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Evidence for α-Nitrogen Participation in the Internal C−H Activation Reaction at ((Dimethylamino)methyl)cyclopentadienyl-Derived Methylzirconocene Cations

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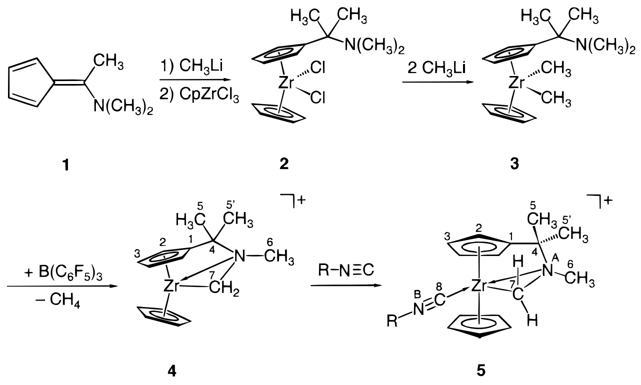
Treatment of 6-(dimethylamino)-6-methylfulvene (**1**) with methyllithium followed by the reaction of the resulting $[C_5H_4{-}CMe_2NMe_2]Li$ reagent with $CpZrCl_3$ gave the complex $[(\eta^5\text{-}C_5H_4{-}CMe_2NMe_2)CpZrCl_2]$ (**2**). Its treatment with 2 molar equiv of methyllithium furnished $[(\eta^5\text{-}C_5H_4{-}CMe_2NMe_2)CpZr(CH_3)_2]$ (**3**). Complex **3** reacted with $B(C_6F_5)_3$ by methyl group transfer. The in situ $[Zr]^+{-}CH_3$ cation system generated in this manner proved to be unstable under the reaction conditions and instantaneously eliminated methane with formation of **4**. In the course of this reaction a $N{-}CH_3$ hydrogen atom was abstracted. Complex **4** was stabilized by the addition of 1 equiv of the alkyl isocyanide $RN{\equiv}C$ ($R = CMe_3$, $n\text{-}C_4H_9$, $-CMe_2CH_2CMe_3$) to yield the respective adducts **5**. The complex $[(\eta^5{:}\eta^2(C,N)\text{-}C_5H_4{-}CMe_2N({=}CH_2)CH_3)CpZr(\kappa C\text{-}C{\equiv}N{-}CMe_3)]^+[CH_3B(C_6F_5)_3]^-$ (**5a**) was characterized by an X-ray crystal structure analysis. It exhibits an η^2-coordination of the pendant formaldiminium moiety to zirconium ($d(Zr{-}N) = 2.318(7)$ Å, $d(Zr{-}C) = 2.272(7)$ Å). The $(\eta^2\text{-}R_2NCH_2)Zr$ moiety shows a characteristic ^{15}N NMR chemical shift (δ −376 ppm), deshielded by ca. $\Delta\delta \approx -40$ ppm relative to the $^{15}NMe_2$ NMR resonance found for **3**. Complex **4** reacts with butadiene or isoprene by insertion into the $Zr{-}CH_2$ bond of the (η^2-formaldiminium)Zr moiety to form the metallacyclic (π-allyl)metallocene complexes **6a**,**b**. The X-ray crystal structure analysis of **6b** shows a close Zr−N contact at 2.491(4) Å. A corresponding ^{15}N NMR feature was found at δ −357 ppm. The complex $[(\eta^5\text{-}C_5H_4{-}CMe_2NMe_2)_2Zr(CH_3)_2]$ reacts analogously: upon treatment with $B(C_6F_5)_3$ in a 1:1 ratio, CH_3 is transferred from zirconium to boron, and 1 equiv of methane is liberated to give complex **8** (^{15}N NMR signals at δ −357 and −372 ppm). Complex **8** was also characterized by X-ray diffraction. It shows coordination of both nitrogen atoms to zirconium: i.e., the presence of a $(\eta^2\text{-}R_2NCH_2)Zr^+$ three-membered-ring system, formed by C−H activation, and a κN-coordinated intact pendant $-CMe_2{-}NMe_2$ group. The latter is displaced upon the addition of *tert*-butyl isocyanide to yield the (κ*C*-isonitrile)(η^2-formaldiminium)metallocene cation complex **9**.

Introduction

The chemistry of organometallic group 4 metal complex cations that bear pendant donor groups (e.g. $-(CR_2-)_nNR_2$, $-(CR_2-)_nPR_2$, or $-(CR_2-)_nOR$) is attracting increased interest due to their potential importance in the development of active carbon−carbon coupling catalysts.[1] We have recently described the generation of methylzirconocene cations bearing substituted ((dimethylamino)methyl)cyclopentadienyl ligands at the group 4 metal and found that such systems are not stable but instantaneously eliminate methane.[2] This involves rupture of a C−H bond at one of the *N*-methyl groups with formation of a pendant iminium moiety that coordinates to zirconium (see Scheme 1). The resulting products were characterized by ^1H and ^{13}C NMR spectroscopy (including their dynamic behavior) and by elemental analysis, but it had remained open whether the nitrogen atom was involved in the coordination of

Scheme 1



Complexes **4** and **5** with $[CH_3B(C_6F_5)_3]^-$ anion $R = -C(CH_3)_3$ (**a**), $-n\text{-}C_4H_9$ (**b**), $-C(CH_3)_2CH_2C(CH_3)_3$ (**c**)

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[†] NMR spectroscopy.

[‡] X-ray crystal structure analyses.

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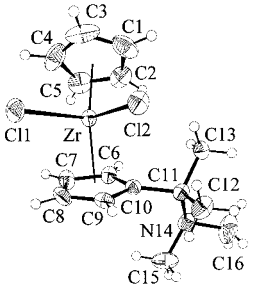

Figure 1. View of the molecular structure of **2**. Selected bond lengths (Å) and angles (deg): Zr−Cl1 = 2.4398(6), Zr−Cl2 = 2.4438(6), Zr−C_{Cp} = 2.511(3), C10−C11 = 1.526(3), C11−N14 = 1.499(3); Cl1−Zr−Cl2 = 94.97(2), C10−C11−N14 = 105.3(2).

the newly formed iminium-type functionality. We have actively pursued this question in the meantime and obtained evidence by X-ray crystal structure analyses and ^{15}N NMR spectroscopy for a variety of such systems indicating a varying degree of nitrogen-donor participation as an important structural and potentially kinetic factor in this chemistry.

Results and Discussion

For the first part of this study we have used the (η^5-C_5H_4−CMe_2NMe_2)CpZr bent-metallocene framework. The synthesis and some chemistry of its derivatives had been mentioned in a recent review by us[3] but will briefly be outlined here for clarity. The C_5H_4−CMe_2NMe_2 ligand system was prepared by a fulvene route. Methyllithium was added to 6-(dimethylamino)-6-methylfulvene (**1**) to give the 1-methyl-1-(dimethylamino)ethyl-substituted cyclopentadienide. Treatment with $CpZrCl_3$ furnished the metallocene dichloride **2**. Subsequent treatment with methyllithium gave **3**. Both metallocene complexes were characterized by X-ray diffraction studies. The structure of **3** was depicted in the review mentioned above. The molecular structure of **2** is shown in Figure 1. The bonding features around zirconium are unexceptional. It should be noted that there is clearly no interaction between the nucleophilic dimethylamino nitrogen center of the functionalized side chain and the group 4 metal center. The −CMe_2−NMe_2 substituent in **2** is oriented toward the lateral sector of the bent-metallocene unit, and the −NMe_2 group is oriented away from the bent-metallocene nucleus (dihedral angle C6−C10−C11−N14 = −56.6(3)°).

Complex **3** was then treated with $B(C_6F_5)_3$ (1 molar equiv) in dichloromethane at low temperature (−50 °C). A methyl group is transferrred from zirconium to boron, followed by an instantaneous formation of methane to give the cation complex **4**. This product was not isolated but only characterized spectroscopically. We will come to its characterization later. The complex could be stabilized by adding a suitable donor ligand. Thus, treatment of in situ generated **4** with 1 molar equiv of an alkyl isocyanide cleanly yielded the 1:1 addition products **5a**−**c** (50−60% isolated yields). Diffusion of pentane vapor into a solution of **5a** in dichloromethane gave single crystals that were suitable for an X-ray crystal structure analysis.

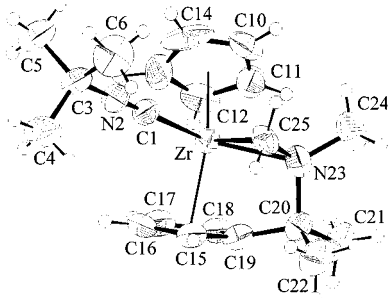

Figure 2. Molecular structure of **5a** (cation only) with (unsystematic) atom-numbering scheme. Selected bond lengths (Å) and angles (deg): Zr−C1 = 2.312(8), Zr−N23 = 2.318(7), Zr−C25 = 2.272(7), C1−N2 = 1.157(10), N2−C3 = 1.435(9), N23−C24 = 1.453(10), N23−C25 = 1.438(11), N23−C20 = 1.554(10), C20−C19 = 1.498(11); C1−Zr−N23 = 114.8(3), C1−Zr−C25 = 78.3(3), Zr−C1−N2 = 178.8(6), C1−N2−C3 = 179.1(8), Zr−N23−C25 = 70.0(4), Zr−C25−N23 = 73.5(4), N23−Zr−C25 = 36.5(3), Zr−N23−C24 = 130.0(6), Zr−N23−C20 = 99.9(4), C20−N23−C24 = 117.8(7), C19−C20−N23 = 101.3(5).

In the crystal, the cation and anion of **5a** are clearly separated (Figure 2). The cation shows a bent-metallocene unit (Cp(centroid)−Zr−Cp(centroid) angle 135.8°) that has three close contacts in the σ-ligand plane. The methane elimination reaction has removed a hydrogen atom from one of the former methyl groups at nitrogen. This has resulted in a new zirconium−carbon bond, but at the same time a bonding contact between zirconium and the adjacent nitrogen atom has been established. The structure of **5a** shows the presence of a three-membered ring containing Zr, C, and N atoms. The formaldiminium unit formed by the methane extrusion has become bonded to zirconium, in an η^2 manner similar to that for an olefin.[4] The bond lengths within the three-membered metallacycle are Zr−C25 = 2.272(7) Å, Zr−N23 = 2.318(7) Å, and C25−N23 = 1.438(11) Å, which are in the ranges of the respective σ-bonds.[5,6] The angles inside the three-membered ring are 36.5-

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(3)° (C25−Zr−N23), 73.5(4)° (Zr−C25−N23), and 70.0(4)° (Zr−N23−C25). The remaining angles at N23 are found at 130.0(6)° (Zr−N23−C24), 114.5(7)° (C25−N23−C24), 117.8(7)° (C20−N23−C24), and 116.2(6)° (C20−N23−C25), indicating the ammonium character of the four-coordinate nitrogen center. The respective N23−C24 (1.453(10) Å) and N23−C20 (1.554(10) Å) bond lengths are in the expected range.[7] The bonding of the nitrogen to zirconium has led to some distortion of the C15−C19 Cp ring with a slight bending of the C19−C20 vector toward Zr (Zr−C19 = 2.395(7) Å, Zr−C16 = 2.538(7) Å). The C19−C20−N23 angle is compressed (101.3(5)°). The η^2-formaldiminium nitrogen atom (N23) occupies a lateral coordination site in the central σ-ligand plane at the bent-metallocene wedge[8] in complex **5a**, and the H_2C25 group is located in the corresponding central position. The *tert*-butyl isocyanide ligand is attached to zirconium using the remaining lateral position opposite to N23, cis to C25 (angle C1−Zr−N23 114.8(3)°). The Zr−C1 bond length is 2.312(8) Å; the adjacent C1−N2 bond length is 1.157(10) Å. The κC-isonitrile ligand framework is linear (Zr−C1−N2 = 178.8(6)°, C1−N2−C3 = 179.1(8)°). Together with the observed IR $\tilde{\nu}(C{\equiv}NR)$ band at 2201 cm^{-1}, this indicates the absence of any significant metal to isonitrile ligand back-bonding[9] at this d^0-metallocene cation complex.[10] The (isonitrile)Zr^+ bonding features in **5a** are similar to those observed previously for a variety of other early-transition-metal isonitrile complexes,[10,11] where electrostatic bonding contributions sometimes seem to prevail.[12]

In solution, the complexes **5** adopt analogous structures. The κC-isonitrile ligand is still present. For **5a** this is evident from the δ(*C*N) ^{13}C NMR feature at 148.5 ppm and a characteristic ^{15}N NMR isonitrile resonance at δ −161.0 ppm (relative to external nitromethane, δ 0; free $Me_3C{-}N{\equiv}C$ values δ −186.5 (^{15}N), δ 153.5 (^{13}C), both in dichloromethane-d_2). **5** is also chiral in solution. For **5a** this leads to the observation of four ^1H NMR methine resonances of the monosubstituted Cp−R moiety (at δ 6.07, 5.88, 5.83, and 5.49 in dichloromethane-d_2). The adjacent $C(CH_3)_2$ group exhibits diastereotopic methyl substituents (^1H, δ 1.63, 1.20 ppm; ^{13}C, δ 25.4 ($^1J_{CH}$ = 129 Hz), 17.7 ($^1J_{CH}$ = 128 Hz)). There is a single CH_3 group bonded to the nitrogen atom (^{13}C, δ 44.2 ppm, with a typical slightly enhanced $^1J_{CH}$ coupling constant of 138 Hz). Most interesting are the NMR spectroscopic features of the η^2-$CH_2{-}NR_2$ group. Due to the persistent chiral molecular structure, the methylene hydrogens at the CH_2−[N] unit are diastereotopic (^1H NMR, δ 2.00, 1.39 ppm, $^2J_{HH}$ = 8.8 Hz). The corresponding ^{13}C NMR signal is observed at δ 43.5 ppm. The CH coupling constant amounts to $^1J_{CH}$ = 153 Hz. This is significantly higher than that for the adjacent $N{-}CH_3$ methyl group signal (see above). We assume that this increase (of ca. 15 Hz relative to the intramolecular [N]−CH_3 reference) is due to the heterocyclopropane character and, thus, may serve as a diagnostic feature for the (η^2-$CH_2{-}NR_2$)-Zr bonding.[13]

In addition, we have observed the ^{15}N NMR resonance of the (η^2-$CH_2{-}NR_2$)Zr moiety in the cation complex **5a** at δ −375.9 ppm. This may be compared with the respective value of the three-coordinate nitrogen center in the neutral starting material **3** (^{15}N NMR, δ −338.7).[14] We assume that the pronounced shifting of the ^{15}N NMR resonance to more negative δ values on going from **3** to **5** (**5a**, $\Delta\delta$ = −37 ppm; **5c**, −38 ppm) may also serve as a diagnostic tool to recognize such a (η^2-$CH_2{-}NR_2$)Zr coordinative situation. We tried to use these spectroscopic indications derived from the complexes **5** to evaluate the NMR features of the reactive intermediate **4**. The cation of **4** shows diastereotopic CH_2−[N] hydrogen atom signals at δ 2.23 and 1.67 ($^2J_{HH}$ = 8.8 Hz). The corresponding ^{13}C NMR resonance is observed at δ 46.5 with $^1J_{CH}$ = 152 Hz. This is increased by ΔJ = +13 Hz relative to the $^1J_{CH}$ = 139 Hz reference of the adjacent $N{-}CH_3$ ^{13}C NMR feature. The ^{15}N NMR signal of **4** is monitored at δ −358.8 ($\Delta\delta$ = −20 ppm relative to the reference of **3**). From these data we assume that complex **4** also contains an intramolecularly coordinated (η^2-$CH_2{-}NR_2$)Zr structural subunit, although the Zr−N interaction is probably weaker than in the complexes **5**. Whether ion pairing with the $[CH_3B(C_6F_5)_3]^-$ anion[15] is also important for stabilizing the system **4** is hard to ascertain from these data.

It is surprising that the isonitrile ligands in **5** just simply coordinate to the electrophilic zirconium center but do not insert into the adjacent metal−carbon σ-bond,[16] although analogous insertion reactions have

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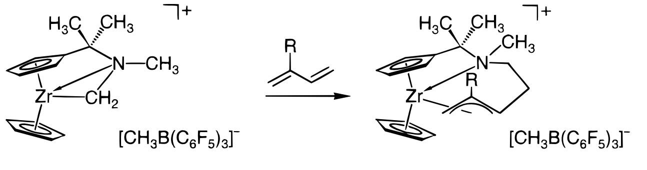
frequently been observed to occur readily, e.g. at (η^2-aldehyde)zirconocene complexes.[17] We assume that steric factors may hinder a facile RN≡C insertion reaction under the applied reaction conditions in the case of **5**, potentially because considerable strain would be built up in the resulting product formation. We have, therefore, treated the in situ generated system **4** with conjugated dienes which could give rise to the formation of much less strained insertion products.[18] This is in fact observed.

The reactive system **4** was generated at −50 °C and then treated with 1,3-butadiene. Warming of the mixture to room temperature leads to the precipitation of the 1:1 addition product **6a** (Scheme 2). The NMR spectra indicate that carbon−carbon coupling of the butadiene has occurred with the CH$_2$−[N] carbon atom. This has resulted in the formation of a metallacyclic (π-allyl)zirconium complex. A single stereoisomer is observed in solution. This is characterized by the typical NMR features of the substituted Cp ligand (^{1}H, δ 6.59, 6.12, 5.89, 5.74 in dichloromethane-d_2), a diastereotopic pair of methyl groups at C4 (i.e. Cp−C*Me*$_2$−: ^{13}C, δ 26.0 ($^1J_{CH}$ = 128 Hz), 22.8 ($^1J_{CH}$ = 129 Hz)), and ^{13}C NMR signals of the π-allyl moiety at δ 47.7 ($^1J_{CH}$ = 154 Hz, C^{11}H$_2$), 130.5 (C^{10}H), and 105.4 ($^1J_{CH}$ = 156 Hz, C^{9}H). The hydrogen atoms at the C^{7}H$_2$−[N] group are again diastereotopic (^{1}H, δ 3.30 and 2.68 ppm). The corresponding ^{13}C NMR resonance is observed at δ 66.6 with $^1J_{CH}$ = 140 Hz. The $^1J_{CH}$ coupling constant in this case is identical with that of the internal [N]−C^{6}H$_3$ reference (^{13}C, δ 41.4, $^1J_{CH}$ = 140 Hz). Complex **6a** features a ^{15}N NMR resonance at δ −358.6 ppm, which indicates a nitrogen to zirconium interaction.

Scheme 2



4 **6**

R = H (**a**), CH$_3$ (**b**)

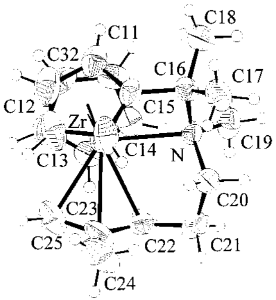


Figure 3. Molecular structure of **6b** (cation only, with unsystematic atom-numbering scheme). Selected bond lengths (Å) and angles (deg): Zr−N = 2.491(4), Zr−C22 = 2.484(6), Zr−C23 = 2.562(7), Zr−C25 = 2.424(7), C15−C16 = 1.515(8), C16−N = 1.549(7), N−C20 = 1.496(7), C20−C21 = 1.522(9), C21−C22 = 1.493(9), C22−C23 = 1.383(10), C23−C24 = 1.509(10), C23−C25 = 1.405(10); N−Zr−C25 = 124.5(2), N−Zr−C23 = 92.0(2), N−Zr−C22 = 69.7(2), C22−Zr−C23 = 31.8(2), C22−Zr−C25 = 58.2(3), C23−Zr−C25 = 32.6(2), Zr−N−C20 = 108.2(3), Zr−C25−C23 = 79.1(4), Zr−C23−C25 = 68.3(4), Zr−C23−C22 = 71.0(4), C25−C23−C22 = 117.9(6), C23−C22−C21 = 127.2(7), C22−C21−C20 = 111.2(5), C21−C20−N = 110.8(5). Additional values are given in the text.

Treatment of **4** with isoprene proceeds analogously and results in the formation of the CC-coupling product **6b**. Again, a single regio- and stereoisomer was observed in solution. The characteristic spectroscopic data are very similar to those for **6a** (^{15}N NMR, δ −357.0 ppm).

Single crystals suitable for the X-ray crystal structure analysis were obtained from complex **6b**. This analysis has established the proposed structural properties from the spectroscopic studies. Complex **6b** shows the expected metallacyclic (π-allyl)metallocene-type structure in the solid state (Figure 3).[18] The allyl-containing hydrocarbon chain is attached to a Cp ring by means of the CMe$_2$−N(Me)−CH$_2$− unit that was derived from the −CMe$_2$−NMe$_2$ substituent by C−H activation. The isoprene reagent has reacted with **4** by carbon−carbon coupling with the [N]-CH$_2$− group. This has taken place regioselectively:[19] the isoprene vinyl group was coupled with the CH$_2$−[N] carbon, with the isoprene methyl group becoming placed at the central carbon atom (C23) of the resulting zirconium-bound π-allyl moiety.

The π-allyl group in **6b** is rather symmetrically bonded to zirconium (Zr−C25 = 2.424(7) Å, Zr−C23 = 2.562(7) Å, Zr−C22 = 2.484(6) Å), which is not often observed for (π-allyl)zirconium complexes.[18−20] The C23-bonded, isoprene-derived methyl group is oriented toward the sector of the substituted Cp ring of the bent metallocene unit in **6b**. The π-allyl ligand in **6b** is syn-

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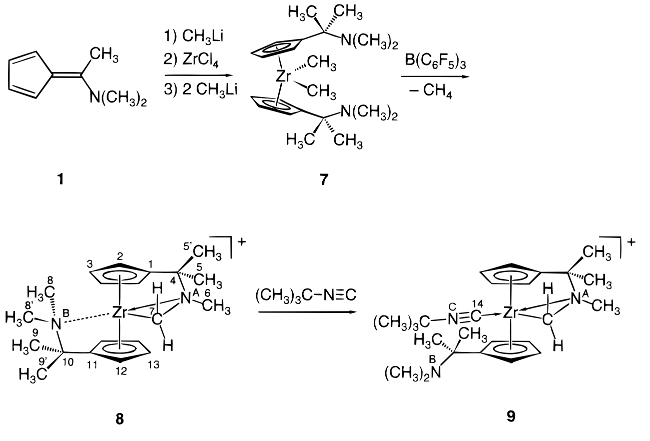
configurated. The newly formed carbon−carbon bond C20−C21 is in the typical single-bond range (1.522(9) Å). The overall framework seems to be rather unstrained. This becomes evident upon inspection of the Zr−C(Cp) distances of the monosubstituted Cp−R ligand, which are in close range with one minor deviation (Zr−C13 = 2.544(7), Zr−C12 = 2.497(8), Zr−C11 = 2.471(7), Zr−C15 = 2.431(7), Zr−C14 = 2.496(6) Å). Complex **6b** also features a close contact between zirconium and the nitrogen atom in the Cp side chain, although the Zr−N distance in **6b** (2.491(4) Å) is markedly larger than the corresponding interaction observed in complex **5a** (2.312(8) Å, see above). The sum of angles around nitrogen in **6b** is 656.7°, which is close to the limiting value of an ideal tetrahedron, but some of the individual bond angles deviate greatly from the 109° angle (C16−N−C19 = 114.3(5)°, C19−N−C20 = 106.1(5)°, C16−N−C20 = 111.8(4)°, Zr−N−C19 = 118.6(3)°, Zr−N−C20 = 108.2(3)°, and Zr−N−C16 = 97.7(3)°).

Then we turned again to the (η^5-C_5H_4−CMe_2NMe_2)$_2$-Zr-derived systems that we had investigated earlier.[2] The (η^2-C_5H_4−CMe_2NMe_2)$_2$Zr(CH_3)$_2$ starting material **7** was prepared analogously to the reaction sequence depicted in Scheme 1 by treatment of the fulvene **1** with methyllithium followed by the reaction of the resulting [C_5H_4−CMe_2NMe_2]Li reagent with $ZrCl_4$ in a 2:1 ratio. Finally, metathetical σ-ligand exchange by treatment with methyllithium yielded **7**. Again, B(C_6F_5)$_3$ was used for abstracting a methyl anion from **7**, and the resulting Zr−CH_3-containing cation was not stable but instantaneously eliminated methane to give **8**. In this present study, complex **8** was also characterized by ^{15}N NMR spectroscopy and by X-ray diffraction. It shows two prominent ^{15}N NMR resonances at δ −357.6 and −373.7 ppm (in dichloromethane-d_2). Both features indicate the presence of tetracoordinate pseudotetrahedral nitrogen centers. We attribute the former resonance to the [C]−NMe_2−[Zr] nitrogen (N^B; see Scheme 3) and suggest that the latter corresponds to N^A and is part of a metallacyclic three-membered ring. The C^7H_2 group adjacent to N^A shows a ^1H NMR AB-type pattern (δ 2.27 and 1.57 (at 263 K in dichloromethane-d_2), $^2J_{HH}$ = 9.8 Hz) and a ^{13}C NMR resonance at δ 49.1 ppm with a characteristically enhanced $^1J_{CH}$ coupling constant of 147 Hz (N−C^6H_3 reference: δ 43.5, $^1J_{CH}$ = 139 Hz).

Scheme 3



Complexes **8** and **9** with [$CH_3B(C_6F_5)_3$]$^-$ anion

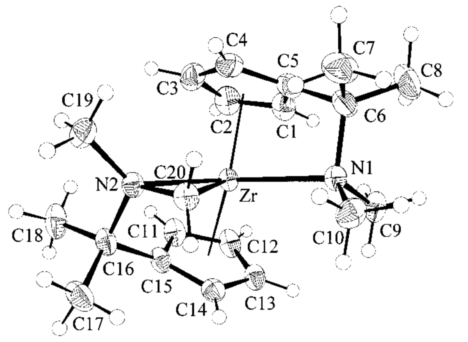


Figure 4. Molecular structure of **8** (cation only, with unsystematic atom-numbering scheme). Selected bond lengths (Å) and angle (deg): Zr−N1 = 2.4692(12), Zr−N2 = 2.2930(12), Zr−C20 = 2.2510(14), N1−C6 = 1.552(2), C6−C5 = 1.515(2), C20−N2 = 1.4640(18), N2−C16 = 1.514(2), C16−C15 = 1.516(2); N1−Zr−N2 = 123.61(4), N1−Zr−C20 = 86.43(5), N2−Zr−C20 = 37.58(5), Zr−N1−C6 = 97.36(8), N1−C6−C5 = 101.57(12), Zr−N2−C20 = 69.66(7), Zr−N2−C16 = 102.10(8), Zr−C20−N2 = 72.77(7), C20−N2−C16 = 116.78(12), N2−C16−C15 = 101.14(11).

This structural description is supported by the result of the X-ray crystal structure analysis of **8**. It shows the presence of the two monosubstituted η^5-cyclopentadienyl ligands. There are five close contacts in the σ-ligand plane at the front side of the bent-metallocene moiety. Most importantly, the [N]−CH_2− group is again η^2-coordinated to zirconium with its methylene carbon atom (C20) occupying the central coordination site (Zr−C20 = 2.2510(14) Å). The η^2-iminium nitrogen atom is bonded closely to the metal center (Zr−N2 = 2.2930(12) Å). The remaining C20−N2 bond inside the three-membered ring has a length of 1.4640(18) Å. The angles inside the Zr,N2,C20 three-membered ring are 37.58(5)° (C20−Zr−N2), 69.66(7)° (Zr−N2−C20), and 72.77(7)° (Zr−C20−N2). The tight Cp−$C^{16}Me_2$−N^2($C^{19}H_3$)−$C^{20}H_2$ chelate ligand leads to marked distortions of the ligand arrangement at the bent-metallocene nucleus. The C15−C16 vector at the C11−C15 Cp ring is tilted toward zirconium (Zr−C15 = 2.4135(15) Å vs Zr−C12 = 2.5497(16) and Zr−C13 = 2.5693(16) Å). The Zr−N2−C16 angle is 102.10(8)°, C20−N2−C16 is 116.78(12)°, and Zr−N2−C19 is 132.66(10)°. The nitrogen atom N1 of the Cp-CMe_2−NMe_2 ligand also coordinates to zirconium, although the Zr−N1 bond is markedly longer at 2.4692(12) Å. The −NMe_2 ligand occupies the other lateral coordination site[8,21] at the bent metallocene wedge, trans to N2. It can be seen from the projection of the molecular structure of complex **8**, as it is depicted in Figure 4, that the N1,Zr,C20,N2 plane is markedly tilted (by ca. 17°) from the ideal Cp−M−Cp bisecting major bent metallocene σ-ligand plane to avoid the building up of considerable strain energy inside the overall ligand system.[22]

Treatment of **8** with *tert*-butyl isocyanide resulted in the displacement of the −NMe_2 donor ligand from the coordination sphere of the zirconium atom to yield the isonitrile adduct **9**. This was evident from the observation of only a single ^1H (δ 1.90 ppm) and ^{13}C NMR

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(21) Erker, G.; Rosenfeldt, F. *J. Organomet. Chem.* **1980**, *188*, C1. Review: Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103.

(22) For an analogous structural situation see e.g.: Bosch, B. E.; Erker, G.; Fröhlich, R.; Meyer, O. *Organometallics* **1997**, *16*, 5449.

resonance (δ 39.2 ppm, $^1J_{CH} = 133$ Hz) for the pendant dimethylamino moiety. The corresponding ^{15}N NMR signal of **9** is observed at δ −338.5 ppm (N^B, in dichloromethane-d_2 at 223 K). This corresponds to a "downfield" shift of $\Delta\delta = +19$ ppm relative to N^B in the precursor complex **8** (δ −357.6; for comparison, see ^{15}N NMR of **7** at δ −338.4 ppm). In addition, we must assume a η^2-$C^7H_2-N^AR_2$ coordination to zirconium in complex **9**. This is evident from the typical ^{15}N NMR resonance of N^A at δ −375.1 ppm and is supported by the observed C^7H_2 ^{13}C NMR feature at δ 44.1 ppm ($^1J_{CH}$ = 155 Hz) (internal reference $[N^A]-C^6H_3$: δ 43.1 ppm, $^1J_{CH} = 138$ Hz).

The κC-isonitrile ligand ^{15}N NMR resonance in **9** is observed at δ −161.3 ppm; the corresponding $RN\equiv C$ ^{13}C NMR resonance is at δ 150.0. Complex **9** shows an IR $\tilde{\nu}(C\equiv NR)$ band at 2193 cm^{-1} (in KBr), which is ca. $\Delta\tilde{\nu} \approx 50$ cm^{-1} above the free alkyl isocyanide value.

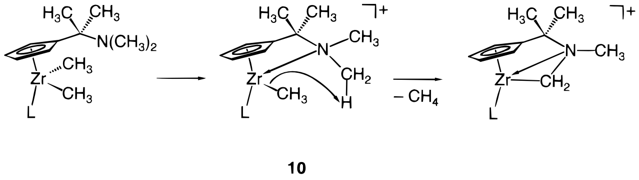
Conclusions

Nitrogen to metal coordination seems to play an important role in the thermal decomposition chemistry of the alkylmetallocene cation systems derived by methylanion abstraction from **3** or **7** and related systems. The obtained products (i.e. **5** or **8**/**9**) greatly benefit from the electronic stabilization that comes along with the formation of a new Zr−N bond in these products. C−H activation at the $N-CH_3$ group of these starting materials has led to the formation of a formaldiminium moiety ($R_2N^+{=}CH_2$) that has become intramolecularly η^2-coordinated to the electron-deficient zirconium center in these products. The overall bonding of the (η^2-$R_2N{=}CH_2$)Zr^+ subunit seems to be similar to that observed previously in a few examples of pendant (η^2-alkene)-zirconocene cations[4] or in the (η^2-aldehyde)- or (η^2-ketone)$ZrCp_2$ type complexes.[6]

Of course, the η^2-coordination of the pendant $R_2N^+{=}CH_2$ unit is easily detected and characterized by X-ray diffraction, but it seems that ^{13}C and especially ^{15}N NMR spectroscopy may serve as suitable methods to identify such a bonding situation. From the result of the X-ray crystal structure analyses of **5** and **8** it may be deduced that the (η^2-$R_2N^+{=}CH_2$)Zr moiety exhibits a pronounced metallaaziridine character, which is probably due to a substantial back-bonding contribution to the overall bonding situation.[23] We notice that this "heterocyclopropane character" seems to show up in the ^{13}C NMR features of the $-CH_2$ group in the expected way, namely by a small but significant increase of the corresponding $^1J_{CH}$ coupling constant (by ca. 10−15 Hz, relative to an acyclic reference). The changes in the ^{15}N NMR spectra are equally pronounced. Upon ring formation, we observe an "upfield" shift of $\Delta\delta$ between ca. −20 to −40 ppm of the ($R_2N{=}CH_2$)Zr nitrogen atom relative to a suitable acyclic trigonal $-CR_2NR_2$ reference. Unfortunately, the magnitude of $\Delta\delta(^{15}N)$ does not seem to correlate directly with the observed Zr−N bond length. Thus, ^{15}N NMR chemical shifts of δ ∼−338 ppm seem to be typical for the $-CMe_2$-NMe_2 reference in complexes **3** and **7**. The ^{15}N NMR chemical shift goes up to δ ∼−375 ppm in complex **5**, which exhibits a strong Zr−N interaction (d(Zr−N) = 2.318(7) Å). A similar structural situation is found in **8** with a short Zr−N bond (2.2930(12) Å) of the (η^2-$R_2N^+{=}CH_2$)Zr unit. However, this corresponds to a ^{15}N NMR signal at δ −357 ppm, and the slightly longer metal−nitrogen bond of the Zr−N(Me_2)R linkage (2.4692(12) Å) coincides with a ^{15}N NMR chemical shift of δ −372 ppm. The observed ^{15}N NMR shift of the isoprene insertion product **6b** (d(Zr−N) = 2.491(4) Å) is again observed at δ −357 ppm.

Amine coordination probably also plays an important role in the formation of the (η^2-$R_2N^+{=}CH_2$)Zr coordination products. In view of the very favorable N−Zr coordination pattern observed, we assume that at the stage of the likely intermediates (e.g. **10;** Scheme 4) in the formation of these complexes amine bonding to zirconium induces a substantial ammonium character and thus leads to the marked increase in N−C*H* acidity that seems to dominate this chemistry to a great extent. The resulting (η^2-formaldiminium)zirconocene complexes show a selective insertion behavior toward added unsaturated substrates. We are probing if this can be developed into a synthetic tool in organometallic chemistry and catalysis.

Scheme 4



Experimental Section

The reactions were carried out under an inert atmosphere (argon) using Schlenk type glassware or in a glovebox. ^{15}N NMR spectra (60.7 MHz) were recorded on a Varian Unity Plus 600 NMR spectrometer by using a GHMBC pulse sequence ($^nJ(^{15}N,^1H) = 5$ Hz, $n = 3, 4$). The ^{15}N chemical shift is given with respect to a 2% benzamide-^{15}N−0.2% $Cr(acac)_3$ sample in DMSO ($\delta(^{15}N)$ −279.3 ppm, relative to neat CH_3NO_2, $\delta(^{15}N)$ 0; $\Xi(^{15}N) = 10.1367$ MHz). ESI-MS was carried out on a Micromass Quattro LC-Z mass spectrometer. For additional general information see ref 2. 6-(Dimethylamino)-6-methylfulvene (**1**) was prepared according to the procedure of Hafner et al.[24] Complexes **2** and **3** (including their structures) were briefly mentioned by us previously in a review.[3] Some of the data for these compounds are listed below for comparison. The preparation of **8** was described by us previously.[2] Additional structural and spectroscopic data for **8** are given below. Complex **7**,[2] $B(C_6F_5)_3$,[25] and $CpZrCl_3$[26] were prepared as described by us in the literature. For a compilation of the NMR experiments used for characterization, see ref 27. Atom

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(23) Dewar, M. J. S.; Dougherty, R. C. *The PMO Theory of Organic Chemistry*; Plenum Press: New York, 1975; p 300. Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* **1979**, *101*, 783 and references therein. Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3800.

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(25) Massey, A. G.; Park, A. J.; Stone, F. G. A. *Proc. Chem. Soc.* **1963**, 212. Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1964**, *2*, 245. Massey, A. G.; Park, A. J. In *Organometallic Syntheses*; King, R. B., Eisch, J. J., Eds.; Elsevier: Amsterdam, 1986; Vol. 3, p 461.

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(27) Braun, S.; Kalinowski, H.; Berger, S. *100 and More Basic NMR Experiments*; VCH: Weinheim, Germany, 1996, and references therein.

numbering is as given in the schemes. For RN≡C reference NMR values see ref 28.

Preparation of [η^5-(1-(Dimethylamino)-1-methylethyl)cyclopentadienyl](η^5-cyclopentadienyl)zirconium Dichloride (2). A solution of 1.70 g (10.8 mmol) of ((1-(dimethylamino)-1-methylethyl)cyclopentadienyl)lithium (generated by treatment of **1** with methyllithium) in 50 mL of a 1:1 mixture of tetrahydrofuran and ether was added dropwise at −20 °C to a suspension of 2.84 g (10.8 mmol) of $CpZrCl_3$ in 100 mL of ether. The mixture was warmed to room temperature and was then stirred for another 1 h. The LiCl precipitate was removed by filtration through Celite. The orange filtrate was brought to dryness in vacuo. The residue was stirred overnight with pentane (50 mL), and the resulting beige product was collected by filtration to yield 3.11 g (76%) of **2**, mp 119 °C dec. Complex **2** always contained a small amount (ca. 5−10%) of an as yet unidentified byproduct. Anal. Calcd for $C_{15}H_{21}NCl_2Zr$ (377.5): C, 47.73; H, 5.61; N, 3.71. Found: C, 46.13; H, 5.19; N, 3.10. ^{1}H NMR (dichloromethane-d_2, 599.99 MHz): δ 6.50, 6.39 (m, each 2H, Cp′ H), 6.48 (s, 5H, Cp H), 1.98 (s, 6H, 6-H), 1.50 (s, 6H, 5-H). ^{13}C NMR (dichloromethane-d_2, 50.32 MHz): δ 137.3 (C1), 117.5, 113.0 (C_5H_4−), 116.5 (C−Cp), 57.8 (C4), 39.1 (C6), 24.4 (C5). ^{15}N,^{1}H-GHMBC NMR (dichloromethane-d_2, 60.72/599.99 MHz): δ −337.8/1.53 (N/5-H).

X-ray Crystal Structure Analysis of 2. Crystal data and refinement details: formula $C_{15}H_{21}NCl_2Zr$, $M_r = 377.45$, 0.80 × 0.50 × 0.20 mm, $a = 12.827(1)$ Å, $b = 9.452(1)$ Å, $c = 13.594(1)$ Å, $\beta = 103.56(1)°$, $V = 1602.2(2)$ Å^3, $\rho_{calcd} = 1.565$ g cm^{-3}, $\mu = 10.06$ cm^{-1}, empirical absorption correction via ψ scan data ($0.846 \leq C \leq 0.999$), $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 0.710\ 73$ Å, $T = 223$ K, $\omega/2\theta$ scans, 3384 reflections collected ($+h$, $-k$, $\pm l$), $(\sin\theta)/\lambda = 0.62$ Å^{-1}, 3238 independent and 2835 observed reflections [$I \geq 2\sigma(I)$], 176 refined parameters, R1 = 0.028, wR2 = 0.077, maximum residual electron density 0.40 (−0.92) e Å^{-3}, hydrogens calculated and riding. These data have been deposited with the Cambridge Structural Data Base under the deposition number CSD 101801.

Preparation of [η^5-(1-(Dimethylamino)-1-methylethyl)cyclopentadienyl](η^5-cyclopentadienyl)dimethylzirconium (3). An 8.3 mL (15.9 mmol) amount of a 1.93 M ethereal methyllithium solution was added dropwise at −40 °C to a suspension of **2** (3.00 g, 7.95 mmol) in 50 mL of ether. The mixture was warmed to −20 °C over 2 h with stirring and then brought to room temperature and stirred for an additional 30 min. A precipitate (LiCl) was removed by filtration through Celite. Solvent was then removed from the clear filtrate in vacuo, pentane (20 mL) added, and the product collected by filtration. After this product was washed with pentane (5 mL) and dried in vacuo, 1.78 g (67%) of **3** was obtained; mp 114 °C (dec at 175 °C). Anal. Calcd for $C_{17}H_{27}NZr$ (336.6): C, 60.66; H, 8.08; N, 4.16. Found: C, 60.03; H, 7.98; N, 3.89. ^{1}H NMR (benzene-d_6, 200.13 MHz): δ 5.79 (s, 5H, Cp H), 5.76 (m, 4H, C_5H_4), 1.98 (s, 6H, 6-H), 1.19 (s, 6H, 5-H), −0.06 (s, 6H, 7-H). ^{1}H NMR (dichloromethane-d_2, 200.13 MHz): δ 6.10 (s, 5H, Cp H), 6.08, 6.04 (m, each 2H, C_5H_4), 2.02 (s, 6H, 6-H), 1.28 (s, 6H, 5-H), −0.36 (s, 6H, 7-H). ^{13}C NMR (benzene-d_6, 50.32 MHz): δ 132.3 (C1), 110.8 (C−Cp), 109.7, 109.2 (each C_5H_4), 56.6 (C4), 39.2 (C6), 31.3 (C7), 25.1 (C5). ^{15}N,^{1}H-GHMBC NMR (dichloromethane-d_2, 60.72/599.99 MHz): δ −338.7/2.02 (N/6-H), −338.7/1.28 (N/5-H).

X-ray Crystal Structure Analysis of 3. Crystal data and refinement details: formula $C_{17}H_{27}NZr$, $M_r = 336.62$, 0.30 × 0.20 × 0.10 mm, $a = 12.891(4)$ Å, $b = 9.427(5)$ Å, $c = 13.985(4)$ Å, $\beta = 103.32(2)°$, $V = 1653.8(11)$ Å^3, $\rho_{calcd} = 1.352$ g cm^{-3}, $\mu = 6.54$ cm^{-1}, empirical absorption correction via ψ scan data ($0.969 \leq C \leq 0.999$), $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 0.710\ 73$ Å, $T = 223$ K, $\omega/2\theta$ scans, 3490 reflections collected ($\pm h$, $+k$, $-l$), $(\sin\theta)/\lambda = 0.62$ Å^{-1}, 3345 independent and 1664 observed reflections [$I \geq 2\sigma(I)$], 178 refined parameters, R1 = 0.055, wR2 = 0.076, maximum residual electron density 0.74 (−0.82) e Å^{-3}, hydrogens calculated and riding. These data have been deposited with the Cambridge Structural Data Base under the deposition number CSD 101802.

Treatment of 3 with $B(C_6F_5)_3$. Generation of 4. In an NMR-controlled experiment a sample of 11 mg (29.1 μmol) of **3** was dissolved in 0.5 mL of dichloromethane-d_2 and this mixture added at −78 °C to 15 mg (29.1 mmol) of solid $B(C_6F_5)_3$. The resulting solution was slowly raised in temperature and monitored by NMR. At −50 °C the clean formation of **4** was thus observed, which was complete after ca. 1 h at that temperature. ^{1}H NMR (dichloromethane-d_2, 599.99 MHz, 223 K): δ 6.69, 5.52 (m, each 1H, C_5H_4), 6.17 (s, 5H, Cp H), 5.93 (m, 2H, C_5H_4), 2.55 (s, 3H, 6-H), 2.23, 1.67 (d, each 1H, $^2J_{HH} = 8.8$ Hz, 7-H, 7-H′), 1.52, 1.29 (s, each 3H, 5-H, 5′-H), 0.39 (br s, 3H, $(C_6F_5)_3B{-}CH_3$). ^{13}C NMR (dichloromethane-d_2, 150.84 MHz, 223 K): δ 114.9 (C1), 113.2 ($^1J_{CH} = 175$ Hz), 110.9 ($^1J_{CH} = 174$ Hz), 108.1 ($^1J_{CH} = 169$ Hz), 97.7 ($^1J_{CH} = 173$ Hz) (C_5H_4), 110.0 ($^1J_{CH} = 174$ Hz, C−Cp), 59.0 (C4), 46.5 ($^1J_{CH} = 152$ Hz, C7), 44.3 ($^1J_{CH} = 139$ Hz, C6), 24.6 ($^1J_{CH} = 127$ Hz), 17.7 ($^1J_{CH} = 127$ Hz) (C5, C5′), 9.5 ($B(C_6F_5)_3{-}CH_3$), 147.7 (d, $^1J_{CF} = 239$ Hz, *o*-$B(C_6F_5)_3$), 137.0 (d, $^1J_{CF} = 252$ Hz, *p*-$B(C_6F_5)_3$), 136.0 (d, $^1J_{CF} = 244$ Hz, *m*-$B(C_6F_5)_3$), 127.8 (br, *ipso*-$B(C_6F_5)_3$). ^{15}N,^{1}H-GHMBC NMR (dichloromethane-d_2, 60.72/599.99 MHz, 223 K): δ −358.8/1.52, −358/1.29 (N/5-H, N/5′-H).

Reaction of 4 with *tert*-Butyl Isocyanide: Preparation of 5a. A sample of **3** (100 mg, 0.30 mmol) was dissolved in 3 mL of dichloromethane. The solution was cooled to −36 °C and then added to 152 mg (0.30 mmol) of solid $B(C_6F_5)_3$. After 30 min 23 mg (0.30 mmol) of *tert*-butyl isocyanide was added, and then the reaction mixture was warmed to room temperature with stirring. The product was precipitated as a dark brown oil by the dropwise addition of pentane (9 mL). The supernatant organic phase was carefully decanted. The remaining oil was washed with pentane (3 × 3 mL). Then 9 mL of pentane was added and the product stirred overnight to give a solid, which was collected to yield 164 mg of **5a** (60%). Single crystals of **5a** suitable for the X-ray crystal structure analysis (see below) were obtained by allowing pentane vapor to diffuse into a solution of **5a** in dichloromethane at −36 °C; mp 115 °C. Anal. Calcd for $C_{39}H_{32}N_2BF_{15}Zr$ (915.7): C, 51.16; H, 3.52; N, 3.06. Found: C, 50.96; H, 3.61; N, 3.15. ^{1}H NMR (dichloromethane-d_2, 599.99 MHz): δ 6.07, 5.88, 5.83, 5.49 (m, each 1H, C_5H_4), 5.96 (s, 5H, Cp H), 2.49 (s, 3H, 6-H), 2.00 (d, $^2J_{HH} = 8.8$ Hz, 1H, 7-H), 1.63, 1.20 (s, each 3H, 5-H, 5′-H), 1.57 (s, 9H, 10-H), 1.39 (d, $^2J_{HH} = 8.8$ Hz, 1H, 7-H′), 0.49 (br s, 3H, $B(C_6F_5)_3{-}CH_3$). ^{13}C NMR (dichloromethane-d_2, 150.84 MHz): δ 148.5 (C8, from GHMBC NMR), 111.7 (C1), 109.0 ($^1J_{CH} = 175$ Hz), 106.7 ($^1J_{CH} = 175$ Hz), 104.2 ($^1J_{CH} = 174$ Hz), 96.6 ($^1J_{CH} = 173$ Hz) (C_5H_4), 107.0 ($^1J_{CH} = 174$ Hz, C−Cp), 59.8 (C9), 58.9 (C4), 44.2 ($^1J_{CH} = 138$ Hz, C6), 43.5 ($^1J_{CH} = 153$ Hz, C7), 30.0 ($^1J_{CH} = 130$ Hz, C10), 25.4 ($^1J_{CH} = 129$ Hz), 17.7 ($^1J_{CH} = 128$ Hz) (C5, C5′), 10.1 ($B(C_6F_5)_3{-}CH_3$), 148.7 (d, $^1J_{CF} = 230$ Hz, *o*-$B(C_6F_5)_3$), 137.8 (d, $^1J_{CF} = 238$ Hz, *p*-$B(C_6F_5)_3$), 136.6 (d, $^1J_{CF} = 243$ Hz, *m*-$B(C_6F_5)_3$), 129.6 (br, *ipso*-$B(C_6F_5)_3$). ^{15}N,^{1}H-GHMBC NMR (dichloromethane-d_2, 60.72/599.99 MHz): δ −161.0/1.57 (N^B/10-H), −375.9/1.63 (N^A/5-H), −375.9/1.20 (N^A/5′-H). IR (KBr): $\tilde{\nu}$ 2201 cm^{-1} (C≡NR).

X-ray Crystal Structure Analysis of 5a. Crystal data and refinement details: formula $C_{39}H_{32}N_2BF_{15}Zr$, $M_r = 915.70$, 0.50 × 0.30 × 0.20 mm, $a = 14.325(1)$ Å, $b = 21.496(1)$ Å, $c = 12.460(1)$ Å, $V = 3836.8(4)$ Å^3, $\rho_{calcd} = 1.585$ g cm^{-3}, $\mu = 3.92$ cm^{-1}, absorption correction via SORTAV ($0.828 \leq T \leq 0.926$), $Z = 4$, orthorhombic, space group $Pna2_1$ (No. 33), $\lambda = 0.710\ 73$ Å, $T = 198$ K, ω and φ scans, 25 552 reflections collected ($\pm h$, $\pm k$, $\pm l$), $(\sin\theta)/\lambda = 0.62$ Å^{-1}, 7629 independent and 6271 observed reflections [$I \geq 2\sigma(I)$], 530 refined parameters, R1 = 0.068, wR2 = 0.169, maximum residual electron density 4.06 (−0.92) e Å^{-3} close to Zr (<0.9 Å), Flack parameter 0.00(6), hydrogens calculated and riding.

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(28) Gifford, M.; Cousseau, J.; Martin, G. M. *J. Chem. Soc., Perkin Trans. 2* **1985**, 157.

Reaction of 4 with *n*-Butyl Isocyanide: Preparation of 5b. Analogously as described above a sample of 150 mg (0.45 mmol) of **3** (in 3 mL of dichloromethane) was treated subsequently with 228 mg (0.45 mmol) of $B(C_6F_5)_3$ (in 3 mL of dichloromethane) and 39 mg (0.45 mmol) of n-$C_4H_9{-}N{\equiv}C$ to yield the product **5b** (231 mg, 56%) as a viscous red oil. The oily product was only characterized spectroscopically. ^1H NMR (dichloromethane-d_2, 599.99 MHz): δ 6.06, 5.88, 5.85, 5.51 (m, each 1H, C_5H_4), 3.74 (t, $^3J_{HH} = 6.8$ Hz, 2H, 9-H), 2.49 (s, 3H, 6-H), 2.02 (d, $^2J_{HH} = 8.8$ Hz, 1H, 7-H), 1.80 (quint., $^3J_{HH} = 7.3$ Hz, 2H, 10-H), 1.63, 1.19 (s, each 3H, 5-H, 5′-H), 1.48 (sext, $^3J_{HH} = 7.5$ Hz, 2H, 11-H), 1.38 (d, $^2J_{HH} = 8.8$ Hz, 1H, 7-H′), 1.00 (t, $^3J_{HH} = 7.5$ Hz, 3H, 12-H), 0.50 (br s, 3H, $B(C_6F_5)_3{-}CH_3$). ^{13}C NMR (dichloromethane-d_2, 150.84 MHz): δ 152.2 (C8), 111.7 (C1), 109.0, 106.6, 104.1, 96.6 (C_5H_4), 106.9 (C−Cp), 58.9 (C4), 45.2 (C9), 44.2 (C6), 43.5 (C7), 30.8 (C10), 25.4, 17.7 (C5, C5′), 20.0 (C11), 13.2 (C12), 10.5 ($B(C_6F_5)_3{-}CH_3$), 148.7 (d, $^1J_{CF} = 242$ Hz, *o*-$B(C_6F_5)_3$), 137.9 (d, $^1J_{CF} = 242$ Hz, *p*-$B(C_6F_5)_3$), 136.7 (d, $^1J_{CF} = 247$ Hz, *m*-$B(C_6F_5)_3$), 129.2 (br, *ipso*-$B(C_6F_5)_3$). IR (KBr): $\tilde{\nu}$ 2213 cm^{-1} (C≡NR).

Reaction of 4 with 2,4,4-Trimethyl-2-pentyl Isocyanide: Preparation of 5c. Analogously as described above complex **4** (150 mg, 0.45 mmol) was treated with $B(C_6F_5)_3$ (228 mg, 0.45 mmol) in dichloromethane and then (after 15 min) with 62 mg of 2,4,4-trimethyl-2-pentyl isocyanide. Workup as described above yielded 228 mg (52%) of complex **5c**, mp 208 °C. Anal. Calcd for $C_{43}H_{40}N_2BF_{15}Zr$ (971.8): C, 53.15; H, 4.15; N, 2.88. Found: C, 52.15; H, 3.98; N, 2.87. ^1H NMR (dichloromethane-d_2, 599.99 MHz, 298 K): δ 6.06, 5.89, 5.84, 5.47 (m, each 1H, C_5H_4), 5.96 (s, 5H, Cp H), 2.49 (s, 3H, 6-H), 2.01 (d, $^2J_{HH} = 8.8$ Hz, 1H, 7-H), 1.73 (s, 2H, 11-H), 1.63, 1.20 (s, each 3H, 5-H, 5′-H), 1.62 (s, 6H, 10-H), 1.38 (d, $^2J_{HH} = 8.8$ Hz, 1H, 7-H′), 1.10 (s, 9H, 13-H), 0.50 (br s, 3H, $B(C_6F_5)_3{-}CH_3$). ^{13}C NMR (dichloromethane-d_2, 150.84 MHz, 298 K): δ 111.7 (C1), 109.0, 106.5, 103.9, 96.7 (C_5H_4), 106.9 (C−Cp), 62.6 (C9), 58.9 (C4), 51.8 (C11), 44.2 (C6), 43.4 (C7), 31.1 (C12), 31.1 (C10), 30.9 (C13), 25.4, 17.6 (C5, C5′), 10.5 ($B(C_6F_5)_3{-}CH_3$), 148.7 (d, $^1J_{CF} = 242$ Hz, *o*-$B(C_6F_5)_3$), 137.9 (d, $^1J_{CF} = 242$ Hz, *p*-$B(C_6F_5)_3$), 136.7 (d, $^1J_{CF} = 247$ Hz, *m*-$B(C_6F_5)_3$), 129.2 (br, *ipso*-$B(C_6F_5)_3$). C8 not detected. $^{15}N,^1H$-GHMBC NMR (dichloromethane-d_2, 60.72/599.99 MHz, 298 K): δ −160.5/1.73 (N^B/11-H), −160.5/1.62 (N^B/10-H), −376.4/1.63, −376.4/1.20 (N^A/5-H, N^A/5′-H). IR (KBr): $\tilde{\nu}$ 2195 cm^{-1} (C≡NR).

Reaction of 4 with Butadiene: Preparation of 6a. A cold solution (−50 °C) containing 150 mg (0.45 mmol) of **3** in 3 mL of dichloromethane was added to a solution of 228 mg (0.45 mmol) of $B(C_6F_5)_3$ in 3 mL of dichloromethane at −50 °C. The mixture was stirred for 30 min to generate **4**. Then 9 mL of gaseous 1,3-butadiene was introduced into the solution. After 45 min at −50 °C the mixture was warmed to room temperature and the product precipitated by the addition of pentane (6 mL). The organic phase was decanted off. The residue was washed 4 times with pentane (3 mL each) and then solidified by stirring it with 6 mL of pentane for 12 h. The product is obtained as a pale yellow solid; yield of **6a** 239 mg (60%); mp 210 °C dec. Anal. Calcd for $C_{38}H_{29}NBF_{15}Zr$ (886.7): C, 51.48; H, 3.30; N, 1.58. Found: C, 50.17; H, 3.44; N, 1.30. ESI-MS: $C_{19}H_{26}NZr^+$ (found/calcd relative intensity in %) *m*/*z* 358 (100/100), 359 (42.1/43.7), 360 (38.4/40.4), 361 (7.3/7.8), 362 (31.5/34.4), 363 (6.6/7.4), 364 (5.7/6.1). ^1H NMR (dichloromethane-d_2, 599.99 MHz): δ 6.59, 6.12, 5.89, 5.74 (m, each 1H, C_5H_4), 6.10 (s, 5H, Cp H), 6.15 (m, 1H, 10-H), 5.70 (m, 1H, 9-H), 3.30 (m, 1H, 7-H), 2.68 (m, 1H, 7-H′), 2.62 (m, 1H, 11-H), 2.60 (m, 1H, 11-H′), 2.39 (m, 1H, 8-H), 2.31 (pd, 1H, 6-H), 2.13 (m, 1H, 8-H′), 1.61, 1.36 (s, each 3H, 5-H, 5′-H), 0.50 (br s, 3H, $B(C_6F_5)_3{-}CH_3$). ^{13}C NMR (dichloromethane-d_2, 150.84 MHz): δ 130.3 (C10), 119.2 ($^1J_{CH} = 178$ Hz), 104.2 ($^1J_{CH} = 179$ Hz), 100.6 ($^1J_{CH} = 174$ Hz), 99.0 ($^1J_{CH} = 172$ Hz) (C_5H_4), 118.1 (C1), 110.3 ($^1J_{CH} = 175$ Hz, C−Cp), 105.4 ($^1J_{CH} = 156$ Hz, C9), 66.6 ($^1J_{CH} = 140$ Hz, C7), 62.2 (C4), 47.7 ($^1J_{CH} = 154$ Hz, C11), 41.4 ($^1J_{CH} = 140$ Hz, C6), 26.0 ($^1J_{CH} = 128$ Hz), 22.8 ($^1J_{CH} = 129$ Hz) (C5, C5′), 25.6 ($^1J_{CH} = 129$ Hz, C8), 10.5 ($B(C_6F_5)_3{-}CH_3$), 148.6 (d, $^1J_{CF} = 249$ Hz, *o*-$B(C_6F_5)_3$), 137.8 (d, $^1J_{CF} = 244$ Hz, *p*-$B(C_6F_5)_3$), 136.7 (d, $^1J_{CF} = 246$ Hz, *m*-$B(C_6F_5)_3$), 129.2 (br, *ipso*-$B(C_6F_5)_3$). $^{15}N,^1H$-GHMBC NMR (dichloromethane-d_2, 60.72/599.99 MHz): $\delta = -358.6/1.61$, $-358.6/1.36$ (N/5-H, N/5′-H).

Reaction of 4 with Isoprene: Preparation of 6b. Complex **4** was generated analogously as described above by treatment of 150 mg (0.45 mmol) of **3** with 228 mg (0.45 mmol) of $B(C_6F_5)_3$ in 3 mL of dichloromethane at −36 °C. Isoprene (31 mg, 0.45 mmol) was added. The mixture was kept at −36 °C for 30 min and then warmed to room temperature. The product was precipitated with pentane (9 mL). Workup analogously as described above gave 318 mg (78%) of **6b**. Single crystals of **6b** that were suitable for the X-ray crystal structure analysis were obtained by crystallization from dichloromethane; mp 137 °C (dec at 197 °C). Anal. Calcd for $C_{39}H_{31}NBF_{15}Zr$ (900.7): C, 52.01; H, 3.47; N, 1.56. Found: C, 51.47; H, 3.20; N, 1.59. ESI-MS: $C_{20}H_{28}NZr^+$ (found/calcd relative intensity in %) *m*/*z* 372 (100/100), 373 (42.5/44.9), 374 (38.6/38.2), 375 (7.6/7.6), 376 (30.7/33.7), 377 (6.6/7.8), 378 (5.5/5.4). ^1H NMR (dichloromethane-d_2, 599.99 MHz): δ 6.55, 6.09, 5.76, 5.27 (m, each 1H, C_5H_4), 6.13 (s, 5H, Cp H), 5.47 (m, 1H, 9-H), 3.44 (m, 1H, 7-H), 2.86 (d, $^2J_{HH} = 4.8$ Hz, 1H, 11-H), 2.68 (m, 1H, 7-H′), 2.39 (m, 1H, 8-H), 2.38 (pd, 3H, 6-H), 2.35 (d, $^2J_{HH} = 4.8$ Hz, 1H, 11-H′), 2.19 (m, 1H, 8-H′), 2.11 (s, 3H, 12-H), 1.65, 1.39 (s, each 3H, 5-H, 5′-H), 0.49 (br s, 3H, $B(C_6F_5)_3{-}CH_3$). ^{13}C NMR (dichloromethane-d_2, 150.84 MHz): δ 152.4 (C10), 118.6 ($^1J_{CH} = 177$ Hz), 104.0 ($^1J_{CH} = 177$ Hz), 102.6 ($^1J_{CH} = 175$ Hz), 102.4 ($^1J_{CH} = 173$ Hz) (C_5H_4), 117.7 (C1), 111.3 ($^1J_{CH} = 174$ Hz, C−Cp), 94.1 ($^1J_{CH} = 143.9$ Hz, C9), 68.4 ($^1J_{CH} = 138$ Hz, C7), 62.3 (C4), 50.1 ($^1J_{CH} = 150$ Hz, C11), 41.9 ($^1J_{CH} = 139$ Hz, C6), 25.8 ($^1J_{CH} = 129$ Hz), 23.1 ($^1J_{CH} = 128$ Hz) (C5, C5′), 24.2 (C8), 23.9 (C12), 10.2 ($B(C_6F_5)_3{-}CH_3$), 148.6 (d, $^1J_{CF} = 249$ Hz, *o*-$B(C_6F_5)_3$), 137.8 (d, $^1J_{CF} = 244$ Hz, *p*-$B(C_6F_5)_3$), 136.7 (d, $^1J_{CF} = 246$ Hz, *m*-$B(C_6F_5)_3$), 129.2 (br, *ipso*-$B(C_6F_5)_3$). $^{15}N,^1H$-GHMBC NMR (dichloromethane-d_2, 60.72/599.99 MHz): δ −357.0/1.65, −357.0/1.39 (N/5-H, N/5′-H).

X-ray Crystal Structure Analysis of 6b. Crystal data and refinement details: formula $C_{39}H_{31}NBF_{15}Zr{\cdot}CH_2Cl_2$, $M_r = 985.60$, 0.30 × 0.20 × 0.10 mm, $a = 10.114(1)$ Å, $b = 19.244(1)$ Å, $c = 20.443(1)$ Å, $\beta = 101.36(1)°$, $V = 3900.9(5)$ Å^3, $\rho_{calcd} = 1.678$ g cm^{-3}, $\mu = 5.23$ cm^{-1}, absorption correction via SORTAV ($0.859 \le T \le 0.950$), $Z = 4$, monoclinic, space group $P2_1/n$ (No. 14), $\lambda = 0.710\,73$ Å, $T = 198$ K, ω and φ scans, 19 299 reflections collected ($\pm h, \pm k, \pm l$), $(\sin\theta)/\lambda = 0.59$ Å^{-1}, 6831 independent and 4301 observed reflections [$I \ge 2\sigma(I)$], 552 refined parameters, R1 = 0.066, wR2 = 0.145, maximum residual electron density 1.89 (−0.59) e Å^{-3} close to Zr (<1.0 Å), hydrogens at C25 from difference Fourier map, others calculated and all refined riding.

Treatment of 7 with $B(C_6F_5)_3$: Preparation of 8. Complex **8** was prepared by treatment of 680 mg (1.61 mmol) of **7** with 824 mg (1.61 mmol) of $B(C_6F_5)_3$ in 20 mL of toluene at −20 °C analogously as described by us in the literature[2] to give a yield of 1.04 g (71%) of **8**. Anal. Calcd for $C_{39}H_{34}N_2BF_{15}Zr$ (917.7): C, 51.04; H, 3.73; N, 3.05. Found: C, 50.35; H, 3.67; N, 2.77. Single crystals of **8** were obtained by diffusion of pentane vapor into a solution of **8** in dichloromethane at −36 °C. ^1H NMR (dichloromethane-d_2, 599.99 MHz, 263 K): δ 6.57, 6.52, 6.26, 5.95, 5.93, 5.76, 5.75, 5.55 (m, each 1H, Cp′ H), 2.45 (s, 3H, 6-H), 2.31, 2.30 (s, each 3H, 8-H, 8′-H), 2.27 (d, $^2J_{HH} = 9.8$ Hz, 1H, 7-H), 1.61, 1.49 (s, each 3H, 9-H, 9′-H), 1.57 (d, $^2J_{HH} = 9.8$ Hz, 1H, 7-H′), 1.50, 1.36 (s, each 3H, 5-H, 5′-H), 0.45 (br s, 3H, $(C_6F_5)_3B{-}CH_3$). ^1H NMR (dichloromethane-d_2, 599.99 MHz, 223 K): δ 6.54, 6.24, 5.73, 5.52 (m, each 1H, 2-H, 2′-H, 3-H, 3′-H), 6.53, 5.91, 5.90, 5.73 (m, each 1H, 12-H, 12′-H, 13-H, 13′-H), 2.42 (s, 3H, 6-H), 2.27 (s, 6H, 8-H, 8-H′), 2.20 (d, $^2J_{HH} = 9.8$ Hz, 1H, 7-H), 1.58, 1.47 (s, each 3H, 9-H, 9′-H), 1.53 (d, $^2J_{HH} = 9.8$ Hz, 1H, 7-H′), 1.48, 1.33 (s, each 3H, 5-H, 5′-H), 0.40 (br s, 3H, $B(C_6F_5)_3-CH_3$). ^{13}C NMR (dichloromethane-d_2, 150.84 MHz, 223 K): δ 123.7 (C11), 115.3 (C1), 113.2 ($^1J_{CH}$ = 173 Hz), 112.0 ($^1J_{CH}$ = 175 Hz), 104.1 ($^1J_{CH}$ = 173 Hz), 99.3 ($^1J_{CH}$ = 170 Hz) (C12, C12′, C13, C13′), 110.1 ($^1J_{CH}$ = 174 Hz), 109.6 ($^1J_{CH}$ = 174 Hz), 106.7 ($^1J_{CH}$ = 174 Hz), 99.6 ($^1J_{CH}$ = 171 Hz) (C2, C2′, C3, C3′), 60.6 (C10), 58.2 (C4), 49.1 ($^1J_{CH}$ = 147 Hz, C7), 47.7 ($^1J_{CH}$ = 139 Hz), 47.3 ($^1J_{CH}$ = 139 Hz) (C8, C8′), 43.5 ($^1J_{CH}$ = 139 Hz, C6), 24.8 ($^1J_{CH}$ = 128 Hz), 17.5 ($^1J_{CH}$ = 128 Hz) (C5, C5′), 24.4 ($^1J_{CH}$ = 128 Hz), 24.2 ($^1J_{CH}$ = 128 Hz) (C9, C9′) 9.4 ($B(C_6F_5)_3-CH_3$), 147.7 (d, $^1J_{CF}$ = 237 Hz, *o*-$B(C_6F_5)_3$), 137.0 (d, $^1J_{CF}$ = 242 Hz, *p*-$B(C_6F_5)_3$), 135.9 (d, $^1J_{CF}$ = 247 Hz, *m*-$B(C_6F_5)_3$), 128.0 (br, *ipso*-$B(C_6F_5)_3$). ^{15}N,^{1}H-GHMBC NMR (dichloromethane-d_2, 60.72/599.99 MHz, 263 K): δ −357.6/1.52, −357.6/1.40 (N^B/5-H, N^B/5′-H), −373.7/1.63, −373.7/1.52 (N^A/9-H, N^A/9′-H). ^{15}N,^{1}H-GHMBC NMR (dichloromethane-d_2, 60.72/599.99 MHz, 223 K): δ −357.9/1.47, −357.9/1.33 (N^B/5-H, N^B/5′-H), −372.9/1.58, −372.9/1.47 (N^A/9-H, N^A/9′-H).

X-ray Crystal Structure Analysis of 8. Crystal data and refinement details: formula $C_{39}H_{34}N_2BF_{15}Zr$, M_r = 917.71, 0.50 × 0.35 × 0.30 mm, a = 12.032(1) Å, b = 17.476(1) Å, c = 17.479(1) Å, β = 91.57(1)°, V = 3674.0(4) Å^3, ρ_{calcd} = 1.659 g cm^{-3}, μ = 4.09 cm^{-1}, absorption correction via SORTAV (0.821 ≤ T ≤ 0.887), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.710 73 Å, T = 198 K, ω and φ scans, 33 281 reflections collected (±h, ±k, ±l), (sin θ)/λ = 0.71 Å^{-1}, 11 048 independent and 9648 observed reflections [$I \geq 2\sigma(I)$], 531 refined parameters, R1 = 0.033, wR2 = 0.080, maximum residual electron density 0.37 (−0.50) e Å^{-3}, hydrogens calculated and refined riding.

All data sets were collected with Enraf-Nonius CAD4, MACH3, or KappaCCD diffractometers. Programs used: data collection, EXPRESS and COLLECT; data reduction, MolEN and DENZO-SMN; absorption correction for CCD data, SORTAV; structure solution, SHELXS-86 and SHELXS-97; structure refinement, SHELXL-93 and SHELXL-97; graphics (with unsystematical numbering schemes), SCHAKAL-92 and DIAMOND.[29]

Reaction of 8 with *tert*-Butyl Isocyanide: Preparation of 9. A sample of 150 mg (0.17 mmol) of **8** was dissolved in 6 mL of dichloromethane and cooled to −36 °C. *tert*-Butyl isocyanide (14 mg, 0.17 mmol) was added and the mixture kept for 30 min at −36 °C. Then it was warmed to room temperature. The product was precipitated by the addition of pentane (15 mL). The organic liquid phase was decanted from the solid. The residue was washed with pentane (4 × 3 mL) and dried in vacuo to yield 80 mg (47%) of **9**, mp 199 °C. Anal. Calcd for $C_{44}H_{43}N_3BF_{15}Zr$ (1000.9): C, 52.80; H, 4.33; N, 4.20. Found: C, 51.14; H, 4.65; N, 4.20. ^{1}H NMR (dichloromethane-d_2, 599.99 MHz, 223 K): δ 6.29, 6.26, 5.73, 5.36 (12-H, 12-H′, 13-H, 13-H′), 6.08, 5.89, 5.76, 5.44, (2-H, 2-H′, 3-H, 3-H′), 2.44 (6-H), 1.92 (d, $^2J_{HH}$ = 8.7 Hz, 1H, 7-H), 1.90 (s, 6H, 8-H), 1.59, 1.14 (s, each 3H, 5-H, 5′-H), 1.50 (s, 9H, CMe_3), 1.37 (d, $^2J_{HH}$ = 8.7 Hz, 1H, 7-H′), 1.30, 1.27 (s, each 3H, 9-H, 9′-H), 0.40 (br s, 3H, $B(C_6F_5)_3-CH_3$). ^{13}C NMR (dichloromethane-d_2, 150.84 MHz, 298 K): δ 151.6 (C14), 128.8 (C11), 112.0 (C1), 111.3 ($^1J_{CH}$ = 172 Hz), 107.7 ($^1J_{CH}$ = 172 Hz), 105.2 ($^1J_{CH}$ = 173 Hz), 102.9 ($^1J_{CH}$ = 173 Hz) (C12, C12′, C13, C13′), 110.3 ($^1J_{CH}$ = 174 Hz), 106.3 ($^1J_{CH}$ = 174 Hz), 104.4 ($^1J_{CH}$ = 174 Hz), 97.0 ($^1J_{CH}$ = 173 Hz) (C2, C2′, C3, C3′), 59.9 (C15), 58.7 (C4), 56.5 (C10), 44.1 ($^1J_{CH}$ = 155 Hz, C7), 43.1 ($^1J_{CH}$ = 138 Hz, C6), 39.2 ($^1J_{CH}$ = 133 Hz, C8), 29.9 ($^1J_{CH}$ = 129 Hz, C16), 27.3 ($^1J_{CH}$ = 126 Hz), 25.4 ($^1J_{CH}$ = 126 Hz) (C9, C9′), 25.4 ($^1J_{CH}$ = 126 Hz), 17.8 ($^1J_{CH}$ = 128 Hz) (C5, C5′), 9.4 ($B(C_6F_5)_3-CH_3$); 148.6 (d, $^1J_{CF}$ = 247 Hz, *o*-$B(C_6F_5)_3$), 137.8 (d, $^1J_{CF}$ = 244 Hz, *p*-$B(C_6F_5)_3$), 136.6 (d, $^1J_{CF}$ = 246 Hz, *m*-$B(C_6F_5)_3$), 128.9 (br, *ipso*-$B(C_6F_5)_3$). ^{15}N,^{1}H-GHMBC NMR (dichloromethane-d_2, 60.72/599.99 MHz, 223 K): δ −161.3/1.50 (N^C/16-H), −338.5/1.30, −338.5/1.27 (N^B/9-H, N^B/9′-H), −375.1/1.59, −375.1/1.14 (N^A/5-H, N^A/5′-H). IR (KBr): $\tilde{\nu}$ 2193 cm^{-1} (C≡NR).

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Supporting Information Available: Figures giving NMR spectra of selected compounds and text and tables giving additional information about the X-ray crystal structure analyses of complexes **2**, **3**, **5a**, **6b**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(29) Programs used: EXPRESS: Nonius BV, 1994. COLLECT: Nonius BV, 1998. MolEN: Fair, K. Enraf-Nonius BV, 1990. Denzo-SMN: Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307−326. SORTAV: Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33−37; *J. Appl. Crystallogr.* **1997**, *30*, 421−426. SHELXS-86 and SHELXS-97: Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473. Sheldrick, G. M. Universität Göttingen, 1997. SHELXL-93 and SHELXL-97: Sheldrick, G. M. Universität Göttingen, 1997. SCHAKAL: Keller, E. Universität Freiburg, 1997. DIAMOND: Brandenburg, K. Universität Bonn, 1996.