−N2−C17 = 123.2(2)°).

Eventually we substituted the $-NMe_2$ Group in complex **7a** by the bulky $-P(mesityl)_2$ substituent. This was achieved by the typical two-step process.[11,13,15−19] N-methylation generated the leaving group. Then the two-step substitution process with anchimeric assistance by the iron center gave the phosphine **8** with overall retention of configuration at the [3]ferrocenophane α-carbon at the bridge (see Scheme 1).

Frustrated Lewis Pair Reactions with Dihydrogen. We had recently shown that the α-dimesitylphosphino[3]ferrocenophane system **9** formed a frustrated Lewis pair with the strongly electrophilic borane $B(C_6F_5)_3$, which rapidly reacted with dihydrogen under ambient conditions.[20] We isolated the dephosphorylated product **11** along with the P/B adduct $Mes_2(H)P\cdot B(C_6F_5)_3$. We assumed that heterolytic splitting of dihydrogen had resulted in the formation of the reactive intermediate **10**, which contained a good leaving group ($-P(H)Mes_2^+$) at a substitution-sensitive position at the [3]ferrocenophane framework. This was consequently replaced by hydride under the reaction conditions to give **11** (see Scheme 2)

We then reacted the imino-/phosphine-substituted [3]ferrocenophane complex **8** with $B(C_6F_5)_3$ (1.1 equiv) and dihydrogen under analogous conditions. Within a few hours the bright red solution turned yellow and we isolated the product **12** in good yield. The analysis of the system revealed that the $-PMes_2$ substituent had been replaced by hydride and that the imine was reduced to the corresponding secondary amine.

Compound **12** contains three chirality elements. Two of them are dependent on each other (p-*R**, 6-*R**). The stoichiometric reduction/dephosphorylation gave two diastereoisomers in a ca. 1.2 : 1 ratio. We employed the Lewis acid hexyl$B(C_6F_5)_2$ in a catalytic version of this hydrogenation reaction. Treatment of the imine **8** with dihydrogen in the presence of 10 mol % of the hexyl$B(C_6F_5)_2$ activator gave an 88% yield of **12** with two diastereoisomers in a 2.2:1 ratio. Reduction of the imine has created an additional chirality center (C15). The formation of this center was unselective under the catalytic frustrated Lewis pair/H_2 reduction conditions. We have observed the formation of two diastereoisomers of **12** (see Scheme 2), which have the relative configurations p-*R**,6-*R**,15-*R** and p-*R**,6-*R**,15-*S**, respectively. Consequently, we have observed two sets of ^{1}H/^{13}C NMR data of the pair of diastereoisomers (e.g., δ 1.11/1.18 (6-CH_3), δ 1.27/1.26 (15-CH_3); δ 1.71, 1.98/1.61, 2.00 ($H_2C(9)$)).

Single crystals were obtained for one diastereoisomer of **12**. The X-ray crystal structure analysis (see Figure 3) revealed that it has the relative configuration p-*R**,6-*R**,15-*R**. It contains the methyl substituent at carbon atom C6 in a pseudo-equatorial orientation and features the newly formed secondary amine substituent at the "lower" ferrocene Cp ring oriented such that the bulky phenyl group is arranged toward the outside of the molecule (C14−N1 = 1.397(3) Å, C14−N1−C15 = 116.9(2)°, dihedral angle θ(C10−C14−N1−C15) = −147.6(2)°).

For the catalytic Lewis pair reduction of the [3]ferrocenophane imines **7a**,**b** we employed the Lewis acid hexyl$B(C_6F_5)_2$.[21] This Lewis acid is readily available by hydroboration of 1-hexene with "Piers' borane" [$HB(C_6F_5)_2$].[22] Catalytic

(16) Ruano, J. L. G.; Aleman, J.; Parra, A.; Cid, M. B. *Org. Synth.* **2007**, *84*, 129–138.

(17) (a) Chhor y Sok, K.; Tainturier, G.; Gautheron, B. *J. Organomet. Chem.* **1977**, *132*, 173–189. (b) Gokel, G. W.; Marquarding, D.; Ugi, I. *J. Org. Chem.* **1972**, *37*, 3052–3058. (c) Marquarding, D.; Klusacek, H.; Gokel, G.; Hoffmann, P.; Ugi, I. *J. Am. Chem. Soc.* **1970**, *92*, 5389–5393.

(18) *Ferrocenes: Ligands, Materials and Biomolecules*; Štěpnička, P., Ed.; Wiley, Chichester, U.K., 2008. *Ferrocenes: Homogeneous Catalysis, Organic Synthesis, Materials Science*; Togni, A., Hayashi, T., Eds.; VCH: Weinheim, Germany, 1995.

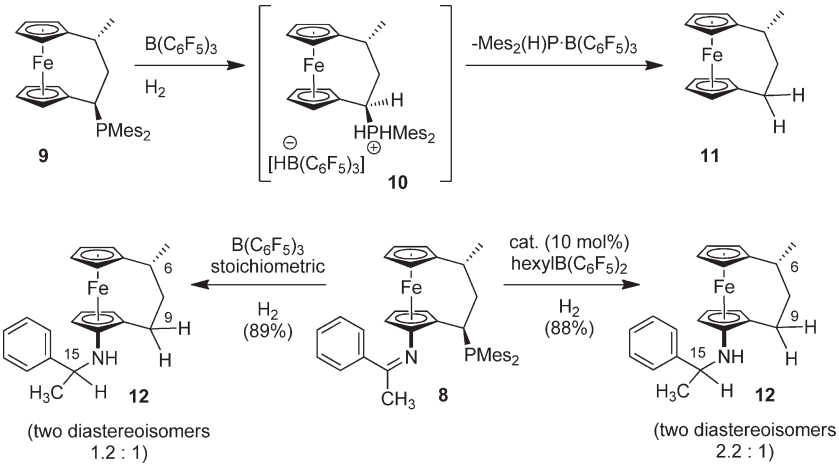
(19) Mernyi, A.; Kratky, C.; Weissensteiner, W.; Widhalm, M. *J. Organomet. Chem.* **1996**, *508*, 209–218.

(20) Huber, D. P.; Tanino, S.; Kehr, G.; Bergander, K.; Fröhlich, R.; Erker, G.; Ohki, Y.; Tatsumi, K. *Organometallics* **2008**, *27*, 5279–5284.

(21) (a) Axenov, K. unpublished results, Münster **2010**. See for a comparison: (b) Parks, D. J.; Spence, R. E. v. H.; Piers, W. E. *Angew. Chem.* **1995**, *107*, 895−897; *Angew. Chem., Int. Ed.* **1995**, *34*, 809−811.

(22) Parks, D. J.; Piers, W. E.; Yap, G. P. A. *Organometallics* **1998**, *17*, 5492–5503.

Scheme 2



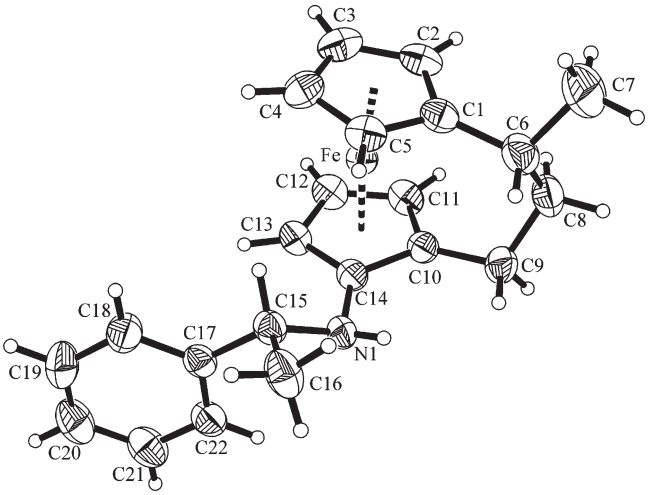
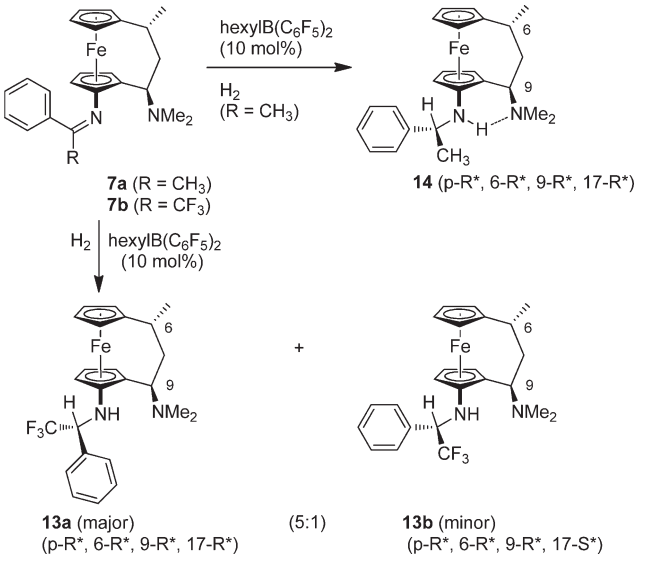


Figure 3. Molecular structure of the p-*R**,6-*R**,15-*R** diastereoisomer of compound **12**.

Scheme 3



hydrogenation of the CF_3-substituted [3]ferrocenophane imine **7b** was carried out under ambient conditions under a dihydrogen atmosphere using 10 mol % of the hexyl-$B(C_6F_5)_2$ Lewis acid. The amine-/imine-substituted substrate in this case itself serves as the complementary Lewis base[9b,10] that is necessary for the heterolytic "metal-free" dihydrogen splitting process. After 12 h at ambient temperature we isolated the product **13** as a mixture of two diastereoisomers in a 5:1 ratio (67% de) in a combined yield of >90%; thus, the reaction is rather unselective (Scheme 3). Both isomers still contain the α-NMe_2 substituent untouched (^{1}H NMR δ 2.12 (major isomer), 2.06 (minor isomer)). The major isomer **13a** features a ^{19}F NMR signal of the $-CF_3$ group at δ −74.5 and the minor isomer at −73.9 ppm.

Single crystals of the major isomer **13a** were obtained by diffusion of pentane vapor into a dichloromethane solution of the mixture. The X-ray crystal structure analysis (see Figure 4) shows the presence of a chairlike conformational orientation of the C_3 bridge of the [3]ferrocenophane unit with the methyl group at C6 and the $-NMe_2$ substituent at C9 attached trans to each other. The methyl group is oriented pseudo-axially and the more bulky dimethylamino substituent pseudo-equatorially. The former imino substituent at the "lower" ferrocenophane Cp ring (C10 to C14) has been reduced to the secondary amino substituent −NHCHPh-(CF_3). The newly formed stereocenter in the major product **13a** has the relative configuration *R**; therefore, this product is characterized by a relative configuration of p-*R**,6-*R**,9-*R**,17-*R** (see Scheme 3 and Figure 4)

The frustrated Lewis pair catalyzed hydrogenation of the [3]ferrocenophane ketimine **7a** (R = CH_3) was initiated by the addition of 10 mol % of hexyl-$B(C_6F_5)_2$. The reduction of the substrate **7a** proceeded smoothly under conditions analogous to those applied to **7b** (see above). However, the reduction of **7a** is much more selective under these conditions. We eventually isolated a single product (**14**) after workup in 80% yield. The ^{1}H NMR spectrum of the product **14** confirmes the presence of the intact dimethylamino substituent at the bridge carbon atom C9 (δ 2.18 (NMe_2)) and of the newly formed $-NHCH(CH_3)Ph$ substituent at the "ortho" position of the lower Cp ring (δ 4.43 (d, NH), δ 4.19 (dq, CH), δ 1.34 (d, CH_3)).

The product **14** was characterized by X-ray diffraction. Single crystals were obtained from dichloromethane/pentane by the diffusion method. In the crystal compound **14** exhibits a bridge conformation that is slightly different from the usually observed one (Figure 5). The twistlike conformation found

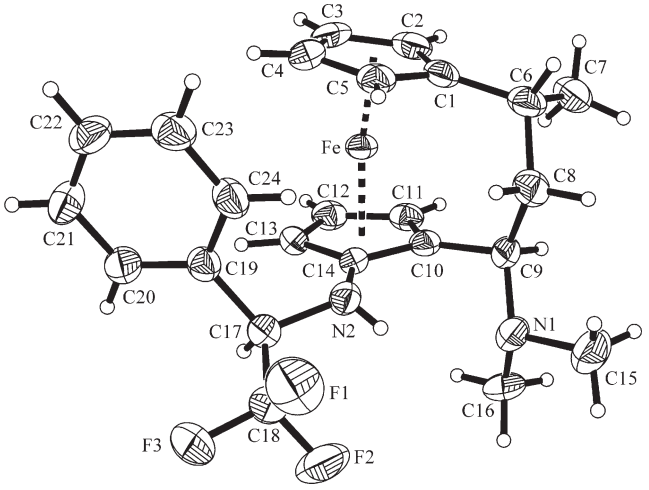


Figure 4. View of the molecular geometry of **13a**, the major diastereoisomer of the [3]ferrocenophane diamine mixture (**13**).

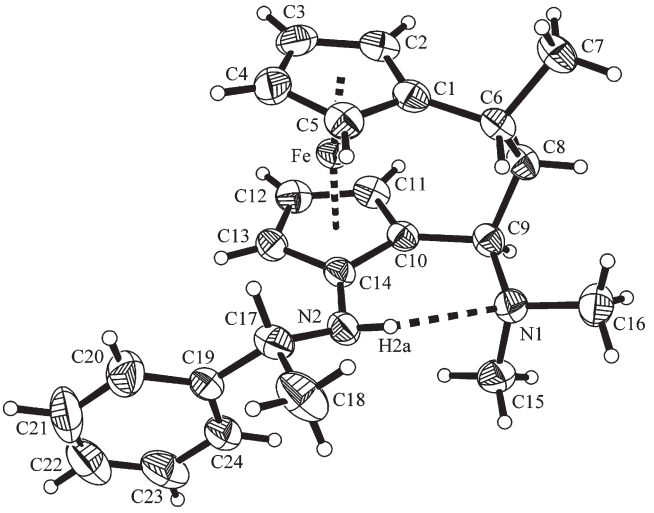
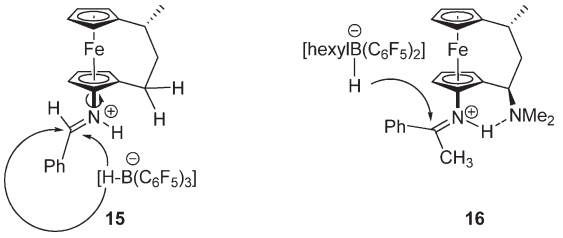


Figure 5. Molecular structure of complex **14**.

here is probably caused by the constraints imposed by the μ-H bridge between N1 of the $-NMe_2$ substituent at C9 (N1−C9 = 1.477(3) Å) and N(2)−H of the newly formed secondary amino substituent at C14. The resulting annelated heterocycle leads to a deviation of the C9−N1 and C14−N2 vectors in **14** (θ(N2−C14···C9−N1) = 9.5°) from coplanarity smaller than that in the related compound **13a** (θ(N2−C14···C9−N1) = 42.1°). The X-ray crystal structure analysis reveals a relative overall configurational assignment of **14** as p-*R**,6-*R**,9-*R**,17-*R**. Note that this correlates to a chemically inverted stereochemical course of hydride addition to the imino carbon in **14** relative to **13a**, since the formal exchange of CH_3 for CF_3 at C17 results in an inverted Cahn−Ingold−Prelog sequence in these two products.

The stereoselectivities of the reduction reactions of the imino groups in the substrates **8** and **7a**,**b** are remarkably different. We assume that the initial heterolytic splitting of the dihydrogen molecule in the frustrated Lewis pair **8**/$B(C_6F_5)_3$ involves the phosphine Lewis base. This will then result in the formation of the $-P(H)Mes_2^+$ leaving group that will be replaced by hydride.[20] It may consequently be assumed that the subsequent reduction of the aldimine function will take place at the dephosphorylated substrate

Scheme 4



already formed in situ. Splitting of H_2 then will require the imine to serve as the necessary Lewis base. The resulting iminium salt (**15**; see Scheme 4) is conformationally unrestricted and will probably be attacked by the borohydride equally well from the *Re* or the *Si* face, leading to the observed ca. equimolar mixture of diastereoisomers (**12**).

In contrast, the frustrated Lewis pair reduction of the chelate ketimine **7a** is diastereospecific within the accuracy of the ^{1}H NMR analysis. Again, the substrate needs to serve as the necessary Lewis base for heterolytic dihydrogen splitting in this case. We assume that pronounced hydrogen bonding between the resulting iminium ion and the almost coplanarly arranged adjacent dimethylamino substituent leads to the necessary conformational fixation of the iminium system to allow a preferred hydride transfer from the *Re* face: for example, as is depicted in Scheme 4.

The reason for the lack of selectivity in the process of the hexyl-$B(C_6F_5)_2$-induced reduction of the related $-CF_3$-containing ketimine is less obvious. It might be assumed that the iminium ion resulting from the heterolytic dihydrogen splitting reaction in this case is so reactive that it may rapidly react by hydride addition before effective conformational fixation by hydrogen bridge formation can occur.

Frustrated Lewis Pair Reactions in the Absence of Dihydrogen. The Lewis acid $B(C_6F_5)_3$ is known to be a good abstractor of hydride in the α-position of amines to form the respective iminium salts.[23] A typical example is the H^- transfer from the α-bridge position of the dimethylamino-[3]ferrocenophane **3** to $B(C_6F_5)_3$ to form the respective iron-stabilized iminium salt.[24]

We now found that treatment of an α-NMe_2 [3]ferrocenophane derivative with $B(C_6F_5)_3$ takes an overall different course when it is carried out in the presence of a suitable nucleophilic trapping reagent. The dimethylamino[3]ferrocenophane aldimine **6** reacts readily at room temperature with 1 molar equiv of $B(C_6F_5)_3$ in toluene to cleanly form the salt **19**. It was isolated in a yield of 86%. The product **19** was characterized by CHN elemental analysis, by spectroscopy, and by X-ray diffraction. Single crystals were obtained by a slow evaporation of the solvent from a toluene solution. In the crystal the salt **19** features discrete cation and anion moieties. We see the presence of the $[HB(C_6F_5)_3^-]$ anion. The cation features a [3]ferrocenophane unit to which a six-membered heterocycle is annelated (Figure 6). Both nitrogen atoms are incorporated into the newly formed heterocycle. It exhibits a delocalized strongly stabilized iminium ion structure in its center (N1−C16 = 1.318(3) Å,

(23) (a) Sumerin, V.; Schulz, F.; Nieger, M.; Leskelä, M.; Repo, T.; Rieger, B. *Angew. Chem.* **2008**, *120*, 6090−6092; *Angew. Chem., Int. Ed.* **2008**, *47*, 6001−6003. (b) Focante, F.; Mercandelli, P.; Sironi, A.; Resconi, L. *Coord. Chem. Rev.* **2006**, *250*, 170–188. (c) Millot, N.; Santini, C. C.; Fenet, B.; Basset, J. M. *Eur. J. Inorg. Chem.* **2002**, 3328–3335.

(24) Liptau, P.; Neumann, M.; Erker, G.; Kehr, G.; Fröhlich, R.; Grimme, S. *Organometallics* **2004**, *23*, 21–25.

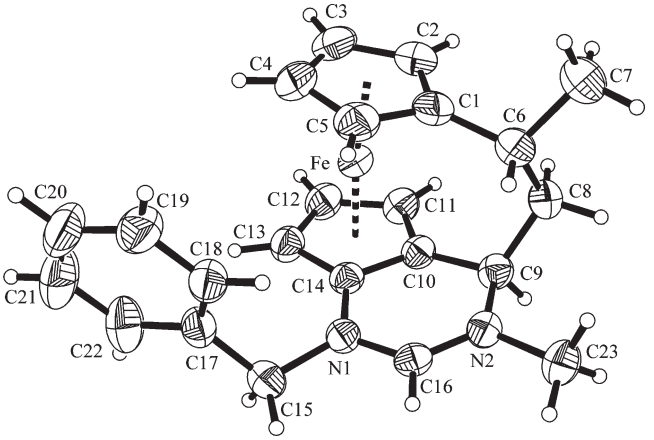
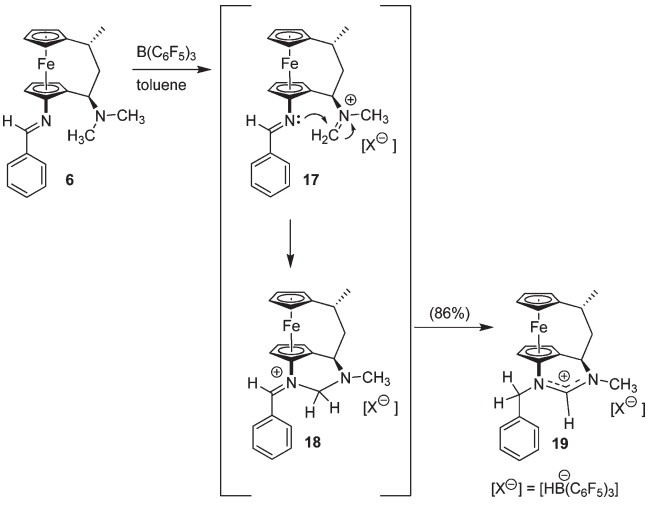


Figure 6. Molecular structure of the annelated iminium [3]ferrocenophane system **19** (only the cation is depicted).

Scheme 5



N2−C16 = 1.309(3) Å, N1−C16−N2 = 125.7(2)°). Consequently, both nitrogen atoms show close to planar three-coordinate coordination geometries (sum of bonding angles: at N1, 359.2°; at N2, 359.8°). The nitrogen atom N1 contains a benzyl substituent that apparently was formed by hydride transfer to the former imine of the starting material **6**.

The NMR spectra show the presence of a single compound in solution. In the ^{1}H NMR spectrum the cation of **19** features an AB spin system of the benzylic CH_2 group at N1 (δ 4.68, 4.78, $^2J_{H,H}$ = 15.0 Hz) and a singlet of the central iminium CH proton (δ 7.91, $\delta(^{13}C)$ 149.5). There is the typical ^{1}H NMR doublet of the 6-CH_3 methyl group at the [3]ferrocenophane bridge (δ 1.31) and a signal at δ 3.28 for the single remaining methyl group at N2 (see Scheme 5). We observe the typical NMR signals of the $[HB(C_6F_5)_3^-]$ counteranion ($\delta(^{11}B)$ −25.6, $\delta(^{19}F)$−132.9 (ortho), −162.3 (para), −165.7 (meta)).

The formation of the product **19** indicates that,under the applied reaction conditions, eventually hydride abstraction by the $B(C_6F_5)_3$ Lewis acid is more favorable from the

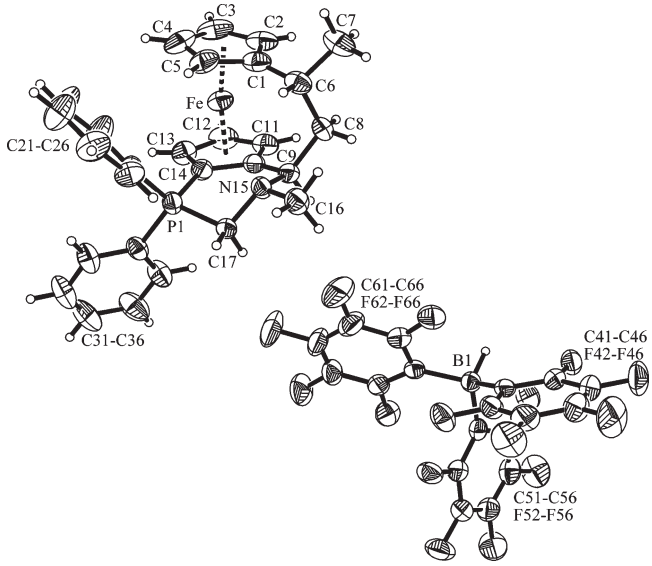
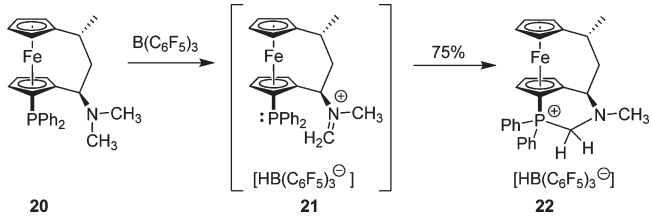


Figure 7. Molecular structure of the salt **22** (both the anion and cation are depicted).

Scheme 6



N-methyl group[25] than the previously observed 9-H hydride abstraction.[24] This new route would initially lead to the reactive iminium ion system **17**.[26] This is apparently not stable under the applied reaction conditions but is rapidly trapped by the adjacent aldimine nucleophile to generate the new (ring-closed) iminium ion **18**. Hydride transfer then converts this to the more stable system **19**, which we have eventually isolated (see Scheme 5).

We have observed a closely related reaction upon treatment of the previously described "ortho"-diphenylphosphino-/α-dimethylamino-disubstituted [3]ferrocenophane system **20**[27] with $B(C_6F_5)_3$. Again we find hydride abstraction at the *N*-methyl group to be favored over the abstraction of the 9-H hydride. The resulting reactive iminium intermediate **21** in this case is effectively trapped by the adjacent phosphorus nucleophile to eventually yield the organometallic phosphonium salt **22** (75% isolated; see Scheme 6).

Compound **22** shows an ^{1}H NMR AB spin system of the methylene group inside the newly formed annelated heterocycle at δ 4.11/3.29 ($\delta(^{13}C)$ 51.1, $^1J_{CP}$ = 75 Hz) and a corresponding ^{31}P NMR resonance at δ 14.6 ($[HB(C_6F_5)_3^-]$ counterion: $\delta(^{11}B)$ −25.4 (d, $^1J_{BH} \approx$ 93 Hz)). The salt **22** was characterized by X-ray diffraction. Single crystals were

(25) (a) Di Saverio, A.; Focante, F.; Camurati, I.; Resconi, L.; Beringhelli, T.; D'Alfonso, G.; Donghi, D.; Maggioni, D.; Mercandelli, P.; Sironi, A. *Inorg. Chem.* **2005**, *44*, 5030–5041. (b) Hughes, R. P.; Kovacik, I.; Lindner, D.; Smith, J. M.; Willemsen, S.; Zhang, D.; Guzei, I. A.; Rheingold, A. L. *Organometallics* **2001**, *20*, 3190–3197.

(26) A reviewer discussed the possibility of radical pathways for the hydride abstraction involving initial electron transfer to the borane. See for a comparison: (a) Harlan, C. J.; Hascall, T.; Fujita, E.; Norton, J. R. *J. Am. Chem. Soc.* **1999**, *121*, 7274–7275. (b) Kwaan, J. K.; Harlan, C. J.; Norton, J R. *Organometallics* **2001**, *20*, 3818–3820. (c) Cummings, S. A.; Iimura, M.; Harlan, C. J.; Kwaan, R. J.; Trieu, I. V.; Norton, J. R.; Bridgewater, B. M.; Jäkle, F.; Sundararaman, A.; Tilset, M. *Organometallics* **2006**, *25*, 1565–1568.

(27) Liptau, P.; Seki, T.; Kehr, G.; Abele, A.; Fröhlich, R.; Erker, G.; Grimme, S. *Organometallics* **2003**, *22*, 2226–2232.

obtained by slow diffusion of pentane into a solution of the compound in diethyl ether. The cation part features a distorted boatlike conformation of the charged [3]ferrocenophane annelated six-membered P/N heterocycle. The six-membered-ring conformation is characterized by the dihedral angles θ(C11−C10−C9−N15) = 171.6(3)°, θ(C9−C10−C14−P1) = −14.0(5)°, and θ(C14−P1−C17−N15) = 50.4(3)°. The bond angles at P1 and at N15 amount to C14−P1−C17 = 100.2(2)° and C17−N15−C9 = 112.0(3)°, respectively (P1−C17−N15 = 107.8(2)°) (see Figure 7).

Some Conclusions

Our study shows that frustrated Lewis pairs derived from simple tertiary amines can successfully be handled and even used for catalytic reactions under the appropriate reaction conditions.[28] In the absence of dihydrogen we observe specific hydride abstraction from an *N*-methyl group with subsequent iminium ion chemistry that involves other functional groups present at the framework. In the presence of dihydrogen one can achieve reaction conditions that lead to very clean and selective catalytic hydrogenation of imine functionalities[9] attached at the chosen organometallic framework. The system behaves "pseudo-autocatalytically"[10] with regard to the necessary Lewis base, which here is derived from the substrate itself. We have also found that under well-defined circumstances a highly stereoselective reduction of the imine functionality can be achieved under frustrated Lewis pair catalysis, which may be of importance in further applications of frustrated Lewis pair chemistry.

Experimental Section

General Information. All reactions were carried out under an argon atmosphere with Schlenk-type glassware or in a glovebox. Solvents (including deuterated solvents used for NMR spectroscopy) were dried and distilled under argon prior to use. The following instruments were used for physical characterization of the compounds. Elemental analyses: Foss-Heraeus CHNO-Rapid. NMR: Bruker AC 200 P (^{1}H, 200 MHz), Varian 500 MHz INOVA (^{1}H, 500 MHz; ^{13}C, 126 MHz), Varian UNITY plus NMR spectrometer (^{1}H, 600 MHz; ^{13}C, 151 MHz). Assignments of the resonances are supported by 2D experiments. Melting points/decomposition temperature: DSC 2010 (TA-Instruments) apparatus. IR: Varian 3100 FT-IR (Excalibur-Series) spectrometer. X-ray diffraction: data sets were collected with a Nonius KappaCCD diffractometer, equipped with a rotating anode generator. Programs used: data collection COLLECT,[31] data reduction Denzo-SMN,[32] absorption correction SORTAV[33] and Denzo,[34] structure solution SHELXS-97,[35] structure refinement SHELXL-97,[36] graphics XP.[37] R1 values are given for the observed reflections and wR2 values for all independent reflections. All figures are drawn with 50% probability ellipsoids.

Materials. Complex **12**,[12] dimesitylphosphine,[29] tris(pentafluorophenyl)borane,[30] bis(pentafluorophenyl)borane,[22] and complex **20**[27] were prepared according to modified literature procedures.

Preparation of Complex 6. Benzaldehyde (5.0 mL, 49.5 mmol, 5.7 equiv) was added to a solution of complex **5** (2.6 g, 8.72 mmol) in tetrahydrofuran (20 mL) at room temperature. The suspension turned from yellow to deep red. After 1 h the solvent was removed in vacuo and the crude product was purified by flash chromatography (SiO_2, methanol) to give **6** as a deep red powder (3.1 g, 8.02 mmol, 92%). Crystals of **6**·HCl suitable for X-ray diffraction were obtained by diffusion of pentane into a saturated solution of **6** in dichloromethane. Anal Calcd for $C_{23}H_{26}FeN_2$: C, 71.51; H, 6.78, N, 7.25. Found: C, 70.60; H, 6.70; N, 6.98. ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K): δ 1.31 (d, $^3J_{H,H}$ = 7.0 Hz, 3H, 7-H), 2.10 (dm, $^2J_{H,H}$ = 12.9 Hz, 1H, 8-H), 2.24 (s, 6H, NMe_2), 2.88 (m, 1H, 6-H), 3.34 (dm, $^3J_{H,H}$ = 11.8 Hz, 1H, 9-H), 3.55 (ddd, $^2J_{H,H}$ = 12.9 Hz, $^3J_{H,H}$ = 11.8 Hz, $^3J_{H,H}$ = 4.3 Hz, 1H, 8′-H), 3.76, 3.84, 4.13, 4.26 (each m, each 1H, C_5H_4), 4.13 (m, 1H, 13-H), 4.15 (m, 1H, 11-H), 4.49 (m, 1H, 12-H), 7.45 (m, 3H, *p*,*m*-C_6H_5), 7.84 (m, 2H, *o*-C_6H_5), 8.53 (s, 1H, 15-H). ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 298 K): δ 17.2 (C7), 28.5 (C6), 43.3 (br, NMe_2), 44.2 (C8), 59.0, 66.8 (br) (C12,13), 59.8 (br, C9), 66.7, 68.7, 70.2, 75.2 (C_5H_4), 73.4 (C11), 78.3 (br, C10), 95.3 (C1), 104.7 (C14), 128.2 (*o*-C_6H_5), 129.1 (*m*-C_6H_5), 130.7 (*p*-C_6H_5), 137.7 (*i*-C_6H_5), 156.8 (C15).

X-ray Crystal Structure Analysis of 6·HCl: formula $C_{23}H_{27}ClFeN_2$, M = 422.77, red crystal, 0.30 × 0.20 × 0.15 mm, a = 9.4638(3) Å, b = 12.4287(4) Å, c = 17.3060(7) Å, β = 97.385(1)°, V = 2018.69(12) Å^3, ρ_{calcd} = 1.391 g cm^{-3}, μ = 0.889 mm^{-1}, empirical absorption correction (0.776 ≤ T ≤ 0.878), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.710 73 Å, T = 223(2) K, ω and φ scans, 16 549 reflections collected (±h,±k,±l), (sin θ)/λ = 0.66 Å^{-1}, 4786 independent (R_{int} = 0.072) and 3002 observed reflections ($I \geq 2\sigma(I)$), 247 refined parameters, R1 = 0.050, wR2 = 0.123, maximum (minimum) residual electron density 0.44 (−0.41) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of Complex 7a. Acetophenone (3.3 mL, 28.2 mol, 1.9 equiv), titanium tetraethoxide (10.12 mL, 48.79 mmol, 3.3 equiv), and compound **5** (4.40 g, 14.8 mmol) were mixed in a Schlenk flask and stirred under vacuum for 15 min. Then dichloromethane (20 mL) was added and the red solution was stirred at 35 °C for 36 h. After addition of a saturated solution of $NaHCO_3$ (100 mL), the organic layer was separated and the aqueous phase was extracted with dichloromethane (3 × 200 mL). The combined organic layers were dried over magnesium sulfate, filtered, and evaporated in vacuo. The residue was purified by column chromatography (SiO_2, methanol) to yield the product as a red solid (2.00 g, 5.00 mmol, 34%). Anal. Calcd for $C_{24}H_{28}FeN_2$: C, 72.00; H, 7.05; N, 7.00. Found: C, 71.65; H, 6.68; N, 6.88. ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ 1.34 (d, $^3J_{H,H}$ = 7.3 Hz, 3H, 7-H), 2.08 (dm, $^2J_{H,H}$ = 12.9 Hz, 1H, 8-H), 2.11 (s, 6H, NMe_2), 2.27 (s, 3H, Me), 2.96 (m, 1H, 6-H), 3.22 (dm, $^3J_{H,H}$ = 11.5 Hz, 1H, 9-H), 3.51 (ddd, $^2J_{H,H}$ = 12.9 Hz, $^3J_{H,H}$ = 11.5 Hz, $^3J_{H,H}$ = 4.2 Hz, 1H, 8′-H), 3.85 (m, 1H, $C_5H_4^{\beta}$), 3.90 (m, 1H, $C_5H_4^{\alpha}$), 3.98 (m, 1H, 13-H), 4.03 (m, 1H, 11-H), 4.05 (m, 1H, 12-H), 4.16 (m, 1H, $C_5H_4^{\alpha}$), 4.25 (m, 1H, $C_5H_4^{\beta}$), 7.45 (m, 3H, *p*,*m*-C_6H_5), 8.01 (m, 2H, *o*-C_6H_5). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K): δ 17.3 (C7), 17.5 (Me), 28.8 (C6), 43.4 (NMe_2, C8), 60.1 (C9), 62.2 (C13), 65.1 (C12), 66.1 ($C_5H_4^{\beta}$), 68.4 ($C_5H_4^{\alpha}$), 70.6 ($C_5H_4^{\beta}$), 71.5 (C11), 76.1 ($C_5H_4^{\alpha}$),

(28) (a) Schulz, F.; Sumerin, V.; Leskelä, M.; Repo, T.; Rieger, B. *Dalton Trans*. **2010**, *39*, 1920–1922. (b) Geier, S. J.; Stephan, D. W. *J. Am. Chem. Soc*. **2009**, *131*, 3476–3477. (c) Geier, S. J.; Gille, A. L.; Gilbert, T. M.; Stephan, D. W. *Inorg. Chem*. **2009**, *48*, 10466–10474. (d) Sumerin, V.; Schulz, F.; Nieger, M.; Atsumi, M.; Wang, C.; Leskelä, M.; Pyykkö, P.; Repo, T.; Rieger, B. *J. Organomet. Chem*. **2009**, *694*, 2654–2660. (e) Sumerin, V.; Schulz, F.; Atsumi, M.; Wang, C.; Nieger, M.; Leskelä, M.; Repo, T.; Pyykkö, P.; Rieger, B. *J. Am. Chem. Soc*. **2008**, *130*, 14117–14119.

(29) Lambert, J. B.; So, J.-H. *J. Org. Chem*. **1991**, *56*, 5962–5964.

(30) (a) Massey, A. G.; Park, A. J. In *Organometallic Syntheses*; King, R. B., Eisch, J. J., Eds.; Elsevier: New York, 1986; Vol. *3*, pp 461−462. (b) Massey, A. G.; Park, A. J. *J. Organomet. Chem*. **1964**, *2*, 245–250.

(31) *COLLECT*; Nonius BV, **1998**.

(32) Otwinowski, Z.; Minor, W. *Methods Enzymol*. **1997**, *276*, 307–326.

(33) Blessing, R. H. *Acta Crystallogr*. **1995**, *A51*, 33−37; *J. Appl. Crystallogr*. **1997**, *30*, 421−426.

(34) Otwinowski, Z.; Borek, D.; Majewski, W.; Minor, W. *Acta Crystallogr*. **2003**, *A59*, 228–234.

(35) Sheldrick, G. M. *Acta Crystallogr*. **1990**, *A46*, 467–473.

(36) Sheldrick, G. M. *Acta Crystallogr*. **2008**, *A64*, 112–122.

(37) *XP*; BrukerAXS, **2000**.

78.3 (C10), 95.2 (C1), 105.8 (C14), 127.1 (*o*-C_6H_5), 128.6 (*m*-C_6H_5), 130.2 (*p*-C_6H_5), 140.8 (*i*-C_6H_5), 165.5 (C15).

Preparation of Complex 7b. Trifluoroacetophenone (3.20 mL, 3.97 g, 22.8 mmol, 2 equiv), titanium tetraethoxide (13.1, 63.0 mmol, 5.5 equiv), and **5** (3.4 g, 11.4 mmol) were mixed in a Schlenk flask and stirred under vacuum for 15 min. Dichloromethane (20 mL) was added, and the red solution was stirred at 35 °C for 36 h. After addition of saturated $NaHCO_3$/water (100 mL) the organic layer was separated and the aqueous phase was extracted with dichloromethane (3 × 200 mL). The combined organic layers were dried over magnesium sulfate, filtered, and evaporated in vacuo. The residue was purified by column chromatography (SiO_2, methanol) to yield the product as a red solid (3.70 g, 8.14 mmol, 71%). Crystals suitable for X-ray diffraction were obtained by slow evaporation of a saturated solution of **7b** in pentane. Anal. Calcd for $C_{24}H_{25}F_3FeN_2$: C, 63.45; H, 5.55; N, 6.17. Found: C, 63.14; H, 5.17; N, 6.12. ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ 1.29 (d, $^3J_{H,H}$ = 7.3 Hz, 3H, 7-H), 2.02 (dm, $^2J_{H,H}$ = 13 Hz, 1H, 8-H), 2.23 (s, 6H, NMe_2), 2.89 (m, 1H, 6-H), 3.17 (m, 1H, 13-H), 3.42 (dm, 1H, $^2J_{H,H}$ = 11.7 Hz, 9-H), 3.54 (dm, $^2J_{H,H}$ = 13.0 Hz, $^3J_{H,H}$ = 11.7 Hz, $^2J_{H,H}$ = 4.3 Hz, 1H, 8′-H), 3.72 (m, 1H, C_5H_4), 3.84 (m, 1H, C_5H_4), 3.93 (m, 1H, 12-H), 4.10 (m, 1H, C_5H_4), 4.17 (m, 1H, 11-H), 4.25 (m, 1H, C_5H_4), 7.29 (m, 2H, *o*-C_6H_5), 7.47 (m, 2H, *m*-C_6H_5), 7.49 (m, 1H, *p*-C_6H_5). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K): δ 17.2 (C7), 28.4 (C6), 43.0 (NMe_2), 44.0 (C8), 59.3 (C9), 62.8 (C13), 66.9 (C_5H_4), 68.2 (C12), 69.3 (C_5H_4), 70.8 (C_5H_4), 73.9 (C11), 76.2 (C_5H_4), 82.8 (C10), 95.7 (C1), 97.0 (C14), 121.2 (q, $^1J_{F,C}$ = 278.0 Hz, CF_3), 128.1 (*o*-C_6H_5), 129.3 (*m*-C_6H_5), 130.4 (*p*-C_6H_5), 132.7 (*i*-C_6H_5), 151.5 (q, $^2J_{F,C} \sim 33$ Hz, C15). ^{19}F NMR (282 MHz, C_6D_6, 300 K): δ −69.3 (s, CF_3).

X-ray Crystal Structure Analysis of 7b: formula $C_{24}H_{25}F_3FeN_2$, M = 454.31, red crystal, 0.30 × 0.20 × 0.07 mm, a = 9.9315(2) Å, b = 13.6542(2) Å, c = 16.0667(4) Å, β = 104.814(1)°, V = 2106.33(7) Å^3, ρ_{calcd} = 1.433 g cm^{-3}, μ = 0.775 mm^{-1}, empirical absorption correction (0.805 ≤ T ≤ 0.949), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.710 73 Å, T = 223(2) K, ω and φ scans, 16 439 reflections collected (±h,±k,±l), (sin θ)/λ = 0.66 Å^{-1}, 4885 independent (R_{int} = 0.051) and 4065 observed reflections ($I \geq 2\sigma(I)$), 274 refined parameters, R1 = 0.057, wR2 = 0.160, maximum (minimum) residual electron density 1.52 (−0.43) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of Complex 8. A solution of compound **7a** (1.00 g, 2.50 mmol) dissolved in anhydrous acetonitrile (10 mL) was treated with methyl iodide (2.27 g, 1.00 mL, 16 mmol, 6.4 equiv). After 1 h of stirring at room temperature the excess methyl iodide and solvent were removed in vacuo. Dimesitylphosphine (675.5 mg, 2.5 mmol, 1 equiv) and anhydrous acetonitrile (10 mL) were added, and the solution was heated to 70 °C and stirred overnight. After removal of the solvent in vacuo, the residue was suspended in pentane. The suspension was filtered, and the filtrate was stored at −32 °C overnight to give the product as a red solid. The precipitate was collected by filtration and dried in vacuo to give **8** as a red powder: yield 0.20 g (0.32 mmol, 13%). Anal. Calcd for $C_{40}H_{44}FeNP$: C, 76.78; H, 7.09; N, 2.24. Found: C, 76.91; H, 6.80; N, 2.19. ^{1}H NMR (500 MHz, C_6C_6, 298 K): δ 1.07 (d, $^3J_{H,H}$ = 7.2 Hz, 3H, 7-H), 1.89 (s, 3H, Me), 1.99 (s, 3H, *p*-CH_3^{Mes}), 2.05 (s, 3H, *p*-$CH_3^{Mes'}$), 2.11 (m, 1H, 8-H), 2.43 (s, 6H, *o*-CH_3^{Mes}), 2.47 (s, 6H, *o*-$CH_3^{Mes'}$), 2.66 (m, 1H, 6-H), 3.19 (m, 1H, 8′-H), 3.88 (m, 1H, 13-H), 3.94 (m, 1H, 12-H), 3.96 (m, 1H, C_5H_4), 3.98 (m, 1H, 11-H), 4.01 (m, 2H, C_5H_4), 4.06 (dm, $^3J_{H,H}$ 1H, 9-H), 4.35 (m, 1H, C_5H_4), 6.56 (d, $^4J_{P,H}$ = 2.6 Hz, 2H, *m*-Mes), 6.71 (d, $^4J_{P,H}$ = 2.4 Hz, 2H, *m*-Mes′), 7.22 (m, 1H, *p*-C_6H_5), 7.26 (m, 2H, *m*-C_6H_5) 8.09 (m, 2H, *o*-C_6H_5). ^{13}C{^{1}H} NMR (126 MHz, 126 Hz, 298 K): δ 17.25 (d, $^4J_{P,C}$ = 5.1 Hz, C7), 17.34 (Me), 20.6 (*p*-CH_3^{Mes}), 20.8 (*p*-$CH_3^{Mes'}$), 23.3 (d, $^3J_{P,C}$ = 15.3 Hz, *o*-$CH_3^{Mes'}$), 23.8 (d, $^3J_{P,C}$ = 14.2 Hz, *o*-CH_3^{Mes}), 26.9 (d, $^3J_{P,C}$ = 10.8 Hz, C6), 28.0 (d, $^1J_{P,C}$ = 25.7 Hz, C9), 45.3 (d, $^2J_{P,C}$ = 25.5 Hz, C8), 61.9 (C13), 64.1 (C12), 67.2 (C_5H_4), 68.2 (C_5H_4), 70.6 (d, $^4J_{P,H}$ = 2.8 Hz, C11), 71.0 (C_5H_4), 76.9 (C_5H_4), 84.6 (d, $^2J_{P,C}$ = 21.5 Hz, C10), 93.4 (C1), 106.0 (d, $^3J_{P,C}$ = 2.4 Hz, C14), 127.5 (*o*-C_6H_5), 128.0 (*m*-C_6H_5), 129.8 (*p*-C_6H_5), 130.1 (d, $^3J_{P,C}$ = 6.7 Hz, *m*-Mes′), 130.2 (d, $^3J_{P,C}$ = 2.4 Hz, *m*-Mes), 133.9 (d, $^1J_{P,C}$ = 41.5 Hz, *i*-Mes), 134.2 (d, $^1J_{P,C}$ = 37.9 Hz, *i*-Mes′), 136.7 (*p*-Mes), 138.1 (*p*-Mes′), 141.1 (*i*-C_6H_5), 142.4 (d, $^2J_{P,C}$ = 15.3 Hz, *o*-Mes), 144.1 (d, $^2J_{P,C}$ = 15.9 Hz, *o*-Mes′), 165.9 (C15). ^{31}P NMR (81.0 MHz, C_6D_6 300 K): δ −7.70.

Preparation of the Amine 12. (a). Stoichiochiometric, with B(C_6F_6)$_3$. Compound **8** (170 mg, 0.27 mmol) and B(C_6F_5)$_3$ (154 mg, 0.30 mmol, 1.1 equiv) were mixed in a Schlenk flask, and anhydrous toluene (10 mL) was added. The red solution was stirred under vacuum for a few seconds. Then the Schlenk flask was connected to a dihydrogen bottle in the glovebox and filled with dihydrogen gas until the pressure inside the Schlenk vessel rose up to 2.5 bar. The reaction mixture was stirred under an atmosphere of dihydrogen for 20 min, and then the connection between the Schlenk flask and the dihydogen bottle was closed. The stirring of the mixture was continued at room temperature overnight under an atmosphere of dihydrogen. Removal of the solvent in vacuo gave the crude product, which was purified by flash chromatography (SiO_2, cyclohexane/triethylamine 30/1) to give a yellow powder (86.0 mg, 0.24 mmol, 89%). A mixture of isomers was obtained (ratio 1:1.2). Anal. Calcd for $C_{22}H_{25}FeN$: C, 73.54; H, 7.01; N, 3.90. Found: C, 73.31; H, 6.72; N, 3.79. Major isomer: ^{1}H NMR (500 MHz, C_6D_6, 298 K) δ 1.18 (d, $^3J_{H,H}$ = 6.9 Hz, 3H, 7-H), 1.27 (d, $^3J_{H,H}$ = 6.5 Hz, 3H, Me), 1.69, 1.87 (each m, 1H, 8-H), 1.71, 1.98 (each m, each 1H, 9-H), 1.89 (m, 1H, 6-H), 3.53, 3.81, 3.99, 4.29 (each m, each 1H, C_5H_4), 3.54 (m, 1H, C_5H_3), 3.62 (m, 2H, C_5H_3), 4.11 (q, $^3J_{H,H}$ = 6.5 Hz, 1H, 15-H), 7.07 (m, 1H, *p*-C_6H_5), 7.18 (m, 2H, *m*-C_6H_5), 7.35 (m, 2H, *o*-C_6H_5); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K) δ 20.9 (C9), 21.4 (C7), 25.6 (Me), 31.1 (C6), 43.5 (C8), 57.8 (C15), 57.76, 62.58, 64.8 (C_5H_3), 64.8, 67.2, 68.9, 74.1 (C_5H_4), 90.6 (C1), 74.2 (C10), 109.4 (C14), 126.4 (*o*-C_6H_5), 127.1 (*p*-C_6H_5), 128.81 (*m*-C_6H_5), 146.6 (*i*-C_6H_5). Minor isomer: ^{1}H NMR (500 MHz, C_6D_6, 298 K) δ 1.11 (d, $^3J_{H,H}$ = 6.9 Hz, 3H, 7-H), 1.26 (d, $^3J_{H,H}$ = 6.5 Hz, 3H, Me), 1.66, 1.85 (each m, each 1H, 8-H), 1.61, 2.00 (each m, each 1H, 9-H), 1.86 (m, 1H, 6-H), 3.31, 3.78, 3.97, 3.98 (each m, each 1H, C_5H_4), 3.66 (m, 1H, C_5H_3), 3.79 (m, 2H, C_5H_3), 3.91 (q, $^3J_{H,H}$ = 6.5 Hz, 1H, 15-H), 7.10 (m, 1H, *p*-C_6H_5), 7.19 (m, 2H, *m*-C_6H_5), 7.29 (m, 2H, *o*-C_6H_5); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K) δ 21.0 (C9), 24.4 (C7), 24.4 (Me), 30.6 (C6), 43.7 (C8), 57.8 (C15), 58.7, 62.57, 65.1, (C_5H_3), 64.6, 67.4, 69.0, 76.0 (C_5H_4), 90.7 (C1), 74.9 (C10), 108.8 (C14), 126.8 (*o*-C_6H_5), 127.4 (*p*-C_6H_5), 128.77 (*m*-C_6H_5), 146.5 (*i*-C_6H_5).

X-ray Crystal Structure Analysis of 12: formula $C_{22}H_{25}FeN$, M = 359.28, yellow crystal, 0.30 × 0.12 × 0.12 mm, a = 8.3870(2) Å, b = 10.1298(2) Å, c = 21.4898(5) Å, β = 93.807(1)°, V = 1821.72(7) Å^3, ρ_{calcd} = 1.310 g cm^{-3}, μ = 0.830 mm^{-1}, empirical absorption correction (0.789 ≤ T ≤ 0.907), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.710 73 Å, T = 223(2) K, ω and φ scans, 12 303 reflections collected (±h,±k,±l), (sin θ)/λ = 0.66 Å^{-1}, 4259 independent (R_{int} = 0.045) and 3639 observed reflections ($I \geq 2\sigma(I)$), 222 refined parameters, R1 = 0.046, wR2 = 0.117, maximum (minimum) residual electron density 0.51 (−0.37) e Å^{-3}, hydrogen atom at N from difference Fourier calculations, others calculated and refined as riding atoms.

(b). Catalytic, with hexyl-B(C_6F_5)$_2$. Compound **8** (150 mg, 0.24 mmol) and hexylB(C_6F_5)$_2$ (11 mg, 0.30 mmol, 1.1 equiv) were mixed in a Schlenk flask, and anhydrous benzene (3 mL) was added. The red solution was stirred under vacuum for a few seconds. Then the Schlenk flask was connected to a dihydrogen bottle in the glovebox and filled with dihydrogen gas until the pressure inside the Schlenk vessel rose to 2.5 bar. The reaction mixture was stirred under an atmosphere of dihydrogen for 20 min, and then the connection between the Schlenk flask and the dihydogen bottle was closed. The stirring of the mixture was

continued at room temperature overnight under an atmosphere of dihydrogen. Removal of the solvent in vacuo gave the crude product, which was purified by flash chromatography (SiO_2, cyclohexane/triethylamine 30/1) to give a yellow powder (74.0 mg, 0.21 mmol, 88%). A mixture of isomers was obtained (ratio 1:2.2). Major isomer: ^{1}H NMR (500 MHz, C_6D_6, 298 K) δ 1.18 (d, $^3J_{H,H}$ = 6.9 Hz, 3H, 7-H), 1.27 (d, $^3J_{H,H}$ = 6.5 Hz, 3H, Me), 1.69, 1.87 (each m, 1H, 8-H), 1.71, 1.98 (each m, each 1H, 9-H), 1.89 (m, 1H, 6-H), 3.53, 3.81, 3.99, 4.28 (each m, each 1H, C_5H_4), 3.54 (m, 1H, C_5H_3), 3.62 (m, 2H, C_5H_3), 4.11 (q, $^3J_{H,H}$ = 6.5 Hz, 1H, 15-H), 7.07 (m, 1H, *p*-C_6H_5), 7.18 (m, 2H, *m*-C_6H_5), 7.35 (m, 2H, *o*-C_6H_5). [1] Minor isomer: ^{1}H NMR (500 MHz, C_6D_6, 298 K) δ 1.11 (d, $^3J_{H,H}$ = 6.9 Hz, 3H, 7-H), 1.26 (d, $^3J_{H,H}$ = 6.5 Hz, 3H, Me), 1.66, 1.85 (each m, each 1H, 8-H), 1.61, 2.00 (each m, each 1H, 9-H), 1.86 (m, 1H, 6-H), 3.31, 3.78, 3.97, 3.98 (each m, each 1H, C_5H_4), 3.66 (m, 1H, C_5H_3), 3.79 (m, 2H, C_5H_3), 3.92 (q, $^3J_{H,H}$ = 6.5 Hz, 1H, 15-H), 7.10 (m, 1H, *p*-C_6H_5), 7.19 (m, 2H, *m*-C_6H_5), 7.29 (m, 2H, *o*-C_6H_5).

Preparation of the Amine 13. Compound **7b** (100 mg, 0.22 mmol) and hexyl-B(C_6F_5)$_2$ (9.47 mg, 0.022 mmol, 10% mol) were mixed in a Schlenk flask, and anhydrous toluene (3 mL) was added. The mixture was treated with dihydrogen gas analogously as described above. Aqueous $NaHCO_3$ was added, and the organic layer was extracted with dichloromethane (3 × 10 mL). The combined organic phases were washed with water (3 × 10 mL) and dried with magnesium sulfate. Filtration and removal of the solvent in vacuo gave the crude product, which was purified by flash chromatography (SiO_2, cyclohexane/triethylamine 95/5) to give the product as a yellow powder (91.0 mg, 0.20 mmol, 91%). Crystals suitable for X-ray crystallography were obtained by diffusion of pentane into a satuarated solution of **13** in dichloromethane. An isomeric mixture was obtained (ratio 1:5). Anal. Calcd for $C_{24}H_{27}F_3FeN_2$: C, 63.17; H, 5.96; N, 6.14. Found: C, 63.28; H, 5.54; N, 6.36. Major isomer: ^{1}H NMR (600 MHz, C_6D_6, 298 K) δ 0.96 (d, $^3J_{H,H}$ = 7.2 Hz, 3H, 7-H), 1.97 (ddd, $^2J_{H,H}$ = 13.3 Hz, $^3J_{H,H}$ = 5.0 Hz, $^3J_{H,H}$ = 3.9 Hz, 1H, 8-H), 2.03 (ddd, $^2J_{H,H}$ = 13.3 Hz, $^3J_{H,H}$ = 10.3 Hz, $^3J_{H,H}$ = 3.0 Hz, 1H, 8′-H), 2.12 (s, 6H, NMe_2), 2.38 (m, 1H, 6-H), 2.49 (dd, $^3J_{H,H}$ = 10.3 Hz, $^3J_{H,H}$ = 3.9 Hz, 1H, 9-H), 3.37, 3.86, 3.89, 4.06 (each m, each 1H, C_5H_4), 3.49 (m, 1H, 11-H), 3.67 (m, 1H, 13-H), 3.73 (m, 1H, 12-H), 4.47 (dq, $^3J_{F,H}$ = 5.7 Hz, $^3J_{H,H}$ = 7.7 Hz, 1H, 15-H), 5.54 (d, $^3J_{H,H}$ = 5.7 Hz, 1H, NH), 7.06 (m, 1H, *p*-C_6H_5), 7.13 (m, 2H, *m*-C_6H_5), 7.41 (m, 2H, *o*-C_6H_5); ^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 298 K) δ 17.7 (C7), 27.6 (C6), 45.10 (NMe_2), 45.7 (C8), 55.08 (C13), 60.1 (C9), 62.1 (C12), 64.1 (q, $^2J_{F,C}$ = 30.2 Hz, C15), 65.9 (C11), 66.5 (C_5H_4), 67.4 (C_5H_4), 70.1 (C_5H_4), 73.1 (C_5H_4), 75.0 (C10), 92.0 (C1), 109.5 (C14), 126.1 (q, $^1J_{F,C}$ = 281.7 Hz, CF_3), 128.5 (*o*-C_6H_5), 128.9 (*m*-C_6H_5), 129.1 (*p*-C_6H_5), 136.1 (*i*-C_6H_5); ^{19}F NMR (282 MHz, C_6D_6, 300 K) δ −74.5 (s, CF_3). Minor isomer: ^{1}H NMR (600 MHz, C_6D_6, 298 K) δ 1.08 (d, $^3J_{H,H}$ = 7.2 Hz, 3H, 7-H), 2.06 (s, 6H, NMe_2), 2.09 (m, 1H, 8-H), 2.44 (ddd, $^2J_{H,H}$ = 13.1 Hz, $^3J_{H,H}$ = 10.1 Hz, $^3J_{H,H}$ = 2.9 Hz, 1H, 8′-H), 2.51 (dd, $^3J_{H,H}$ = 10.1 Hz, $^3J_{H,H}$ = 3.4 Hz, 1H, 9-H), 2.67(m, 1H, 6-H), 3.93, 3.94, 4.07, 4.40 (each m, each 1H, C_5H_4), 3.37 (m, 1H, 13-H), 3.45 (m, 1H,11-H), 3.56 (m, 1H, 12-H), 4.61 (dq, $^3J_{F,H}$ = 5.7 Hz, $^3J_{H,H}$ = 7.7 Hz, 1H, 15-H), 5.51 (d, $^3J_{H,H}$ = 5.7 Hz, 1H, NH), 7.09 (m, 1H, *m*-C_6H_5), n.o. (*p*-C_6H_5), 7.38 (m, 2H, *o*-C_6H_5); ^{13}C{^{1}H} NMR ([D$_6$]benzene, 151 MHz, C_6D_6, 298 K) δ 18.2 (C7), 27.7 (C6), 45.13 (NMe_2), 45.5 (C8), 55.14 (C13), 60.3 (C9), 62.0 (C12), 63.7 (q, $^2J_{F,C}$ = 30.0 Hz, C15), 65.7 (C11), 66.5 (C_5H_4), 67.2 (C_5H_4), 70.2 (C_5H_4), 73.8 (C_5H_4), 75.3 (C10), 92.4 (C1), 108.7 (C14), 125.9 (q, $^1J_{F,C}$ = 281.6 Hz, CF_3), 128.4 (*o*-C_6H_5), 128.8 (*m*-C_6H_5), 129.0 (*p*-C_6H_5), 135.8 (*i*-C_6H_5); ^{19}F NMR (282 MHz, C_6D_6, 300 K) δ −73.9 (s, CF_3).

X-ray Crystal Structure Analysis of 13a. formula $C_{24}H_{27}F_3FeN_2$, M = 456.33, yellow crystal, 0.20 × 0.15 × 0.10 mm, a = 7.4963(2) Å, b = 9.2434(3) Å, c = 15.7850(6) Å, α = 95.678(1)°, β = 100.152(1)°, γ = 99.068(3)°, V = 1054.11(6) Å^3, ρ_{calcd} = 1.438 g cm^{-3}, μ = 0.754 mm^{-1}, empirical absorption correction (0.864 ≤ T ≤ 0.928), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.710 73 Å, T = 223(2) K, ω and φ scans, 8685 reflections collected (±h,±k,±l), (sin θ)/λ = 0.66 Å^{-1}, 4771 independent (R_{int} = 0.049) and 4380 observed reflections ($I \geq 2\sigma(I)$), 278 refined parameters, R1 = 0.084, wR2 = 0.264, maximum (minimum) residual electron density 1.54 (−0.76) e Å^{-3}, hydrogen atom at N2 from difference Fourier calculations, others calculated and refined as riding atoms.

Preparation of the Amine 14. Compound **7a** (100 mg, 0.25 mmol) and hexyl-B(C_6F_5)$_2$ (10.74 mg, 0.025 mmol, 10 mol %) were mixed in a Schlenk flask, and anhydrous toluene (3 mL) was added. The reduction with dihydrogen (analogously as described above) gave the product **14** as a yellow solid (82.0 mg, 0.20 mmol, 80%). Crystals suitable for X-ray crystallography were obtained by diffusion of pentane into a satuarated solution of **14** in dichloromethane. Anal. Calcd for $C_{24}H_{30}FeN_2$: C, 71.64; H, 7.52; N, 6.96. Found: C, 71.14; H, 7.60; N, 6.71. ^{1}H NMR (600 MHz, C_6D_6, 298 K): δ 1.15 (d, $^3J_{H,H}$ = 7.2 Hz, 3H, 7-H), 1.34 (d, $^3J_{H,H}$ = 6.8 Hz, 3H, Me), 2.16 (ddd, $^2J_{H,H}$ = 13.2 Hz, $^3J_{H,H}$ = 5.6 Hz, $^3J_{H,H}$ = 3.3 Hz, 1H, 8-H), 2.18 (s, 6H, NMe_2), 2.37 (ddd, $^2J_{H,H}$ = 13.2 Hz, $^3J_{H,H}$ = 10.1 Hz, $^3J_{H,H}$ = 2.9 Hz, 1H, 8′-H), 2.55 (dd, $^3J_{H,H}$ = 10.1 Hz, $^3J_{H,H}$ = 3.3 Hz, 1H, 9-H), 2.69 (m, 1H, 6-H), 3.39 (m, 1H, 13-H), 3.49 (m, 1H, 11-H), 3.59 (m, 1H, 12-H), 3.87, 3.95, 3.96, 4.40 (each m, each 1H, C_5H_4), 4.19 (qd, $^3J_{H,H}$ = 6.8 Hz, $^3J_{H,H}$ = 3.2 Hz, 1H, 15-H), 4.43 (d, 1H, $^3J_{H,H}$ = 3.2 Hz, NH), 7.07 (m, 1H, *p*-C_6H_5), 7.20 (m, 2H, *m*-C_6H_5), 7.37 (m, 2H, *o*-C_6H_5). ^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 298 K): δ 18.3 (C7), 25.8 (Me), 27.8 (C6), 45.6 (NMe_2), 45.8 (C8), 55.2 (C13), 57.0 (C15), 60.8 (C9), 62.0 (C12), 65.5 (C11), 66.0 (C_5H_4), 67.0 (C_5H_4), 70.2 (C_5H_4), 73.1 (C_5H_4), 74.1 (C10), 92.1 (C1), 110.4 (C14), 126.3 (*o*-C_6H_5), 126.9 (*p*-C_6H_5), 128.8 (*m*-C_6H_5), 147.3 (*i*-C_6H_5).

X-ray Crystal Structure analysis of 14: formula $C_{24}H_{30}FeN_2$, M = 402.35, yellow crystal, 0.30 × 0.25 × 0.03 mm, a = 13.9568(2) Å, b = 9.0606(1) Å, c = 17.0797(3) Å, β = 109.420(1)°, V = 2036.97(5) Å^3, ρ_{calcd} = 1.312 g cm^{-3}, μ = 0.751 mm^{-1}, empirical absorption correction (0.806 ≤ T ≤ 0.978), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.710 73 Å, T = 223(2) K, ω and φ scans, 10 474 reflections collected (±h,±k,±l), (sin θ)/λ = 0.66 Å^{-1}, 4765 independent (R_{int} = 0.030) and 4179 observed reflections ($I \geq 2\sigma(I)$), 251 refined parameters, R1 = 0.044, wR2 = 0.108, maximum (minimum) residual electron density 0.34 (−0.32) e Å^{-3}, hydrogen atom at N2 from difference Fourier calculations, others calculated and refined as riding atoms.

Preparation of the Ferrocenophane Complex 19. Compound **6** (1 g, 2.60 mmol) was added in portions at room temperature to a solution of B(C_6F_3)$_3$ (1.33 g, 2.60 mmol, 1 equiv) in anhydrous toluene (10 mL). The reaction mixture was stirred overnight, and the solvent was removed in vacuo to yield the product as a yellow oil, which solidified after treatment with pentane (2.00 g, 2.23 mmol, 86%). Crystals suitable for X-ray diffraction were grown from slow evaporation of a toluene solution. Anal. Calcd for $C_{41}H_{26}BF_{15}FeN_2$: C, 54.82; H, 2.92; N, 3.12. Found: C, 54.54, H, 2.96; N, 3.26. ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K): δ 1.31 (d, $^3J_{H,H}$ = 6.5 Hz, 3H, 7-H), 2.11 (m, 2H, 6-H, 8-H), 2.61 (dd, $^2J_{H,H}$ = 12.9 Hz, $^3J_{H,H}$ = 4.2 Hz, 1H, 8-H), 3.21 (m, 1H, $C_5H_4^{\alpha}$), 3.28 (s, 3H, NMe_2), 3.92 (Br, 1H, HB), 4.09 (m, 2H, $C_5H_4^{\beta}$), 4.13 (m, 1H, $C_5H_4^{\alpha}$), 4.21 (m, 1H, 12-H), 4.22, 4.33 (each m, each 1H, C_5H_3), 4.57 (m, 1H, 9-H), 4.68 (d, $^2J_{H,H}$ = 15.0 Hz, 15-H), 4.78 (d, $^2J_{H,H}$ = 15.0 Hz, 15′-H), 7.32 (m, 2H, *o*-C_6H_5), 7.43 (m, 3H, *m*-C_6H_5, *p*-C_6H_5), 7.91 (s, 1H, 16-H). ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 298 K): δ 21.4 (C7), 24.6 (C6), 41.1 (Me), 46.2 (C8), 55.5 (C9), 56.3 (C15), 59.1, 64.5, (C_5H_3), 67.6 (C12), 66.9 (C_5H_3, $C_5H_4^{\alpha}$), 70.1 (C10), 70.7 ($C_5H_4^{\beta}$), 71.3 ($C_5H_4^{\beta}$), 78.0 ($C_5H_4^{\alpha}$), 90.3 (C1), 90.5 (C14), 128.9 (*o*-C_6H_5), 129.8 (*m*-C_6H_5), 130.2 (*p*-C_6H_5), 132.2 (*i*-C_6H_5), 149.6 (C16) [C_6F_5 not assigned]. ^{19}F NMR (282 MHz, C_6D_6, 300 K): δ −132.9 (m, 2F, *o*-C_6F_5), −162.3 (m, 1F, *p*-C_6F_5), −165.7 (m, 2F, C_6F_5) ppm. ^{11}B NMR (200 MHz, CD_2Cl_2, 300 K): −25.6 ($\nu_{1/2}$ = 42 Hz).

X-ray Crystal Structure Analysis of 19: formula $C_{41}H_{26}BF_{15}FeN_2$, M = 898.30, yellow-orange crystal, 0.30 × 0.15 × 0.05 mm, a = 12.3616(2) Å, b = 12.4078(2) Å, c = 14.4482(3) Å, α = 88.729(1)°, β = 65.307(1)°, γ = 68.018(3)°, V = 1843.22(6) Å^3, ρ_{calcd} = 1.619 g cm^{-3}, μ = 0.520 mm^{-1}, empirical absorption correction (0.860 ≤ T ≤ 0.974), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.710 73 Å, T = 223(2) K, ω and φ scans, 17 255 reflections collected (±h,±k,±l), (sin θ)/λ = 0.66 Å^{-1}, 8598 independent (R_{int} = 0.045) and 7292 observed reflections ($I \geq 2\sigma(I)$), 546 refined parameters, R1 = 0.056, wR2 = 0.134, maximum (minimum) residual electron density 0.48 (−0.41) e Å^{-3}, hydrogen atom at B1 from difference Fourier calculations, others calculated and refined as riding atoms.

Preparation of the Ferrocenophane Complex 22. Compound **20** (500 mg 1.070 mmol, 1.0 equiv) was dissolved in dichloromethane (10 mL), and $B(C_6F_5)_3$ (546.9 mg (1.070 mmol, 1.0 equiv) was added to the solution (the solution turns red). After the solvent was removed in vacuo, the crude product was dissolved in diethyl ether (5 mL) and cooled to −78 °C. Addition of pentane (5 mL) to the solution leads to the precipitation of the pure product. After drying in vacuo (24 h) the pure product could be obtained as a yellow solid with a yield of 776 mg (0.79 mmol, 75%). Yellow single crystals were obtained by slow diffusion of pentane into a diethyl ether solution of 22 at −32 °C. Anal. Calcd for $C_{46}H_{30}BF_{15}FeNP$: C, 56.41; H; 3.09; N, 1.43. Found: C, 56.13; H, 3.10; N, 1.45. ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K): δ 1.22 (d, $^3J_{H,H}$ = 7.0 Hz, 3H, 7-H), 2.00 (ddd, $^2J_{H,H}$ = 14.9 Hz, $^3J_{H,H}$ = 12.1 Hz, $^3J_{H,H}$ = 1.7 Hz, 1H, 8-H), 2.33 (m, 1H, 6-H), 2.55 (ddd, $^2J_{H,H}$ = 14.9 Hz, $^3J_{H,H}$ = 4.5 Hz, $^3J_{H,H}$ = 2.7 Hz, 1H, 8′-H), 2.70 (d, $^4J_{H,P}$ = 1.8 Hz, 3H, NMe), 2.74 (m, 1H, H-5), 3.29 (ddd, $^2J_{H,H}$ = 15.3 Hz, $^2J_{P,H}$ = 3.2 Hz, $J_{H,H}$ = 0.8 Hz, 1H, PCH_2), 3.41 (dm, $^3J_{H,H}$ = 4.5 Hz, 1H, 9-H), 3.76 (br 1:1:1:1 q, $^1J_{B,H}$ ≈ 93 Hz, BH), 3.92 (m, 1H, H-4), 4.11 (dd, $^2J_{H,H}$ = 15.3 Hz, $^2J_{P,H}$ = 12.7 Hz, 1H, PCH_2), 4.17 (m, 1H, 3-H), 4.21 (m, 1H, H-2), 4.61 (m, 1H, H-13), 4.697 (m, 1H, H-12), 4.701 (m, 1H, H-11), 7.33 (m, 2H, *o*-PPh'_2), 7.54 (m, 2H, *m*-PPh'_2), 7.74 (m, 1H, *p*-PPh'_2), 7.84 (m, 2H, *m*-PPh_2), 7.91 (m, 2H, *o*-PPh_2), 7.94 (m, 1H, *p*-PPh_2). $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2, 298 K): δ 21.3 (C7), 23.5 (C6), 44.6 (d, $^3J_{P,C}$ = 17.1 Hz, NMe), 47.6 (C-8), 51.1 (d, $^1J_{P,C}$ = 75.1 Hz, PCH_2), 58.3 (d, $^{3+4}J_{P,C}$ = 2.2 Hz, C9), 58.7 (d, $^1J_{P,C}$ ≈ 104 Hz, C14), 67.6 (C2), 69.4 (C4), 71.50, 71.56 (each d, $J_{P,C}$ ≈ 7 Hz, C-11, C-13), 72.0 (C3), 76.9 (C5), 75.0 (d, $^{3+4}J_{P,C}$ = 12.1 Hz, C12), 92.1 (C1), 93.2 (d, $^2J_{P,C}$ = 9.7 Hz, C10), 119.98 (d, $^1J_{P,C}$ = 84.1 Hz, *i*-PPh'_2), 120.11 (d, $^1J_{P,C}$ = 91.5 Hz, *i*-PPh_2), 130.4 (d, $^3J_{P,C}$ = 12.7 Hz, *m*-PPh'_2), 130.7 (d, $^3J_{P,C}$ = 12.7 Hz, *m*-PPh_2), 132.6 (d, $^2J_{P,C}$ = 9.4 Hz, *o*-PPh_2), 133.4 (d, $^2J_{P,C}$ = 10.4 Hz, *o*-PPh'_2), 135.7 (d, $^4J_{C,P}$ = 3.2 Hz, *p*-PPh_2, *p*-PPh'_2), n.o. (*i*-C_6F_5), 136.7 (dm, $^1J_{F,C}$ ≈ 245 Hz, C_6F_5), 138.0 (dm, $^1J_{F,C}$ ∼ 244 Hz, C_6F_5), 148.4 (dm, $^1J_{F,C}$ ≈ 239 Hz, C_6F_5). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 298 K,): δ 14.6 ($\nu_{1/2}$ ≈ 7 Hz). $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 298 K): δ −25.4 ($\nu_{1/2}$ ≈ 50 Hz). ^{11}B NMR (160 MHz, CD_2Cl_2, 298 K): δ −25.4 (d, $^1J_{B,H}$ ≈ 93 Hz). ^{19}F NMR (470 MHz, CD_2Cl_2, 298 K): δ −133.7 (2F, *o*-C_6F_5), −164.6 (1F, *p*-C_6F_5), 167.4 (2F, *m*-C_6F_5).

X-ray Crystal Structure Analysis of 22: formula $C_{46}H_{30}BF_{15}FeNP$, M = 979.34, yellow crystal, 0.20 × 0.10 × 0.05 mm, a = 14.0423(2) Å, b = 16.8625(3) Å, c = 17.1947(3) Å, β = 91.934(1)°, V = 4069.18(12) Å^3, ρ_{calcd} = 1.599 g cm^{-3}, μ = 0.516 mm^{-1}, empirical absorption correction (0.904 ≤ T ≤ 0.975), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.710 73 Å, T = 223(2) K, ω and φ scans, 30 115 reflections collected (±h,±k,±l), (sin θ)/λ = 0.66 Å^{-1}, 9527 independent (R_{int} = 0.060) and 6678 observed reflections ($I \geq 2\sigma(I)$), 591 refined parameters, R1 = 0.067, wR2 = 0.155, maximum (minimum) residual electron density 0.35 (−0.45) e Å^{-3}, hydrogen atom at B1 from difference Fourier calculations, others calculated and refined as riding atoms.

Acknowledgment. Financial support from the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft is gratefully acknowledged. We thank the BASF for a gift of solvents.

Supporting Information Available: Text and figures giving further experimental and spectroscopic details and CIF files (**6**·HCl, **7b**, **12**, **13a**, **14**, **19**, **22**) giving crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.