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Article

Functional Group Chemistry at the Group 4 Bent Metallocene Frameworks: Formation and "Metal-Free" Catalytic Hydrogenation of Bis(imino-Cp)zirconium Complexes

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†X-ray crystal structure analyses.

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Treatment of 6-dimethylaminofulvene **1** with lithio-2,6-diisopropylanilide **2** gave the lithiated 6-(2,6-diisopropylanilido)fulvene **3**. Its treatment with Me_3SiCl afforded the N-silylated derivative (C_5H_4)=CH-N(Ar)$SiMe_3$ (**4**), which was characterized by X-ray diffraction. Protonation of **3** was effected by treatment with acetylacetone to yield a mixture of syn- and anti-**5** [(C_5H_4)=CH-N(Ar)H] contaminated with some 2,6-diisopropylaniline. The minor isomer, syn-**5**, was also characterized by an X-ray crystal structure analysis. Treatment of this mixture with $Zr(NMe_2)_4$ led to in situ deprotonation and formation of complex $[(C_5H_4)\text{-}CH{=}NAr]_2Zr(NMe_2)_2$ (**6**) in a mixture with the exchange product $[(C_5H_4)\text{-}CH{=}NAr]_2Zr(NMe_2)(NH\text{-}Ar)$ (**7**) as a minor component (both characterized by X-ray diffraction). The corresponding reaction with the reagent $Zr(benzyl)_4$ or $Cl_2Zr(NMe_2)_2(THF)_2$ resulted in the clean formation of the products $[(C_5H_4)\text{-}CH{=}NAr]_2Zr(benzyl)_2$ (**8**) (also characterized by X-ray diffraction) and $[(C_5H_4)\text{-}CH{=}NAr]_2ZrCl_2$ (**9**), respectively. Complex **9** was subjected to a "metal-free" catalytic hydrogenation reaction by treatment with a substoichiometric amount of $B(C_6F_5)_3$ under mild conditions (2 bar H_2, rt) to yield the product $[(C_5H_4)\text{-}CH_2\text{-}NH\text{-}Ar]_2ZrCl_2$ (**10**), which was also characterized by an X-ray crystal structure analysis. Treatment of **9** with 1 or 2 molar equiv of $B(C_6F_5)_3$ gave "frustrated" Lewis pairs that split dihydrogen heterolytically at near to ambient conditions to give the salts $\{[(C_5H_4)\text{-}CH_2NH_2^+Ar][(C_5H_4)\text{-}CH_2NHAr]\}ZrCl_2/[HB(C_6F_5)_3^-]$ (**11**) and $[(C_5H_4)CH_2NH_2^+Ar]_2ZrCl_2/2\ [HB(C_6F_5)_3^-]$ (**12**), respectively. The system **12** itself was shown to be an active catalyst for the hydrogenation of bulky imines and of a bulky silyl enol ether.

Introduction

Functional group chemistry at the group 4 metallocene complexes is not developed to a great extent due to the sensitivity of these early metal compounds.[1] Usually the choice of reagents and of reaction conditions is restricted. Nevertheless, we had recently described examples of typical organic functional group conversions at the zirconocene framework,[2−6] e.g., a Mannich-type C−C coupling reaction,[2,7] but this required a suitable selection of reagents, reaction conditions, and the actual organic functional groups involved. In the Mannich chemistry we had used an enamino moiety attached at the Cp rings of the metallocene, which was in situ converted catalytically to a reactive iminium ion intermediate for the actual carbon−carbon coupling reaction.[2,7] We have now developed synthetic pathways to related Cp-functionalized group 4 bent metallocenes, namely, zirconocenes that bear neutral imino groups at their Cp rings. In this account we wish to report the development of synthetic entries to a variety of bis(imino-Cp)zirconium complexes, their spectroscopic and structural characterization, and the reduction of the −CH=N−Ar functional group using an interesting novel catalytic reaction.

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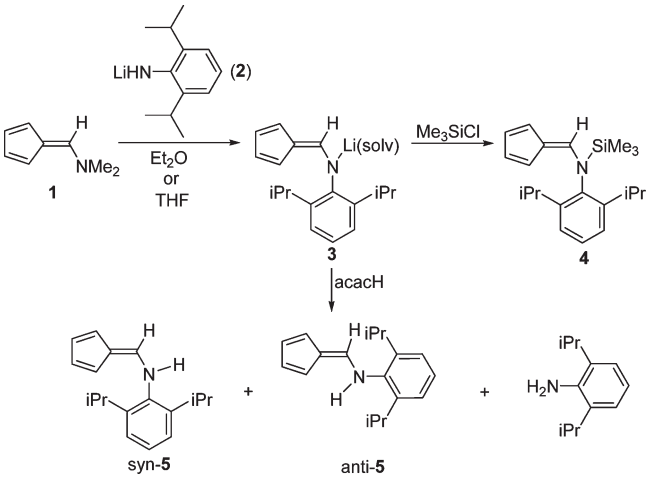
Scheme 1. Syntheses of Bulky Aminopentafulvenes



Results and Discussion

Synthesis and Characterization of the (Imino-Cp)zirconium Complexes. We started our synthetic scheme from 6-dimethylaminofulvene **1**. This in turn was synthesized by treatment of in situ activated *N*,*N*-dimethylformamide (by the addition of dimethylsulfate to DMF) with sodium cyclopentadienide according to Hafner et al.[8] Subsequent nucleophilic replacement of the $-NMe_2$ group was carried out with lithium 2,6-diisopropylanilide **2** to yield the imino-substituted LiCp system **3**. This reaction can be carried out either in THF, as previously described by us,[9] or in ether. In the former case one obtains the reagent $\mathbf{3}\cdot(THF)_3$, the structure of which has been characterized by X-ray diffraction.[9] It features a close Li to imine nitrogen contact and has three stabilizing THF molecules coordinated to the alkali metal in a pseudotetrahedral coordination geometry.

We tried to prepare imino-Cp-containing zirconocene complexes directly from the lithiated reagent **3**. However, the treatment of **3** with $ZrCl_4$ under various reaction conditions in our hands gave a complicated mixture of products, from which we were not able to isolate the desired functionalized metallocene systems. We suspected that the imino function in our reagent might not be compatible with the presence of the strongly Lewis acidic $ZrCl_4$ metal halide substrate. Therefore, we converted **3** to the N-silylated derivative **4** (see Scheme 1 and Figure 1). However, also treatment of **4** with $ZrCl_4$ did not yield the functionalized metallocene product under our typical conditions. The silylated compound **4** was characterized by X-ray diffraction. Suitable single crystals were obtained from pentane at −30 °C. The molecular structure of **4** (see Figure 1 and Table 1) is fulvene like. The five-membered ring shows the respective alternating C=C and C−C bond lengths. The exocyclic C1−C6 linkage is in the typical double-bond range. The adjacent C6−N1 bond is rather short, indicating a pronounced π-conjugation along the C1−C6−N1 unit. The substituents at N1 are in plane with the fulvene backbone. The bulky 2,6-diisopropylphenyl substituent at N1 is rotated almost normal to the central fulvene plane. Consequently, the nonconjugated N1−C7(sp^2) bond is much longer than the conjugated N1−C6-(sp^2) linkage (see Table 1). We note that the aryl substituent is found in a syn-orientation (relative to C1−C6) at the fulvene nitrogen and the $-SiMe_3$ group is consequently anti-oriented.

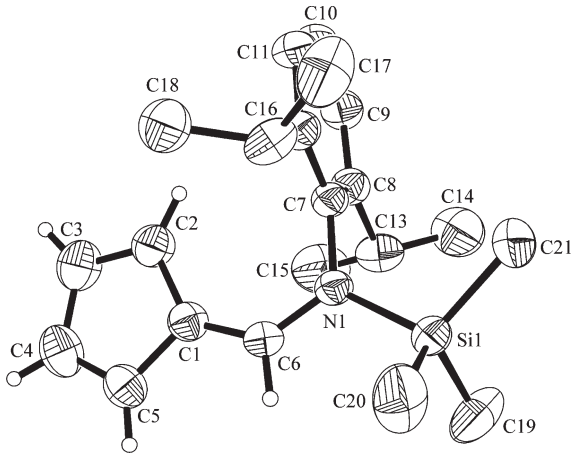


Figure 1. View of the molecular structure of the amino-fulvene derivative **4**. Ellipsoids are given at the 50% probability level. Hydrogen atoms at the substituents were omitted for clarity.

Table 1. Selected Structural Parameters of the Compounds 4, syn-5, and 3[a]

	4	syn-**5**	**3**$(THF)_3$
C1−C5	1.437(2)	1.447(2)	1.418(3)
C1−C2	1.446(2)	1.437(2)	1.434(3)
C2−C3	1.337(3)	1.356(2)	1.385(3)
C3−C4	1.428(3)	1.431(2)	1.416(4)
C4−C5	1.330(3)	1.353(2)	1.345(4)
C1−C6	1.346(2)	1.368(2)	1.408(3)
C6−N1	1.349(2)	1.331(2)	1.301(3)
N1−C7	1.440(2)	1.439(2)	1.430(2)
C1−C6−N1	131.3(1)	130.6(1)	134.4(2)
C6−N1−C7	118.2(1)	125.8(1)	121.3(2)
C1−C6−N1−C7	−2.6(2)	−1.1(3)	−0.3(3)
C6−N1−C7−C8	92.2(2)	86.9(2)	−96.2(2)
N1−Si	1.767(1)		
N−H		0.88	
N−Li			2.005(4)

[a] Bond lengths in Å, angles in deg; the structure of **3**$(THF)_3$ was reported by us previously;[9] the values of **3**$(THF)_3$ listed here are from an independent structural determination carried out in this study.

As we will see below, the solution of our synthetic problem was achieved by means of a route through the neutral fulvene system **5**. However, it was difficult to find suitable reaction conditions to achieve a clean protonation reaction of the salt **3**. After many attempts using various protonation protocols and reagents we found that H^+ transfer from the Brønsted acid acetylacetone gave acceptable results. Under optimized conditions (see the Experimental Section for details) we eventually obtained the neutral substituted aminofulvene derivative **5** as a sensitive, red-brown oil in ca. 70% yield. This product always contained variable amounts of 2,6-diisopropylaniline (typically in the 25% range), the product of further protolytic cleavage of the C6−N1 linkage.

Product **5** was characterized spectroscopically (see below) and by X-ray diffraction. In the crystal we found only the syn-**5** isomer (with an analogous orientation of the bulky

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(9) (a) Kunz, K.; Erker, G.; Fröhlich, R. *Organometallics* **2001**, *20*, 392–400. (b) See also: Erker, G.; Kehr, G.; Fröhlich, R. *Organometallics* **2008**, *27*, 3−14, and references therein.

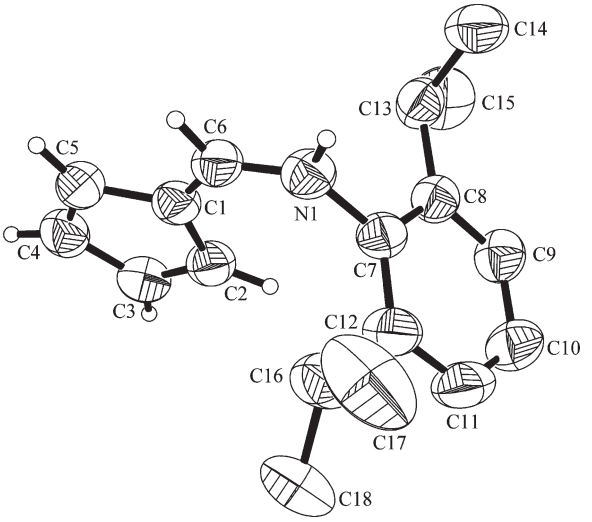


Figure 2. Molecular structure of syn-**5**. Ellipsoids are given at the 50% probability level. Hydrogen atoms at the substituents were omitted for clarity.

2,6-diisopropylphenyl substituent as found in **4**; see above). The structure of syn-**5** (see Figure 2 and Table 1) is very similar to that of **4** (see above). We found a typical aminofulvene framework with the characteristic C=C/C−C bond alternation. Again, the C6−N1 bond is short and the bulky aryl group is rotated out of conjugation with the fulvene core.

It is interesting to compare the structure of the anionic system **3** with the neutral fulvenes **4** and syn-**5**, respectively. We note that in **3** the C6−N1 bond is markedly shorter and the C1−C6 bond considerably longer than in the neutral fulvenes (see Table 1). This may indicate a slightly higher significance of the imine-type resonance structure **3B** for this lithiated system (see Scheme 2). A drawing of the previously reported molecular structure of **3** can be found in the Supporting Information.

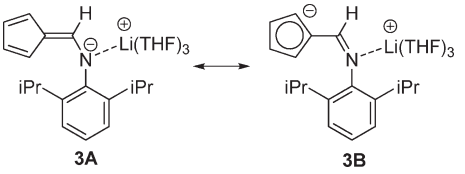
The NMR spectra show the presence of a pair of fulvene isomers in a 2:1 ratio in solution. The compound syn-**5**, which was identified by X-ray diffraction in the solid state, is the minor component in solution. It features a typical =CHN− ^{1}H NMR signal (in CD_2Cl_2) at δ 7.32 with a $^3J_{HH}$ coupling constant of 7.3 Hz, and it shows ^{13}C NMR signals of the fulvene core at δ 125.4, 124.8, 120.5, 115.1 (C_5H_4), 118.1 (*ipso*-C_5H_4), and 143.6 (=*C*HN). The major anti-**5** isomer shows similar core signals (^{13}C) at δ 126.5, 123.5, 121.9, 111.6 (C_5H_4), and 118.3 (*ipso*-C_5H_4) and the =^{13}CHN− resonance at δ 146.5. The corresponding ^{1}H NMR signal is observed as a doublet at δ 6.99 with a typical coupling constant of $^3J_{HH}$ = 14.2 Hz for an anti-conformation.

The silylated compound **4** shows only one set of ^{1}H/^{13}C NMR signals [e.g., =CHN− at δ 7.25 (^{1}H)/δ 144.4 (^{13}C, in C_6D_6)]. There are some trace signals that may originate from a very low populated minor isomer.

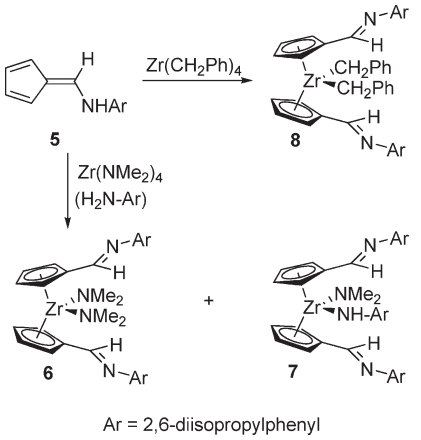
We were able to successfully use the syn-**5**/anti-**5**/2,6-diisopropylaniline mixture for the preparation of zirconocene complexes having the −CH=N-aryl carbaldimino functionalities attached at their Cp ring systems. We treated the reagent mixture with ca. 0.5 molar equiv of $Zr(NMe_2)_4$[10] in benzene at room temperature overnight. The resulting product mixture was separated by treatment with pentane.

(10) Bradley, D. C.; Thomas, I. M. *J. Chem. Soc.* **1960**, 3857–3861.

Scheme 2



Scheme 3



Ar = 2,6-diisopropylphenyl

Extraction with pentane gave the anticipated complex **6** as the major product (ca. 65%). The pentane-insoluble fraction (ca. 35%) consisted mainly of **7**, which was formally formed by exchange of one $-NMe_2$ group of **6** for −NH-2,6-diisopropylphenyl. Both compounds were obtained analytically pure after recrystallization. They were both characterized spectroscopically and by X-ray diffraction (see below).

The major product (**6**) featured an AA′BB′ ^{1}H NMR pattern of the symmetry-equivalent η^5-C_5H_4-moieties (δ 6.71/6.01) and the typical −CH=N− singlet at δ 7.96 (corresponding imine ^{13}C NMR feature at δ 156.5). The ^{1}H NMR $-NMe_2$ singlet (12H) occurs at δ 2.83. In addition we monitored the typical NMR resonances of the 2,6-diisopropylphenyl substituents at the imine nitrogen atoms (for details see the Experimental Section).

The minor substitution product (**7**) shows the ^{1}H NMR −CH=N− feature at δ 7.88 (in C_6D_6, ^{13}C: δ 156.7). There is a $-NMe_2$ singlet of 6H relative intensity at δ 2.85. The signals of the "extra" 2,6-diisopropylanilide σ-ligand are broad at room temperature. At 353 K (in d_8-toluene) the respective ^{1}H NMR signals were observed at 6.95/6.81 (C_6H_3) [^{13}C: δ 153.3, 140.5, 123.2, 122.5] and 3.42/1.12 (*i*Pr) [^{13}C: δ 28.1, 24.5].

In a similar reaction we have treated **5** with tetra(benzyl)zirconium, in situ prepared from $ZrCl_4$ and benzylmagnesium chloride.[11] The product (**8**) was isolated as an orange solid in > 80% yield and purified by recrystallization from pentane. The product was again characterized by C,H elemental analysis, NMR spectroscopy, and an X-ray crystal structure analysis (see below). Together with the typical ^{1}H NMR $-CH_2-$ singlet of the Zr-σ-benzyl moiety (δ 2.18, 4H relative intensity, ^{13}C: δ 63.5), the compound features a η^5-C_5H_4 AA′BB′ pattern at δ 6.53/5.68 and the NMR signals of the −CH=N− functional groups (^{1}H: δ 7.67, ^{13}C: δ 157.0) that are attached at the Cp rings of complex **8**. The NMR spectra show the typical signals of the 2,6-diisopropylphenyl

(11) Zucchini, U.; Albizzati, E.; Giannini, U. *J. Organomet. Chem.* **1971**, *26*, 357–372.

Table 2. Selected Structural Parameters of the (Imino-Cp)zirconium Complexes 6−8

	6	7	8
Zr−C1/C5 range	2.568(2) to 2.637(2)	2.533(4) to 2.626(3)	2.468(5) to 2.575(6)
C−C(Cp) range	1.393(3) to 1.420(3)	1.380(5) to 1.418(5)	1.387(7) to 1.423(6)
C1A−C6A	1.463(3)	1.483(5)	1.508(9)[g]
C1B−C6B	1.460(3)	1.454(5)	1.470(6)
C6A−N1A	1.262(2)	1.218(5)	1.246(8)[g]
C6B−N1B	1.259(3)	1.252(4)	1.243(5)
N1A−C7A	1.432(2)	1.454(5)	1.468(8)
N1B−C7B	1.424(2)	1.434(4)	1.439(5)
C1A−C6A−N1A	123.6(2)	121.3(4)	110.1(7)[g]
C1B−C6B−N1B	121.5(2)	120.9(3)	122.8(5)
C6A−N1A−C7A	118.0(2)	119.7(4)	113.5(7)[g]
C6B−N1B−C7B	122.0(2)	122.6(3)	117.6(4)
Zr−N2A	2.069(2)	2.115(3)[a]	2.322(5)[d]
Zr−N2B	2.075(2)	2.073(3)[b]	2.324(5)[e]
N2A−Zr−N2B	96.2(1)	101.4(1)[c]	97.3(2)[f]

[a] Zr1−N1C. [b] Zr1−N11. [c] N1C−Zr1−N11. [d] Zr−C21A. [e] Zr−C21B, [f] C21A−Zr−C21B, [g] Values taken from the main compound of the disordered group.

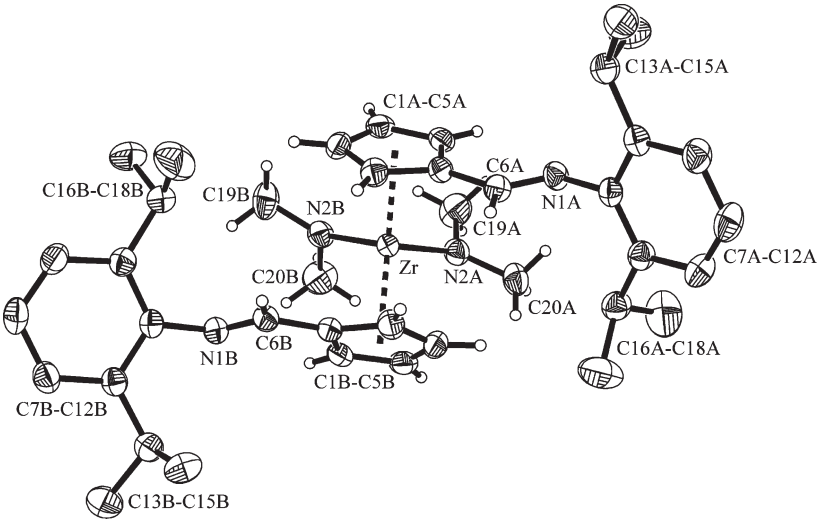


Figure 3. View of the molecular structure of complex **6**. Ellipsoids are given at the 50% probability level. Hydrogen atoms at the substituents were omitted for clarity.

substituents at the imine nitrogen atoms (for details see the Experimental Section).

In the crystal complex **6** features a bent metallocene structure that is characterized by a near to C_2-symmetric metallocene conformation.[12] The Cp(centroid)−Zr−Cp-(centroid) angle amounts to 125.7°. The imino substituents at the Cp rings are both oriented in the hind lateral metallocene sector. This probably leads to a maximal separation of the bulky 2,6-diisopropylphenyl substituents from each other. The −CH=N− π-systems are oriented in plane with their respective Cp rings. The aryl plane of the 2,6-diisopropylphenyl substituent is rotated close to normal to the imine planes.[13] The Zr-amide σ-ligands show near planar tricoordinate nitrogen atoms (sum of bond angles at N2A: 357.4°, N2B: 358.4°).

Complex **7** exhibits similar structural features of the (imino-Cp)$_2$Zr core. Again, the imine −CH=N− π-units are arranged close to coplanar with the adjacent Cp rings to allow for a maximal conjugation. The 2,6-diisopropylphenyl substituents at the imine nitrogens are rotated substantially from that common plane (see Figure 4). However, we notice a slightly different metallocene conformation as compared to **6**. The −NMe$_2$ group at Zr is trigonal planar. Its orientation may allow some ligand to metal π-interaction with the (empty) "ninth" metallocene orbital. The adjacent 2,6-diisopropylanilido σ-ligand is oriented differently; here the observed preferred conformation seems to be governed by steric interaction.

Complex **8** features a metallocene conformation that is similar to that of **7** with one imino substituent at Cp pointing toward a hind lateral sector and the other being oriented toward the more open front side of the bent metallocene wedge. The C6A−N1A imino group exhibits an orientational

(12) For typical conformational features of Cp-substituted bent metallocene systems see for example: (a) Erker, G.; Mühlenbernd, T.; Benn, R.; Rufińska, A.; Tsay, Y.-H.; Krüger, C. *Angew. Chem.* **1985**, *97*, 336–337. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 321−323. (b) Erker, G.; Nolte, R.; Tainturier, G.; Rheingold, A. *Organometallics* **1989**, *8*, 454–460. (c) Erker, G.; Nolte, R.; Krüger, C.; Schlund, R.; Benn, R.; Grondey, H.; Mynott, R. *J. Organomet. Chem.* **1989**, *364*, 119–132. (d) Erker, G.; Aulbach, M.; Knickmeier, M.; Wingbermühle, D.; Krüger, C.; Nolte, M.; Werner, S. *J. Am. Chem. Soc.* **1993**, *115*, 4590–4601. (e) Knickmeier, M.; Erker, G.; Fox, T. *J. Am. Chem. Soc.* **1996**, *118*, 9623–9630. (f) Jödicke, T.; Menges, F.; Kehr, G.; Erker, G.; Höweler, U.; Fröhlich, R. *Eur. J. Inorg. Chem.* **2001**, 2097–2106.

(13) See for a comparison: (a) Nienkemper, K.; Kotov, V. V.; Kehr, G.; Erker, G.; Fröhlich, R. *Eur. J. Inorg. Chem.* **2006**, 366–379. (b) Wallenhorst, C.; Kehr, G.; Luftmann, H.; Fröhlich, R.; Erker, G. *Organometallics* **2008**, *27*, 6547–6556. (c) Wallenhorst, C.; Kehr, G.; Fröhlich, R.; Erker, G. *Organometallics* **2008**, *27*, 6557–6564.

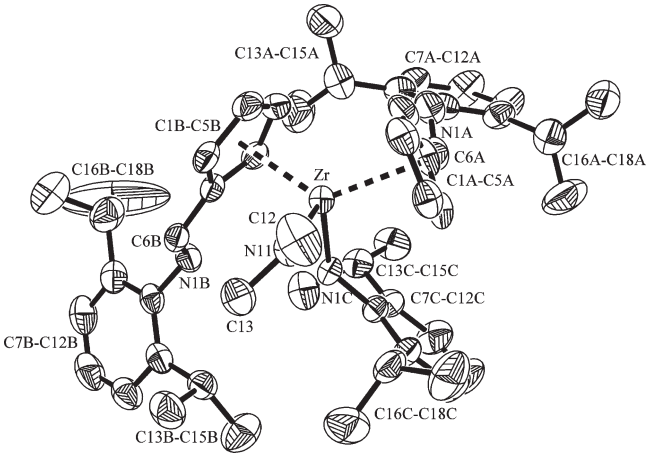


Figure 4. Molecular geometry of complex **7**. Ellipsoids are given at the 50% probability level. Hydrogen atoms were omitted for clarity.

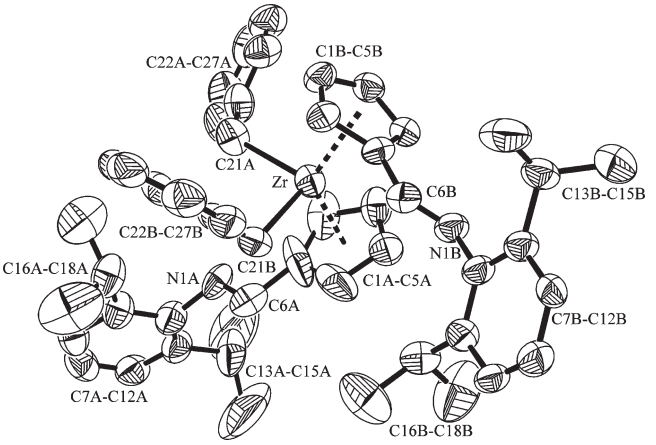


Figure 5. Projection of the molecular structure of complex **8**. Ellipsoids are given at the 50% probability level. Hydrogen atoms were omitted for clarity.

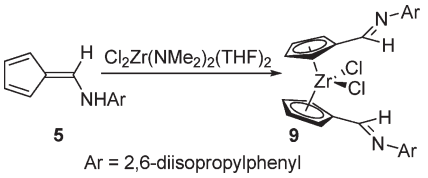
disorder inside its Cp-imino plane. Therefore the structural data of this group will not be discussed. The other π-ligand shows the typical Cp-imino conjugation. Both σ-benzyl groups at zirconium are oriented with their bulky phenyl group toward the latter Cp-imino (B) ligand system (see Figure 5).

We eventually prepared the parent bis(imino-Cp)zirconium dichloride complex (**9**) by a direct route. Treatment of the neutral, protonated ligand system **5** with the $Cl_2Zr(NMe_2)_2(THF)_2$[14] reagent at elevated temperature (3 h, 120 °C) resulted in a rather clean in situ deprotonation by the dimethylamide base with concurrent formation of the (imino-Cp)$_2$ZrCl$_2$ product **9**. This was isolated in $>60\%$ yield after conventional workup. It was characterized by C,H elemental analysis and spectroscopically. It shows the typical ^{1}H/^{13}C NMR imino resonances at δ 7.99 (^{1}H)/δ 156.2 (^{13}C). The isopropyl groups of the symmetry-equivalent 2,6-diisopropylphenyl substituents at nitrogen feature the typical ^{1}H NMR CH septet at δ 3.25 and a corresponding doublet of the methyl group at δ 1.24.

Although complex **9** was not characterized by X-ray diffraction, we chose it as the apparent parent compound in this series as the substrate for reduction with the new "metal-free" hydrogenation method.

Hydrogenation of the Imino-Zirconocene System. We applied a recent novel method for imine hydrogenation at the sensitive group 4 bent metallocene framework. This involved the initial formation of an "antagonistic" Lewis pair[15] (or a "frustrated" Lewis pair as it is more commonly termed[16]) by treatment of the (imino-Cp)$_2$ZrCl$_2$ complex **9** with a catalytic

Scheme 4



quantity of the strong boron Lewis acid B(C$_6$F$_5$)$_3$[17−19] (typically between 0.25 and 0.5 molar equiv). When this mixture was stirred for several hours (typically overnight to ensure complete conversion) under an atmosphere of dihydrogen (2 bar) at room temperature, the −CH=N-aryl imine functionality was cleanly converted to the corresponding −CH$_2$-NH-aryl aminomethyl functional group attached at the Cp rings of the metallocene system. This reaction proceeded in a quasi-autocatalytic fashion. The product **10** in combination with the remaining B(C$_6$F$_5$)$_3$ apparently formed a new amine/borane frustrated Lewis pair,[20] which itself was able to heterolytically cleave the dihydrogen molecule with formation of the organometallic ammonium salt (**11**, with [HB(C$_6$F$_5$)$_3^-$] anion). Consequently, we isolated a mixture of **10** (major) and **11** (minor component) from a typical catalytic "metal-free" hydrogenation reaction[21] using a substoichiometric amount of the B(C$_6$F$_5$)$_3$ Lewis acid component as described above. We were so far not able to separate the products **10** and **11** on a preparative scale, but have obtained single crystals of the (Cp-CH$_2$-NH-aryl)ZrCl$_2$ neutral complex **10** for characterization by an X-ray crystal structure analysis (see below).

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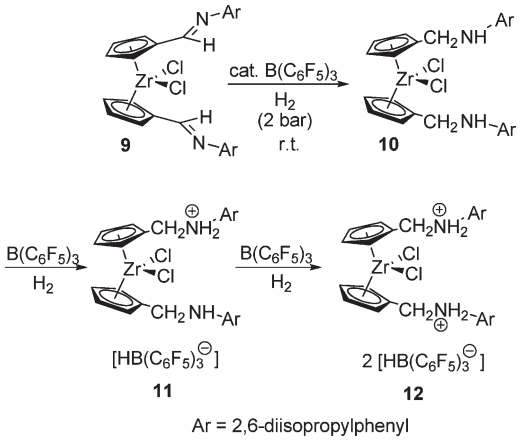
Scheme 5



Since the organometallic secondary amine **10** itself formed a frustrated Lewis pair with $B(C_6F_5)_3$, which was catalytically active in H_2 splitting, the outcome of the overall reaction was determined decisively by the initial ratio of **9**/$B(C_6F_5)_3$. When the components were employed in the hydrogenation reaction in a 1:1 ratio, we obtained the organometallic monoammonium salt **11** as the major product (see Scheme 5). This could be used further for dihydrogen splitting.[22,23] Hydrogenation (2 bar H_2, ambient temperature, overnight, or 60 bar H_2, 2 h) of an initial 1:2 mixture of **9** and $B(C_6F_5)_3$ eventually resulted in a near complete conversion to the organometallic bis-ammonium salt **12** (with two $[HB(C_6F_5)_3^-]$ counteranions).

Solutions containing the ammonium salts **11** and/or **12** showed very broad NMR spectra at ambient temperature due to proton transfer. This became sufficiently slow on the NMR time at 198 K (600 MHz, ^1H) to monitor sharp ^1H and ^{13}C NMR spectra for the characterization of the products **10**–**12**. The aminomethyl-Cp complex **10** shows two sets of ^1H NMR signals (at 198 K in d_8-THF) of the η^5-C_5H_4– moieties at δ 6.00/6.37 (each 4 H relative intensity), a broad Cp-CH_2-N resonance at δ 4.04 (4H, ^{13}C: δ 50.4), and an N*H* signal at δ 4.00 (2H) in addition to the typical resonances of the 2,6-diisopropylphenyl substituent [aryl ^1H resonances at δ 7.06 (4H) and 7.00 (2H)].

We spectroscopically characterized the monoammonium salt **11** from a ca. 5:20:3 mixture of **10**, **11**, and **12**. The salt **11** shows the typical features of the $-CH_2$-NH-aryl group [^1H: δ 4.01 (br, 3H), aryl signals at δ 7.05 (2H) and 6.99 (1H)] in addition to the $-CH_2$-NH_2^+-aryl signals [^1H: δ 4.62 (CH_2), δ 9.65 (NH_2^+), corresponding aryl signals at δ 7.56 (1H) and δ 7.48 (2H)]. Complex **11** shows four η^5-C_5H_4 ^1H NMR signals (δ 6.75/6.14, 6.60/6.33; each 2H) as expected. The $[HB(C_6F_5)_3^-]$ counteranion shows the characteristic ^{19}F NMR features (in d_8-THF at 298 K) at δ −133.4, −166.4, and −168.8 for the *o,p,m*-C_6F_5 fluorine nuclei. The ^{11}B NMR spectrum shows the broad H[B] doublet at δ −25.5 ($^1J_{BH}$ = 94 Hz).

The NMR characterization of the bis-ammonium salt **12** was carried out at 198 K in d_8-THF from a ca. 5:1 mixture of **12** and **11**. Complex **12** shows ^1H NMR signals of the aryl-NH_2^+-CH_2– groups at δ 9.65 and 4.59, respectively [with corresponding characteristic aryl resonances at δ 7.55 (1H) and 7.48 (2H)]. It features ^1H NMR η^5-C_5H_4 resonances at δ 6.76 and 6.19 and a broad signal of the counteranion $[HB(C_6F_5)_3^-]$ at δ 3.70. For further details of the characterization of the compounds **10**–**12** see the Experimental Section and the Supporting Information.

Complex **10** was also characterized by X-ray diffraction (see Figure 6).[24] It shows a bent metallocene unit with a pseudotetrahedral coordination geometry of the central group 4 transition metal [angles Cp(centroid)–Zr–Cp(centroid): 130.3°, Cl1–Zr–Cl2: 98.0(1)°]. The Zr–C(Cp) bond lengths were found in a range between 2.470(2) and 2.594(3) Å. The $-CH_2$-NH-aryl substituents at the pair of Cp ligands are oriented in a close to C_2-symmetric arrangement both toward the open front side of the bent metallocene wedge. Thereby, the C1A–C6A (1.502(3) Å) vector in the projection is oriented toward the Zr–Cl1 (2.447(1) Å) side, whereas its C1B–C6B (1.494(3) Å) counterpart is found in the projection above Zr–Cl2 (2.426(1) Å). The C6A–N7A (1.466(3) Å) and C6B–N7B (1.471(3) Å) bond lengths are in the C(sp^3)–N single bond range. The bond angle at the CH_2 groups amounts to 111.9(2)° (C1A–C6A–N7A) and 110.8(2)° (C1B–C6B–N7B), respectively. The angles at the NH groups amount to C6A–N7A–C8A 116.4(2)° and C6B–N7B–C8B 117.8(2)°, respectively. The $-CH_2$-NH vectors are conformationally oriented close to in-plane with their adjacent Cp rings (dihedral angles C5A–C1A–C6A–N7A: −11.1(3)°, C5B–C1B–C6B–N7B: −25.0(4)°), whereas the NH-aryl vector is markedly rotated from that plane (dihedral angles C1A–C6A–N7A–C8A: 151.0(2)°, C6A–N7A–C8A–C9A: −75.7(3)°, and correspondingly C1B–C6B–N7B–C8B: 162.2(2)°, C6B–N7B–C8B–C9B: −76.0(3)°).

The zirconocene-based ammonium salt **12** itself is an active hydrogenation catalyst, e.g., for bulky imines, as expected.[18–20] These reactions were described in some detail in our preliminary communication about this chemistry[25] and its Supporting Information. We achieved a close to quantitative hydrogenation of each of the bulky aldimines **13** by treatment with H_2 (2 bar) at room temperature in C_6D_6 using 5.6 mol % (for **13a**) or 2.3 mol % (for **13b**) of the catalyst system **12** (see Scheme 6). Complex **12** was also an active catalyst for the hydrogenation of a bulky silyl enol ether.[26] With 4.8 mol % of the catalyst **12** the product **16** was obtained in 85% yield from the catalytic hydrogenation of **15** (see Scheme 6). In a control experiment we exposed a 20:1 mixture of the silyl enol ether **15** and complex **9** to H_2 (2 bar, rt) overnight in the absence of $B(C_6F_5)_3$. This did not result in hydrogenation of any of these compounds.

Conclusions

We note that there has been some progress in the development of an organic functional group chemistry at the sensitive group 4 bent metallocenes and related compounds, but in detail this still meets with a lot of difficulties.[1] Group 4

(22) For mechanistic aspects of this reaction (theoretic analysis) see for example: (a) Rokob, T. A.; Hamza, A.; Stirling, A.; Soós, T.; Pápai, I. *Angew. Chem.* **2008**, *120*, 2469–2472. *Angew. Chem., Int. Ed.* **2008**, *47*, 2435–2438. (b) Stirling, A.; Hamza, A.; Rokob, T. A.; Pápai, I. *Chem. Commun.* **2008**, 3148–3150. (c) Guo, Y.; Li, S. *Inorg. Chem.* **2008**, *47*, 6212–6219.

(23) Early reviews: (a) Stephan, D. W. *Org. Biomol. Chem.* **2008**, 1535–1539. (b) Kenward, A. L.; Piers, W. E. *Angew. Chem.* **2008**, *120*, 38–42. *Angew. Chem., Int. Ed.* **2008**, *47*, 38–41.

(24) For related substituted (1-aminoethyl-Cp) group 4 metallocene complexes see for example: Erker, G. *Coord. Chem. Rev.* **2006**, *250*, 1056–1070, and references therein.

(25) Axenov, K. V.; Kehr, G.; Fröhlich, R.; Erker, G. *J. Am. Chem. Soc.* **2009**, 3454–3455.

(26) See for a comparison: Wang, H.; Fröhlich, R.; Kehr, G.; Erker, G. *Chem. Commun.* **2008**, 5966–5968.

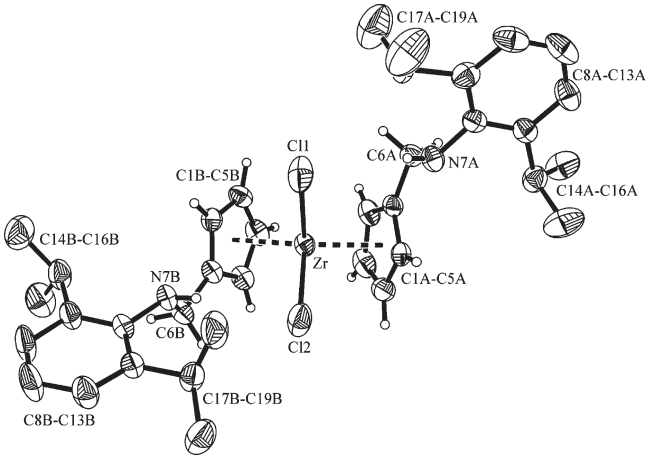
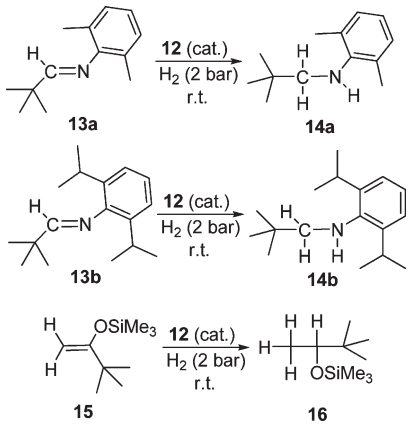


Figure 6. View of the molecular structure of complex **10**. Ellipsoids are given at the 50% probability level. Hydrogen atoms at the substituents were omitted for clarity.

Scheme 6



metallocene functional group chemistry is still nowhere near, for example, ferrocene-based synthetic chemistry. The systems described here may serve as some typical examples. It seems that we had mastered, at least to some extent, imino-Cp chemistry at the ligand stage. The respective secondary amino-fulvene precursors are now available by established routes. The imino-Cp systems can be constructed at their anion stage **3**. The anions **3** exhibit a considerable [Cp-CH=N-aryl]−character, as exemplified by the spectroscopic properties and the structural features of the respective lithium compound **3**·$(THF)_3$ (see Scheme 2 and Table 1). However, transmetalation to zirconium still met with considerable difficulties. Even well-established alternative routes via the corresponding silyl derivative failed under our experimental conditions.

Nevertheless, we were able to prepare the imino-Cp-functionalized zirconocene complexes **6**−**9** starting from the neutral secondary fulvene derivatives. The C_5H_4(=CH-NH-aryl) fulvene **5** has become available by means of the "detour" via the $[C_5H_4(CHN\text{-aryl})]^-$ anion system **3**. To achieve a sufficiently selective protonation was more difficult than expected. Eventually treatment of **3** in ether with acacH (serving as a Brønsted acid) solved the problem to give syn-/anti-**5** in a good yield, albeit contaminated with 2,6-diisopropylaniline. In situ deprotonation of **5** by suitable [Zr]-NMe_2 or [Zr]-benzyl reagents then opened the synthetic pathways for the preparation of the anticipated functionalized (Cp-CH=N-aryl)$_2ZrX_2$ systems **6**−**9**. This shows that the synthesis of even such functionalized group 4 metallocenes can be achieved by means of acceptably short, but admittedly sometimes rather special routes.

The subsequent catalytic hydrogenation of the pair of imine functional groups at the bent metallocene framework of the zirconocene complex **9** is a quite remarkable application of the new method of "metal-free" hydrogen activation and hydrogenation catalysis by frustrated Lewis pairs.[16,21,23] Our example indicates some potentially useful application of this new chemistry, of which currently more and more examples of suitable Lewis acid/Lewis base pairs are emerging from the literature.[27]

In our case, it is likely that we are generating a series of non-self-quenched N/B Lewis pairs.[18−20] First, the attached imine probably serves as the bulky Lewis base necessary for heterolytic dihydrogen splitting. At later stages this may be complemented by the metallocene-attached secondary amine base, which was itself formed in this rather efficient catalytic "metal-free" hydrogenation process. The overall process may, therefore, well have some quasi-autocatalytic features. Eventually, the product **10** serves as a component of an efficient hydrogenation catalyst of this novel general type itself. So it seems that developing functional group chemistry at the sensitive group 4 bent metallocenes is not just a more complex repeat of, for example, established organic ferrocene-type chemistry, but can in cases lead to new and unexpected observations, which may encourage us and others to continue with this development.

Experimental Section

General Information. All reactions were carried out under 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; ^{11}B, 64 MHz), ARX 300 (^{1}H, 300 MHz; ^{19}F, 282 MHz), Varian 500 MHz INOVA (^{1}H, 500 MHz; ^{11}B, 160.4 MHz; ^{19}F, 470.2 MHz), Varian UNITY plus NMR spectrometer (^{1}H, 600 MHz; ^{13}C, 151 MHz; ^{19}F, 564 MHz). Assignments of the resonances are supported by 2D experiments and chemical shift calculations. ^{11}B NMR spectra were referenced to an external $Et_2O\cdot BF_3$ sample; ^{19}F NMR spectra were referenced to an external $CFCl_3$ sample. X-ray diffraction: Data sets were collected with Nonius KappaCCD diffractometers, in the case of Mo-radiation equipped with a rotating anode generator. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307−326), absorption correction SORTAV (R. H. Blessing,

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6-Dimethylaminofulvene (**1**),[8] $Zr(NMe_2)_4$,[10] $Zr(NMe_2)_2Cl_2\cdot(THF)_2$, and $B(C_6F_5)_3$[17] were prepared according to modified literature procedures. The THF-free lithium {[(*N*-2,6-diisopropylphenyl)formimidoyl]cyclopentadienide} (**3**) was synthesized on the basis of the procedure published by us previously,[9a] only with Et_2O used as solvent instead of THF.

Preparation of 6-(*N*-2,6-Trimethylsilyl-2,6-diisopropylanilino)-fulvene, 4. Me_3SiCl (0.43 g, 0.5 mL, 3.93 mmol) was added to the solution of $Li[C_5H_4CH{=}N(2,6\text{-}iPr_2C_6H_3)]\cdot THF$[9a] (**3**·THF) (1.30 g, 3.93 mmol) in Et_2O (20 mL) at −78 °C. The reaction mixture was allowed to warm slowly to room temperature and stirred overnight. Et_2O was evaporated in vacuo, and the residue was extracted with pentane (30 mL). After filtration, pentane was removed under vacuum, which gave the product in the form of an orange-brown crystalline solid (1.28 g, 78%). Single crystals of **4** suitable for X-ray crystal structure analysis were grown from pentane solution at −30 °C. Anal. Calcd for $C_{21}H_{31}SiN$: C, 77.47; H, 9.60; N, 4.30. Found: C, 77.17; H, 9.68; N, 4.35. ^{1}H NMR (600 MHz, C_6D_6, 298 K): δ 7.25 (s, 1H, =C*H*N), 7.19 (m, 1H, *p*-Ar), 7.09 (m, 2H, *m*-Ar), 6.58 (α′), 6.49 (β′), 6.42 (β), 5.09 (α) (each m, each 1H, C_5H_4), 3.06 (sept, 2H, $^3J_{HH}$ = 6.8 Hz, C*H*(*i*Pr)), 1.09 (d, 12H, $^3J_{HH}$ = 6.8 Hz, CH_3(*i*Pr)), 0.03 (s, 9H, CH_3Si). ^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 298 K): δ 146.0 (*o*-Ar), 144.4 (=*C*HN), 138.9 (*i*-Ar), 128.4 (*p*-Ar), 128.0 (β-C_5H_4), 126.3 (α′-C_5H_4), 125.1 (*m*-Ar), 124.2 (*i*-C_5H_4), 122.4 (β′-C_5H_4), 117.0 (α-C_5H_4), 28.6 (*C*H(*i*Pr)), 25.1 (*C*H_3(*i*Pr)), 24.3 (*C*H_3(*i*Pr)), −0.4 (*C*H_3Si).

X-ray Crystal Structure Analysis of Compound 4. Formula $C_{21}H_{31}NSi$, M = 325.56, yellow-red crystal 0.50 × 0.45 × 0.05 mm, a = 8.657(1) Å, b = 8.942(1) Å, c = 14.169(1) Å, α = 82.22(1)°, β = 88.91(1)°, γ = 66.88(1)°, V = 998.8(2) Å^3, ρ_{calc} = 1.083 g cm^{-3}, μ = 1.011 mm^{-1}, empirical absorption correction (0.632 ≤ T ≤ 0.951), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 11 543 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.60 Å^{-1}, 3544 independent (R_{int} = 0.039) and 3331 observed reflections [$I \geq 2\sigma(I)$], 215 refined parameters, R = 0.049, wR^2 = 0.137, max. residual electron density 0.25(−0.29) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of 6-(2,6-Diisopropylanilino)fulvene, 5. The THF-free Li salt **3** (6.31 g, 24.38 mol) was placed into a Schlenk flask, and Et_2O (150 mL) was added. The resulting solution was cooled to −40 °C, and dry acetylacetone (2.44 g, 2.6 mL, 24.4 mmol) was slowly added via syringe. The reaction mixture was stirred at −40 °C for 10 min, then warmed slowly to room temperature and finally stirred for 1 h. After filtration all volatiles were removed from the filtrate in vacuo. The brown oily residue was extracted with pentane (100 mL). The filtered pentane solution was dried in vacuo to yield the product as a red-brown oil, which slowly crystallized (5.22 g, 72%) at low temperature. Despite all precautions, the compound was always contaminated with ca. 25 mol % of 2,6-di-isopropylaniline. Based on the integration of the CH protons of the *i*Pr groups, the ratio of the major to the minor ligand isomer to free 2,6-di-isopropylaniline was 2:1:1. Crystals of **5** suitable for crystal structure analysis were obtained from a heptane solution at −30 °C. Anal. Calcd for 3 × $C_{18}H_{23}N$ + $C_{12}H_{19}N$: C, 84.56; H, 9.46, N, 5.98. Found: C, 84.45; H, 9.45; N, 5.94.

Major Isomer (anti-5). ^{1}H NMR (600 MHz, CD_2Cl_2, 253 K): δ 7.36 (t, $^3J_{HH}$ = 7.8 Hz, 1H, *p*-Ar), 7.26 (d, $^3J_{HH}$ = 7.8 Hz, 2H, *m*-Ar), 6.99 (d, $^3J_{HH}$ = 14.2 Hz, 1H, =C*H*N), 6.91 (br d, $^3J_{HH}$ = 14.2 Hz, 1H, N*H*), 6.71 (dm, J_{HH} = 4.7 Hz, β′), 6.51 (m, α′), 6.41 (ddd, J_{HH} = 4.7 Hz, 2.1 Hz, 1.7 Hz, β), 6.27 (ddd, J_{HH} = 4.6 Hz, 2.4 Hz, 1.4 Hz, α) (each 1H, C_5H_4), 3.29 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*(*i*Pr)), 1.23 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH_3(*i*Pr)). ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 253 K): δ 146.5 (=C*H*N), 145.7 (*o*-Ar), 135.0 (*i*-Ar), 128.4 (*p*-Ar), 126.5 (α′-C_5H_4), 124.0 (*m*-Ar), 123.5 (β-C_5H_4), 121.9 (α-C_5H_4), 118.3 (*i*-C_5H_4), 111.6 (β′-C_5H_4), 28.3 (*C*H(*i*Pr)), 23.6 (*C*H_3(*i*Pr)).

Minor Isomer (syn-5). ^{1}H NMR (600 MHz, CD_2Cl_2, 253 K): δ 7.45 (t, $^3J_{HH}$ = 7.8 Hz, 1H, *p*-Ar), 7.32 (d, $^3J_{HH}$ = 7.3 Hz, 1H, =C*H*N), 7.30 (d, $^3J_{HH}$ = 7.8 Hz, 1H, *m*-Ar), 6.49 (d, $^3J_{HH}$ = 7.3 Hz, 1H, N*H*), 6.35 (dm, J_{HH} = 4.7 Hz, β′), 6.12 (ddd, J_{HH} = 4.6 Hz, 2.3 Hz, 1.4 Hz, α′), 6.05 (m, α), 4.97 (dm, J_{HH} = 4.7 Hz, β) (each 1H, C_5H_4), 3.13 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*(*i*Pr)), 1.18, 1.10 (each d, each $^3J_{HH}$ = 6.8 Hz, each 6H, CH_3(*i*Pr)). ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 253 K): δ 146.4 (*o*-Ar), 143.6 (=C*H*N), 134.2 (*i*-Ar), 129.1 (*p*-Ar), 125.4 (α-C_5H_4), 124.8 (β′-C_5H_4), 124.3 (*m*-Ar), 120.5 (α′-C_5H_4), 118.1 (*i*-C_5H_4), 115.1 (β-C_5H_4), 28.4 (*C*H(*i*Pr)), 24.4 (*C*H_3(*i*Pr)), 23.0 (*C*H_3(*i*Pr)).

X-ray Crystal Structure Analysis of syn-5. Formula $C_{18}H_{23}N$, M = 253.37, yellow crystal 0.30 × 0.20 × 0.15 mm, a = 8.5993(2) Å, b = 17.2910(5) Å, c = 10.7919(3) Å, β = 100.022(2)°, V = 1580.17(7) Å^3, ρ_{calc} = 1.065 g cm^{-3}, μ = 0.457 mm^{-1}, empirical absorption correction (0.875 ≤ T ≤ 0.935), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 11 264 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.60 Å^{-1}, 2747 independent (R_{int} = 0.035) and 2423 observed reflections [$I \geq 2\sigma(I)$], 200 refined parameters, R = 0.046, wR^2 = 0.123, max. residual electron density 0.15(−0.13) e Å^{-3}, isopropyl group C16−C18 refined with split positions, hydrogen atom at N1 from difference Fourier calculation, others calculated and refined as riding atoms.

Preparation of the Bis(amido)zirconocene Complexes 6 and 7. Compound 7. A solution of $Zr(NMe_2)_4$ (2.63 g, 9.84 mmol) in dry benzene (20 mL) was added to the solution of ligand **5** (6.64 g, 19.68 mmol) in dry benzene (30 mL) at room temperature. The reaction mixture was stirred overnight. After removal of all volatiles under vacuum the brown residue was washed with pentane (50 mL). After decantation of the pentane phase the residue was washed again with pentane (20 mL) and dried under vacuum, which gave 2.8 g (35%) of the product **7** as a yellow-brown powder. Crystals of **7** suitable for X-ray single-crystal diffraction analysis were grown from an Et_2O solution at −30 °C. Anal. Calcd for $C_{50}H_{68}ZrN_4$: C, 73.57; H, 8.40; N, 6.86. Found: C, 74.26; H, 8.70; N, 6.31. At 298 K: ^{1}H NMR (600 MHz, C_6D_6, 298 K): δ 7.88 (s, 2H, N=C*H*), 7.12 (m, 4H, *m*-Ar), 7.09 (m, 2H, *p*-Ar), 7.06 (m, 2H, *m*-Ar^{Zr}), 6.96 (m, 1H, *p*-Ar^{Zr}), 6.94 (α′), 6.46 (α), 6.10 (β′), 5.96 (β) (each br m, each 2H, C_5H_4), 3.47 (br, 2H, C*H*(*i*Pr)^{Zr}), 3.18 (sept, 4H, $^3J_{HH}$ = 6.8 Hz, C*H*(*i*Pr)), 2.85 (s, 6H, CH_3N), 1.21 (br, 12H, CH_3-(*i*Pr)^{Zr}), 1.20 (d, 12H, $^3J_{HH}$ = 6.8 Hz, CH_3(*i*Pr)), 1.13 (d, 12H, $^3J_{HH}$ = 6.8 Hz, CH_3(*i*Pr)). ^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 298 K): δ 156.7 (*C*H=N), 153.1 (*i*-Ar^{Zr}), 149.5 (*i*-Ar), 138.1 (*o*-Ar), 124.8 (*p*-Ar), 123.5 (*m*-Ar), 123.1 (br, *m*-Ar^{Zr}), 122.2 (*p*-Ar^{Zr}), 119.9 (*i*-C_5H_4), 117.7 (α-C_5H_4), 113.1 (br, β′-C_5H_4), 112.7 (α′-C_5H_4), 109.9 (br, β-C_5H_4), 50.9 (*C*H_3N), 28.3 (*C*H(*i*Pr)), 28.2 (br, *C*H(*i*Pr)^{Zr}), 24.5 (br, CH_3(*i*Pr)^{Zr}), 23.9 (*C*H_3(*i*Pr)), 23.8 (*C*H_3(*i*Pr)). At 353 K: ^{1}H NMR (600 MHz, d_8-toluene, 353 K): δ 7.90 (s, 2H, N=C*H*), 7.01 (m, 4H, *m*-Ar), 6.96 (m, 2H, *p*-Ar), 6.95 (br m, 2H, *m*-Ar^{Zr}), 6.83 (α′), 6.81 (m, 1H, *p*-Ar^{Zr}), 6.44 (α), 6.06 (β′), 5.90 (β) (each br s, each 2H, C_5H_4), 3.42 (br sept, 2H, $^3J_{HH}$ = 6.7 Hz, C*H*(*i*Pr)^{Zr}), 3.08 (sept, 4H, $^3J_{HH}$ = 6.8 Hz, C*H*(*i*Pr)), 2.83 (s, 6H, CH_3N), 1.12 (d, 12H, $^3J_{HH}$ = 6.8 Hz, CH_3(*i*Pr)), 1.12 (d, 12H, $^3J_{HH}$ = 6.7 Hz, CH_3(*i*Pr)^{Zr}), 1.05 (d, 12H, $^3J_{HH}$ = 6.8 Hz, CH_3(*i*Pr)). ^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 353 K): δ 156.8 (*C*H=N), 153.3 (*i*-Ar^{Zr}), 149.8 (*i*-Ar), 140.5 (*o*-Ar^{Zr}), 138.5 (*o*-Ar), 124.9 (*p*-Ar), 123.6 (*m*-Ar), 123.2 (*m*-Ar^{Zr}), 122.5 (*p*-Ar^{Zr}), 120.9 (*i*-C_5H_4), 117.4 (α-C_5H_4), 113.7 (br, β′-C_5H_4), 113.3 (α′-C_5H_4), 109.8 (β-C_5H_4), 51.1 (*C*H_3N), 28.5 (*C*H(*i*Pr)), 28.1 (*C*H(*i*Pr)^{Zr}), 24.5 (*C*H_3(*i*Pr)^{Zr}), 23.9 (*C*H_3(*i*Pr)), 23.9 (*C*H_3(*i*Pr)).

X-ray Crystal Structure Analysis of Complex 7. Formula $C_{50}H_{68}N_4Zr$, M = 816.30, yellow crystal 0.45 × 0.40 × 0.10 mm,

a = 20.3145(3) Å, b = 10.6737(2) Å, c = 21.4606(4) Å, β = 100.071(1)°, V = 4581.6(1) Å^3, ρ_{calc} = 1.183 g cm^{-3}, μ = 0.276 mm^{-1}, empirical absorption correction (0.886 ≤ T ≤ 0.973), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 23 874 reflections collected (±h, ± k, ± l), [(sin θ)/λ] = 0.60 Å^{-1}, 8041 independent (R_{int}=0.078) and 5437 observed reflections [$I \geq 2\sigma(I)$], 513 refined parameters, R = 0.053, wR^2 = 0.119, max. residual electron density 0.63(−0.41) e Å^{-3}, hydrogen atom at N1C from difference Fourier calculation, others calculated and refined as riding atoms.

Compound 6. The pentane solution decanted from the precipitation of complex **7** was filtered through Celite and evaporated under vacuum, to give 4.40 g (65%) of the target complex **6** as a yellow-brown solid. Crystals of **6** suitable for the X-ray single-crystal diffraction analysis were grown from pentane solution at −30 °C. Anal. Calcd for $C_{40}H_{56}ZrN_4$: C, 70.23; H, 8.25. Found: C, 70.78; H, 8.64. ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 7.96 (s, 2H, N=C*H*), 7.18 (m, 4H, *m*-Ar), 7.13 (m, 2H, *p*-Ar), 6.71 (α), 6.01 (β) (each m, each 4H, C_5H_4), 3.28 (sept, 4H, $^3J_{HH}$ = 6.9 Hz, C*H*(*i*Pr)), 2.83 (s, 12H, CH_3N), 1.22 (d, 24H, $^3J_{HH}$ = 6.9 Hz, CH_3(*i*Pr)). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K): δ 156.5 (*C*H=N), 150.0 (*i*-Ar), 138.2 (*o*-Ar), 124.6 (*p*-Ar), 123.5 (*m*-Ar), 121.3 (*i*-C_5H_4), 114.4 (α-C_5H_4), 111.3 (β-C_5H_4), 49.1 (*C*H_3N), 28.1 (*C*H(*i*Pr)), 24.1 (*C*H_3(*i*Pr)).

X-ray Crystal Structure Analysis of Complex 6. Formula $C_{40}H_{56}N_4Zr$, M = 684.11, yellow crystal 0.50 × 0.20 × 0.10 mm, a = 8.8885(1) Å, b = 13.7423(2) Å, c = 16.0742(3) Å, α = 75.012(1)°, β = 76.547(1)°, γ = 89.272(2)°, V = 1842.25(5) Å^3, ρ_{calc} = 1.233 g cm^{-3}, μ = 0.330 mm^{-1}, empirical absorption correction (0.852 ≤ T ≤ 0.968), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 12 856 reflections collected (±h, ± k, ± l), [(sin θ)/λ] = 0.66 Å^{-1}, 8708 independent (R_{int} = 0.031) and 7122 observed reflections [$I \geq 2\sigma(I)$], 418 refined parameters, R = 0.040, wR^2 = 0.093, max. residual electron density 0.36(−0.54) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of the Dibenzylzirconocene Complex 8. Et_2O (15 mL) was added to $ZrCl_4$ (0.31 g, 1.33 mmol) at −78 °C, and the resulting mixture was stirred at −78 °C until a homogeneous suspension was formed. To this suspension of $ZrCl_4$ in Et_2O was added a 1 M solution of $PhCH_2MgCl$ (5.34 mmol) in Et_2O (5.34 mL) at −78 °C. The reaction was protected from direct light, allowed to warm to room temperature, and stirred for 1 h. To the resulting mixture was added an ethereal solution (20 mL) of the ligand **5** (0.91 g, 2.68 mmol) by syringe at −78 °C. The reaction was warmed to room temperature, stirred for 1 h, and then kept in the freezer at −20 °C overnight. After removal of all volatiles under vacuum the residue was extracted with pentane (2 × 20 mL). The combined extracts were filtered, and the solvent was evaporated in vacuo. The remaining red-orange residue was washed with pentane (10 mL) and dried under vacuum, which gave the product as an orange solid (0.7 g). An additional amount of the product (0.2 g) precipitated from the pentane washings upon keeping it at room temperature for several days. The total yield of the complex was 0.9 g (87%). Crystals of **8** suitable for X-ray single-crystal diffraction analysis were grown from Et_2O solution at −33 °C. Anal. Calcd for $C_{50}H_{58}ZrN_2$: C, 77.17; H, 7.51; N, 3.60. Found: C, 77.72; H, 7.82; N, 3.46. ^{1}H NMR (600 MHz, C_6D_6, 298 K): δ 7.67 (s, 2H, N=C*H*), 7.15 (m, 4H, *m*-Ph), 7.13 (m, 4H, *m*-Ar), 7.11 (m, 2H, *p*-Ar), 6.97 (m, 4H, *o*-Ph), 6.82 (m, 2H, *p*-Ph), 6.53 (α), 5.68 (β) (each m, each 4H, C_5H_4), 3.16 (sept, 4H, $^3J_{HH}$ = 6.9 Hz, C*H*(*i*Pr)), 2.18 (s, 4H, CH_2Ph), 1.18 (d, 24H, $^3J_{HH}$ = 6.9 Hz, CH_3(*i*Pr)). ^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 298 K): δ 157.0 (*C*H=N), 151.3 (*i*-Ph), 149.4 (*i*-Ar), 137.9 (*o*-Ar), 128.7 (*m*-Ph), 126.2 (*o*-Ph), 125.0 (*p*-Ar), 123.5 (*m*-Ar), 123.0 (*i*-C_5H_4), 121.9 (*p*-Ph), 116.0 (α-C_5H_4), 113.2 (β-C_5H_4), 63.5 (*C*H_2Ph), 28.4 (*C*H(*i*Pr)), 23.9 (*C*H_3(*i*Pr)).

X-ray Crystal Structure Analysis of Complex 8. Formula $C_{50}H_{58}N_2Zr$, M = 778.20, orange crystal 0.30 × 0.30 × 0.12 mm, a = 11.620(1) Å, b = 12.127(1) Å, c = 31.003(1) Å, V = 4368.8(5) Å^3, ρ_{calc} = 1.183 g cm^{-3}, μ = 0.286 mm^{-1}, empirical absorption correction (0.919 T ≤ 0.967), Z = 4, orthorhombic, space group $P2_12_12_1$ (No. 19), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 32 769 reflections collected (±h, ± k, ± l), [(sin θ)/λ] = 0.62 Å^{-1}, 8831 independent (R_{int} = 0.078) and 5228 observed reflections [$I \geq 2\sigma(I)$], 501 refined parameters, R = 0.056, wR^2 = 0.141, max. residual electron density 0.53(−0.53) e Å^{-3}, Flack parameter 0.03(5), imino group C6A−N1A refined with split positions, hydrogens calculated and refined as riding atoms.

Preparation of the Dichlorozirconocene Complex 9. $(Me_2N)_2ZrCl_2(THF)_2$ (0.78 g, 1.98 mmol) was mixed in a glovebox with ligand **5** (1.20 g, ∼4.74 mmol). Then 20 mL of toluene was added. The reaction mixture was first stirred for 3 h at 120 °C and additionally overnight at room temperature. After filtration all volatiles were removed under vacuum, and the resulting brown residue was washed with pentane (12 mL). After removal of the pentane phase by syringe, the oily brown precipitate was dried in vacuo, which gave 0.52 g (39%) of the product **9** as a red-brown solid. The second crop of the product precipitated from the pentane washings at room temperature as a crystalline solid. After removing the pentane solvent by decantation, the crystalline residue was dried in vacuo, which gave an additional amount of the target complex (0.358 g). The combined yield of complex **9** was 0.878 g, 67%. Anal. Calcd for $C_{36}H_{44}N_2Cl_2Zr$: C, 64.84; H, 6.65; N, 4.20. Found: C, 64.72; H, 6.85; N, 4.24. ^{1}H NMR (600 MHz, C_6D_6, 298 K): δ 7.99 (s, 2H, =C*H*N), 7.15 (m, 6H, Ar), 6.72 (α), 5.89 (β) (each m, each 4H, C_5H_4), 3.25 (sept, $^3J_{HH}$ = 6.9 Hz, 4H, C*H*(*i*Pr)), 1.24 (d, $^3J_{HH}$ = 6.9 Hz, 24H, CH_3(*i*Pr)). ^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 298 K): δ 156.2 (N=*C*H), 149.2 (*i*-Ar), 137.9 (*o*-Ar), 125.1 (*p*-Ar), 124.6 (*i*-C_5H_4), 123.5 (*m*-Ar), 119.4 (α-C_5H_4), 114.5 (β-C_5H_4), 28.2 (*C*H(*i*Pr)), 24.0 (*C*H_3(*i*Pr)).

Hydrogenation of the Dichlorozirconocene Complex 9; Generation of Complex 10. In a reference experiment C_6D_6 (1 mL) was added in the glovebox in a Schlenk flask to a mixture of complex **9** (0.2 g, 0.30 mmol) and $B(C_6F_5)_3$ (77 mg, 0.15 mmol). The flask was connected to the hydrogen bottle. The system was flushed with hydrogen and then properly closed with the tap. The hydrogen pressure in the reaction flask was raised to 2 bar, and the reaction mixture was stirred in the glovebox overnight at room temperature. After evaporation of all volatiles in vacuo a mixture of **10** and **11** was obtained as a light yellow solid (ca. 0.27 g, 100%). A similar result was achieved by using a hydrogen pressure of 60 bar and shorter reaction time (3 h). Anal. Calcd for **10**:**11** (1:1) ($C_{90}H_{98}BCl_4F_{15}N_4Zr_2$): C, 58.25; H, 5.32; N, 3.02. Anal. Calcd for **10**:**11** (2:1) ($C_{126}H_{144}BCl_6F_{15}N_6Zr_3$): C, 59.94; H, 5.75; N, 3.33. Found: C, 57.97; H, 4.91; N, 3.33. ^{1}H NMR (600 MHz, C_6D_6, 298 K): δ 7.07 (m, 6H, Ar), 6.13 (α), 5.68 (α) (each m, each 4H, C_5H_4), 4.17 (s, 4H, CH_2), 3.87 (B*H*), 3.32 (sept, $^3J_{HH}$ = 6.5 Hz, 4H, C*H*(*i*Pr)), 1.21 (d, $^3J_{HH}$ = 6.5 Hz, 24H, CH_3(*i*Pr)), n.o. (N*H*). ^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 298 K): δ 148.8 (dm, $^1J_{CF} \approx$ 235 Hz, C_6F_5), 143.0 (*o*-Ar), 140.7 (br, *i*-Ar), 138.8 (dm, $^1J_{CF} \approx$ 243 Hz, *p*-C_6F_5), 137.3 (dm, $^1J_{CF} \approx$ 248 Hz, C_6F_5), n.o. (*i*-C_6F_5), 131.8 (*i*-C_5H_4), 126.0 (*p*-Ar), 124.3 (*m*-Ar), 117.6 (br, α-C_5H_4), 111.8 (β-C_5H_4), 51.0 (*C*H_2), 28.1 (*C*H(*i*Pr)), 24.4 (*C*H_3(*i*Pr)). ^{19}F NMR (470 MHz, C_6D_6, 298 K): δ −133.4 (m, *o*-C_6F_5), −161.7 (t, $^3J_{FF}$ = 20.4 Hz, *p*-C_6F_5), −165.2 (m, *m*-C_6F_5). ^{11}B{^{1}H} NMR (160 MHz, C_6D_6, 298 K): δ −24.4 ($\nu_{1/2} \approx$ 100 Hz). ^{11}B NMR (160 MHz, C_6D_6, 298 K): δ −24.4 (br d, $^1J_{BH} \approx$ 76 Hz).

Crystals of complex **10** suitable for the X-ray single-crystal diffraction analysis were grown from a pentane solution at −33 °C.

X-ray Crystal Structure Analysis of Complex 10. Formula $C_{36}H_{48}Cl_2N_2Zr$, M = 670.88, colorless crystal 0.35 × 0.10 × 0.10 mm, a = 13.6288(2) Å, b = 17.8192(3) Å, c = 14.1609(2) Å, β = 91.922(1)°, V = 3437.10(9) Å^3, ρ_{calc} = 1.296 g cm^{-3}, μ = 0.501 mm^{-1}, empirical absorption correction (0.877 ≤ T ≤ 0.973), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 27 684 reflections

collected ($\pm h, \pm k, \pm l$), [(sin θ)/λ] = 0.66 Å^{-1}, 8167 independent (R_{int} = 0.056) and 5519 observed reflections [$I \geq 2\sigma(I)$], 416 refined parameters, R = 0.044 wR^2 = 0.099, max. (min.) residual electron density 0.44 (−0.62) e Å^{-3}, disorder in the isopropyl group C17A−C19A refined with split positions, hydrogen atoms at nitrogen from difference Fourier map, others calculated and refined as riding atoms.

The following additional experiments were carried out to identify the individual products **10** and **11** from the reaction mixture. The experiment was carried out in a glovebox using a Schlenk flask: C_6D_6 (0.6 mL) was added to a mixture of complex **9** (50 mg, 0.075 mmol) and $B(C_6F_5)_3$ (0.5 equiv, 19 mg, 0.0375 mmol). The flask was connected to the hydrogen bottle. The system was flushed with hydrogen and then properly closed with the tap. The hydrogen pressure in the reaction flask was raised to 2 bar, and the reaction mixture was stirred in a glovebox overnight at room temperature. After evaporation of all volatiles in vacuo a mixture of **10** and **11** (2:1) was obtained as a light yellow solid (∼100%). The sample was redissolved in d_8-THF, and the NMR experiments were measured at low temperature under static conditions ("frozen" proton transfer). Complex **10**: ^{1}H NMR (600 MHz, d_8-THF, 198 K): δ 7.06 (m, 2H, *m*-Ar), 7.00 (m, 1H, *p*-Ar), 6.37 (β), 6.00 (α),(each br, each 2H, C_5H_4), 4.04 (br, 2H, CH_2), 4.00 (br, 1H, N*H*), 3.29 (sept, $^3J_{HH}$ = 6.5 Hz, 2H, C*H*(*i*Pr)), 1.14 (br, 12H, CH_3(*i*Pr)). ^{13}C{^{1}H} NMR (151 MHz, d_8-THF, 198 K): δ 143.1 (*i*-Ar), 142.8 (*o*-Ar), 133.6 (*i*-C_5H_4), 123.8 (*p*-Ar), 123.4 (*m*-Ar), 116.7(α), 112.3(β) (C_5H_4), 50.4 (*C*H$_2$), 27.4 (*C*H(*i*Pr)), 24.2 (*C*H$_3$(*i*Pr)) [data from the ghsqc and ghmbc NMR experiment]. Complex **11**: ^{1}H NMR (600 MHz, d_8-THF, 198 K): δ 7.55 (m, 1H, *p*-Ar$_+$), 7.48 (m, 2H, *m*-Ar$_+$), 7.06 (m, 2H, *m*-Ar), 7.00 (m, 1H, *p*-Ar), 6.74, 6.16 (each br, each 2H, C_5H_{4+}), 6.59, 6.33 (each br, each 2H, C_5H_4), 4.62 (br, 2H, C$H_{2,+}$), 4.04 (br, 2H, CH_2), 4.00 (br, 1H, N*H*), 3.19 (br, 2H, C*H*(*i*Pr)), 2.77 (br, 2H, C*H*(*i*Pr)$_+$), 1.20 (br, 12H, CH_3-(*i*Pr)$_+$), 1.11 (br, 12H, CH_3(*i*Pr)), n.o. (N$H_{2,+}$). Averaged spectra at 298 K: ^{1}H NMR (600 MHz, d_8-THF, 298 K): δ 7.10 (br, 3H, Ar), 6.53, 6.40 (each br, each 2H, C_5H_4), 4.18 (br, 2H, CH_2), 3.78 (br, B*H*), 3.59 (br, 2H, C*H*(*i*Pr)), 1.19 (d, $^3J_{HH}$ = 6.5 Hz, 12H, CH_3(*i*Pr)), n.o. (N*H*). ^{19}F NMR (564 MHz, d_8-THF, 298 K): δ −133.4 (m, *o*-C_6F_5), −166.5 (t, $^3J_{FF}$ = 20.5 Hz, *p*-C_6F_5), −168.9 (m, *m*-C_6F_5);. ^{11}B{^{1}H} NMR (192 MHz, d_8-THF, 298 K): δ −25.5 ($\nu_{1/2} \approx$ 80 Hz). ^{11}B NMR (192 MHz, d_8-THF, 298 K): δ −25.5 (br d, $^1J_{BH} \approx$ 94 Hz).

Generation of Complex 11. The experiment was carried out in a glovebox using a Schlenk flask: D_6-benzene (1 mL) was added to a mixture of complex **9** (0.1 g, 0.15 mmol) and $B(C_6F_5)_3$ (1.2 equiv, 92 mg, 0.18 mmol). The flask was connected to the hydrogen bottle. The system was flushed with hydrogen and then properly closed with the tap. The hydrogen pressure in the reaction flask was raised to 2 bar, and the reaction mixture was stirred in a glovebox overnight at room temperature. After evaporation of all volatiles in vacuo a mixture of **10**, **11**, and **12** (5:20:3) was obtained as a light yellow solid (∼100%). The sample was redissolved in d_8-THF, and the NMR experiments were measured at low temperature under static conditions ("frozen" proton transfer). Complex **11**: ^{1}H NMR (600 MHz, d_8-THF, 198 K): δ 9.65 (br, 2H, N$H_{2,+}$), 7.56 (m, 1H, *p*-Ar$_+$), 7.48 (m, 2H, *m*-Ar$_+$), 7.05 (m, 2H, *m*-Ar), 6.99 (m, 1H, *p*-Ar), 6.75 (β), 6.14 (α) (each br, each 2H, C_5H_{4+}), 6.60 (β), 6.33 (α) (each br, each 2H, C_5H_4), 4.62 (br, 2H, C$H_{2,+}$), 4.01 (br, 3H, CH_2, N*H*), 3.19 (br, 2H, C*H*(*i*Pr)), 2.77 (br, 2H, C*H*(*i*Pr)$_+$), 1.20, 1.17 (each br, each 6H, CH_3(*i*Pr)$_+$), 1.10 (br, 12H, CH_3(*i*Pr)). ^{13}C{^{1}H} NMR (151 MHz, d_8-THF, 198 K): δ 143.1 (*i*-Ar), 142.9 (*o*-Ar, *o*-Ar$_+$), 134.8 (*i*-C_5H_4), 131.5 (*p*-Ar$_+$), 127.8 (*i*-Ar$_+$), 124.6 (*m*-Ar$_+$), 124.4 (*p*-Ar), 124.4(α), 111.9 (β) (C_5H_{4+}), 123.8 (*m*-Ar), 118.2 (α), 113.8 (β) (C_5H_4), 115.4 (*i*-C_5H_{4+}), 51.4 (C$H_{2,+}$), 50.4 (CH_2), 28.8 (C*H*(*i*Pr)$_+$), 27.8 (C*H*(*i*Pr)), 24.4 (CH_3(*i*Pr)), 24.5, 23.3 (CH_3(*i*Pr)$_+$), [data from the ghsqc and ghmbc NMR experiment]. Averaged spectra at 298 K. ^{1}H NMR (600 MHz, d_8-THF, 298 K): δ 9.46 (N$H_{2,+}$), 7.28 (Ar), 6.59, 6.31 (C_5H_4), 4.60, 4.11 (CH_2), 3.08 (C*H*(*i*Pr)), 1.19 (d, $^3J_{HH}$ = 6.5 Hz, 12H, CH_3(*i*Pr)) [all resonances are very broad]. ^{19}F NMR (564 MHz, d_8-THF, 298 K): δ −133.4 (m, *o*-C_6F_5), −166.4 (t, $^3J_{FF}$ = 20.5 Hz, *p*-C_6F_5), −168.8 (m, *m*-C_6F_5). ^{11}B{^{1}H} NMR (192 MHz, d_8-THF, 298 K): δ −25.5 ($\nu_{1/2} \approx$ 60 Hz). ^{11}B NMR (192 MHz, d_8-THF, 298 K): δ −25.5 (br d, $^1J_{BH} \approx$ 94 Hz).

Preparation of Complex 12. C_6D_6 (1 mL) was added in a glovebox to a mixture of complex **9** (0.112 g, 0.168 mmol) and $B(C_6F_5)_3$ (172 mg, 0.336 mmol, 2 equiv). The glass tube containing the reaction mixture was closed with a dual valve Teflon adapter and placed into a steel autoclave inside a glovebox; then the autoclave was properly closed and removed from the glovebox. The autoclave was charged with dihydrogen to a pressure of 60 bar, and the reaction mixture was stirred for 3 h at ambient temperature. After venting hydrogen to ambient pressure inside the autoclave the glass tube was placed in the glovebox. The product is only sparingly soluble in benzene and precipitated as a brown oil. Benzene was removed from the precipitated product by decantation. The oily product was dissolved in 1 mL of dry dichloromethane. After evaporation of all volatiles under vacuum the product **12** was obtained as a light brown solid (160 mg, 81%).

The elemental analysis was obtained from the material prepared analogously from complex **9** (0.112 g, 0.168 mmol) and $B(C_6F_5)_3$ (172 mg, 0.336 mmol, 2 equiv). The procedure was as follows: C_6D_6 (1 mL) was added in the glovebox in a Schlenk flask to a mixture of complex **9** (0.112 g, 0.168 mmol) and $B(C_6F_5)_3$ (172 mg, 0.336 mmol, 2 equiv). The flask was connected to the hydrogen bottle. The system was flushed with hydrogen and then properly closed with the tap. The hydrogen pressure in the reaction flask was raised to 2 bar, and the reaction mixture was stirred in a glovebox overnight at room temperature. The solvent was decanted from the oily precipitate of the product **12**. The oil was transferred into another Schlenk flask with the help of C_6D_6 (1 mL), and the benzene phase was decanted from the oily precipitate. This oily residue was dried in vacuo, which led to the product **12**, obtained as a light yellow solid. Anal. Calcd for $C_{72}H_{52}B_2Cl_2F_{30}N_2Zr$: C, 50.90; H, 3.09; N, 1.65. Found: C, 51.11; H, 3.04; N, 2.05. Other further experiments gave slightly deviated elemental analysis results (up to 2.5% C deviation).

The NMR identification of **12** was achieved from the spectra in d_8-THF under "static" conditions at low temperature. The experiment was carried out in a glovebox using a Schlenk flask: C_6D_6 (1 mL) was added to a mixture of complex **9** (0.1 g, 0.15 mmol) and $B(C_6F_5)_3$ (2.3 equiv, 177 mg, 0.345 mmol). The flask was connected to the hydrogen bottle. The system was flushed with hydrogen and then properly closed with the tap. The hydrogen pressure in the reaction flask was raised to 2 bar, and the reaction mixture was stirred in a glovebox overnight at room temperature. The solvent was decanted from the precipitated oil of the product mixture of **11** and **12**. The oily products were transferred to another Schlenk flask with some C_6D_6 (1 mL), and the benzene phase was decanted from the oily precipitate. This oily residue was dried in vacuo, which led to a mixture of **11** and **12** (1:5), obtained as a light yellow solid (0.100 g). The sample was redissolved in d_8-THF, and the NMR experiments were measured at low temperature under static conditions ("frozen" proton transfer). Complex **12**: ^{1}H NMR (600 MHz, d_8-THF, 198 K): δ 9.65 (br, 2H, N$H_{2,+}$), 7.55 (m, 1H, *p*-Ar$_+$), 7.48 (m, 2H, *m*-Ar$_+$), 6.76 (β), 6.19 (α) (each br, each 2H, C_5H_{4+}), 4.59 (br, 2H, C$H_{2,+}$), 3.70 (br, 1H, B*H*), 2.72 (br, 2H, C*H*(*i*Pr)$_+$), 1.20, 1.13 (each br, each 6H, CH_3 (*i*Pr)$_+$). ^{13}C{^{1}H} NMR (151 MHz, d_8-THF, 198 K): δ 142.9 (*o*-Ar$_+$), 131.5 (*p*-Ar$_+$), 127.7 (*i*-Ar$_+$), 126.3 (*m*-Ar$_+$), 124.4 (α), 113.2 (β) (C_5H_{4+}), 117.5 (*i*-C_5H_{4+}), 51.0 (C$H_{2,+}$), 28.8 (C*H*(*i*Pr)$_+$), 24.6, 23.0 (CH_3(*i*Pr)$_+$) [data from the ghsqc and ghmbc NMR experiment]. Complex **11**: ^{1}H NMR (600 MHz, d_8-THF, 198 K): δ 9.65 (br, 2H, N$H_{2,+}$), 7.55 (m, 1H, *p*-Ar$_+$), 7.48 (m, 2H, *m*-Ar$_+$), 7.05 (m, 2H, *m*-Ar), 6.99 (m, 1H, *p*-Ar), 6.74 (β), 6.14 (α) (each br, each 2H, C_5H_{4+}), 6.59 (β), 6.34 (α) (each br, each 2H, C_5H_4), 4.63 (br, 2H, C$H_{2,+}$), 4.01, 3.98 (br,

3H, CH_2, N*H*), 3.20 (br, 2H, C*H*(*i*Pr)), 2.77 (br, 2H, C*H*(*i*Pr)$_+$), 1.20, 1.13 (each br, each 6H, CH_3(*i*Pr)$_+$), 1.11 (br, 12H, CH_3(*i*Pr)). Averaged spectra at 298 K: ^{1}H NMR (600 MHz, d_8-THF, 298 K): δ 9.49 (NH_{2+}), 7.50, 7.40 (Ar), 6.64, 6.22 (C_5H_4), 4.64 (CH_2), 3.75 (q (1:1:1:1), $^1J_{BH} \approx 100$ Hz, B*H*), 2.80 (C*H*(*i*Pr)), 1.21 (d, $^3J_{HH}$ = 6.4 Hz, 12H, CH_3(*i*Pr)) [all resonances are very broad]. ^{19}F NMR (564 MHz, d_8-THF, 298 K): δ −133.4 (m, *o*-C_6F_5), −166.3 (t, $^3J_{FF}$ = 20.0 Hz, *p*-C_6F_5), −168.8 (m, *m*-C_6F_5). ^{11}B{^{1}H} NMR (192 MHz, d_8-THF, 298 K): δ −25.5 ($\nu_{1/2} \approx 70$ Hz). ^{11}B NMR (192 MHz, d_8-THF, 298 K): δ −25.5 (br d, $^1J_{BH} \approx 95$ Hz).

Synthesis of *N*-(2,2-Dimethylpropylidene)-2,6-xylidine (13a). In a 50 mL round-bottom flask 2,6-xylidine (4.84 g, 0.04 mol) was mixed with pivalic aldehyde (5.16 g, 0.06 mol). A few drops of concentrated H_2SO_4 were added to the mixture. The reaction mixture was heated to 60 °C and stirred at that temperature overnight. The resulting mixture was extracted with 100 mL of pentane. The solvent was removed from the extracts under vacuum, and the residue was distilled under vacuum (bp of product = 61 °C/0.08 bar). The product was isolated as a colorless oil (5.52 g, 73%). Anal. Calcd for $C_{13}H_{19}N$: C, 82.48; H, 10.12; N, 7.40. Found: C, 82.32; H, 10.17; N, 7.48. ^{1}H NMR (600 MHz, C_6D_6, 298 K): δ 7.09 (s, 1H, =C*H*N), 7.00 (m, 2H, *m*-Ar), 6.92 (m, 1H, *p*-Ar), 2.03 (s, 6H, CH_3), 1.04 (s, 9H, *t*-Bu). ^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 298 K): δ 173.7 (=*C*HN), 151.8 (*i*-Ar), 128.3 (*m*-Ar), 126.7 (*o*-Ar), 123.4 (*p*-Ar), 37.0, 26.6 (*t*-Bu), 18.3 (*C*H_3). The data are similar to those reported in the literature.[28]

Synthesis of *N*-(2,2-Dimethylpropylidene)-2,6-bis(1-methylethyl)benzenamine (13b). In a 50 mL round-bottom flask 2,6-di-isopropylaniline (1.6 g, 0.009 mol) was mixed with pivalic aldehyde (3.89 g, 0.045 mol). A few drops of the concentrated H_2SO_4 were added to the mixture. The mixture was heated to 60 °C and stirred at that temperature for 3 h. The resulting mixture was extracted with 100 mL of pentane. Pentane was removed from the extracts under vacuum, and the residue was distilled under vacuum (bp of product = 86 °C/0.02 bar). The product was isolated as a colorless oil (1.73 g, 93%). Anal. Calcd for $C_{17}H_{27}N$: C, 83.20; H, 11.09; N, 5.71. Found: C, 82.32; H, 10.17; N, 7.48). ^{1}H NMR (600 MHz, C_6D_6, 298 K): δ 7.26 (s, 1H, =C*H*N), 7.13 (m, 2H, *m*-Ar), 7.08 (m, 1H, *p*-Ar), 3.05 (sept, $^3J_{HH}$ = 6.9 Hz, 2H, C*H*(*i*Pr)), 1.17 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH_3(*i*Pr)), 1.07 (s, 9H, *t*-Bu). ^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 298 K): δ 173.1 (=*C*HN), 149.8 (*i*-Ar), 137.4 (*o*-Ar), 124.1 (*p*-Ar), 123.2 (*m*-Ar), 37.0 (*t*-Bu), 28.0 (*C*H(*i*Pr)), 26.6 (*t*-Bu), 23.5 (*C*H_3(*i*Pr)). The data are similar to those reported in the literature.[29]

General Procedure for the Hydrogenation of Imines and a Silyl Enolether Catalyzed by 12. In a glovebox the unsaturated substrate was added to a Schlenk flask containing a solution of complex **12** in C_6D_6 (0.6 mL). The system was flushed with hydrogen, then properly closed with the tap. The pressure of hydrogen in the reaction flask was kept at 2 bar, and the reaction mixture was stirred at room temperature in the glovebox overnight. The resulting mixture was evaporated under vacuum. The residue was extracted with pentane (5 mL). The filtered pentane extracts were evaporated in vacuo. The obtained products were characterized by ^{1}H and ^{13}C NMR and exact mass MS measurements (for details see below).

Preparation of *N*-(2,2-Dimethylpropyl)-2,6-xylidine (14a); Catalytic Hydrogenation of *N*-(2,2-Dimethylpropylidene)-2,6-xylidine (13a). About 17 molar equiv of **13a** (150 mg, 0.792 mmol) was catalytically hydrogenated according to the general procedure in the presence of complex **12** (80 mg, 0.0471 mmol). The product **14a** was isolated as a colorless oil (150 mg, ∼100%). ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ 6.87 (d, $^3J_{HH}$ = 7.3 Hz, 2H, *m*-Ar), 6.70 (t, $^3J_{HH}$ = 7.3 Hz, 1H, *p*-Ar), 3.00 (br s, 1H, N*H*), 2.57 (s, 2H, CH_2), 2.17 (s, 6H, CH_3), 0.93 (s, 9H, *t*-Bu). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K): δ 146.0 (*i*-Ar), 129.8 (*o*-Ar), 128.8 (*m*-Ar), 122.1 (*p*-Ar), 60.4 (*C*H_2), 31.9, 27.5 (*t*-Bu), 18.2 (*C*H_3). MS(ESI): found *m*/*z* 192.1760, calcd for $C_{13}H_{21}NH^+$ 192.1747.

Preparation of *N*-(2,2-Dimethylpropyl)-2,6-bis(1-methylethyl)-aniline (14b); Catalytic Hydrogenation of *N*-(2,2-Dimethylpropylidene)-2,6-bis(1-methylethyl)aniline (13b). About 43 molar equiv of **13b** (124 mg, 0.507 mmol) was catalytically hydrogenated according to the general procedure in the presence of complex **12** (20 mg, 0.0118 mmol). The product **14b** was isolated as a colorless oil (124 mg, ∼100%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 7.10 (m, 2H, *m*-Ar), 7.06 (m, 1H, *p*-Ar), 3.28 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*(*i*Pr)), 2.94 (br, 1H, N*H*), 2.61 (s, 2H, CH_2), 1.26 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH_3(*i*Pr)), 1.07 (s, 9H, *t*-Bu). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 298 K): δ 143.3 (br, *i*-Ar), 142.9 (*o*-Ar), 123.9 (*p*-Ar), 123.5 (*m*-Ar), 64.1 (*C*H_2), 31.9, 27.5 (*t*-Bu), 27.4 (*C*H(*i*Pr)), 24.3 (*C*H_3(*i*Pr)). MS(ESI): found *m*/*z* 248.2371, calcd for $C_{17}H_{29}NH^+$ 248.2373; found *m*/*z* 270.2188, calcd for $C_{17}H_{29}N{\cdot}Na^+$ 270.2192.

Preparation of Trimethyl(1,2,2-trimethylpropoxy)silane (16); Catalytic Hydrogenation of 1-*tert*-Butyl-1-trimethylsiloxyethene (15). About 20 molar equiv of **15** (purchased from Aldrich) (163 mg, 0.9478 mmol) was catalytically hydrogenated according to the general procedure in the presence of complex **12** (80 mg, 0.0471 mmol). The product **16** was isolated as a colorless oil (140 mg, 85%). The product is hydroscopic, and its long exposure to air should be avoided. ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 3.36 (q, $^3J_{HH}$ = 6.3 Hz, 1H, *H*C), 1.01 (d, $^3J_{HH}$ = 6.3 Hz, 3H, CH_3), 0.88 (s, 9H, *t*-Bu), 0.11 (s, $^2J_{SiH}$ = 6.6 Hz, 9H, $SiMe_3$). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K): δ 76.2 (*C*H), 35.4, 25.9 (*t*-Bu), 18.7 (*C*H_3), 0.4 (Me_3Si). MS(EI): found *m*/*z* 173.1341 (100%), calcd for $C_9H_{21}OSi$ 173.1362; found *m*/*z* 174.1409, calcd for $C_9H_{22}OSi$ 174.1440.

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Supporting Information Available: Text and figures giving further experimental and spectroscopic details and CIF files giving crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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