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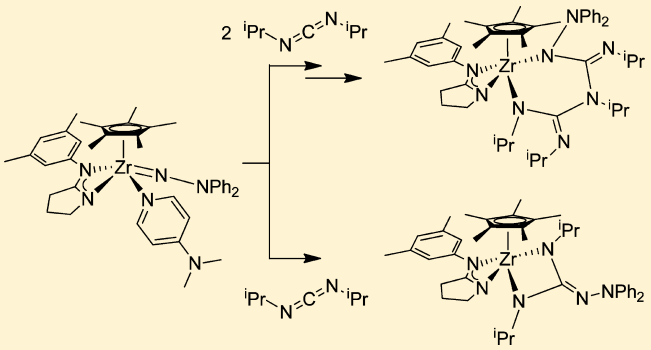
Zirconium and Hafnium Hydrazinediido Half-Sandwich Complexes: Synthesis and Reactivity

Peter D. Schweizer, Hubert Wadepohl, and Lutz H. Gade*

Anorganisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany

Supporting Information

ABSTRACT: The hydrazinediido complexes [Cp*M(N_{xyl}N)($NNPh_2$)(dmap)] (M = Zr, **3a**; M = Hf, **3b**; N_{xyl}N = 2-(*N*-xylylamino)pyrrolinate) have been synthesized, and their reactivity has been investigated. Both complexes were prepared from [Cp*M(N_{xyl}N)Cl_2] (**1a**,**b**) and [Cp*M(N_{xyl}N)($NHNPh_2$)Cl] (**2a**,**b**), respectively, as precursors. While **3a** was obtained by dehydrohalogenation of **2a** using LiHMDS in the presence of dmap, reaction of **2b** with LiHMDS initially afforded a mixture of [Cp*Hf(N_{xyl}N)($NHNPh_2$)$_2$] (**6**) and [Cp*Hf(N_{xyl}N)($NNPh_2$)LiHMDS] (**4**), which was thermolyzed subsequently in the presence of dmap to yield **3b**. [Cp*Zr(N_{xyl}N)($NNPh_2$)(dmap)] (**3a**) reacted with diisopropylcarbodiimide, giving the rearranged [2 + 2] cycloaddition product [Cp*Zr(N_{Xyl}N){κ^2-N^{i}PrC($NNPh_2$)N^{i}Pr}] (**7**) and the six-membered zirconacycle [Cp*Zr(N_{Xyl}N){κ^2-N(NPh_2)C(N^{i}Pr)N^{iPr}C(N^{i}Pr)N^{iPr}}] (**8a**). With *N*-phenylbenzimine the cycloaddition product [Cp*Zr(N_{Xyl}N){κ^2-N(NPh_2)CHPhNPh}] (**9**) was isolated, and upon reaction with diphenylacetylene the seven-membered zirconacycle [Cp*Zr(N_{Xyl}N){κ^2-N(Ph)-*o*-phenylene-C(Ph)=C(Ph)NH}] (**10**) was obtained. Reaction of the previously synthesized compound [Zr($N_2^{TBS}N_{py}$)($NNPh_2$)-py] (**11**) with ^{i}PrNCN^{i}Pr and with PhCH=NPh gave the four-membered zirconacycles [Zr($N_2^{TBS}N_{py}$){κ^2-N(NPh_2)C(N^{i}Pr)-N^{i}Pr}] (**12**) and [Zr($N_2^{TBS}N_{py}$){κ^2-N(NPh_2)CHPhNPh}] (**13**), respectively.



INTRODUCTION

Since the first report of a titanium hydrazinediido complex in 1978,[1] a great variety of such compounds featuring different types of ancillary ligands have been reported,[2−13] and their reactivity has been studied in some detail in recent years.[6−15] Stoichiometric reactions with alkynes,[4,5,7,8,12] allenes,[14] and heteroallenes, such as isocyanates,[3,10,11,14] isothiocyanates,[10,11,14] carbon dioxide,[3,9,11] carbodiimides,[16] and carbon disulfide,[11] resulted in formal [2 + 2] cycloadditions. In some cases this initial reaction step was followed by Ti−X insertion,[10,17] or insertion into the N−N bond of the hydrazinediido unit, depending on the ancillary ligand. Complexes of this type have been employed as catalysts in the hydrohydrazination of alkynes[7,12,18] and carbodiimides[16] and related three-component coupling reactions.[19]

However, zirconium[20−25] and hafnium[21] hydrazinediido complexes remain relatively scarce, despite the interesting and diverse reactive behavior found for some of them.[26−31] For stoichiometric reactions with disubstituted alkynes, formation of seven-membered zirconacycles via N−N-bond scission was observed,[20] which provided the basis for a new catalytic indole synthesis.[23,24,32] This illustrates why further investigation into the chemistry of the heavier group 4 metals is desirable. To this end and in order to investigate the dependence of stoichiometric reactivity on both the ancillary ligand and metal, we have prepared new half-sandwich zirconium and hafnium complexes containing 2-(*N*-xylylamino)pyrrolinate (N_{xyl}N) as a spectator ligand.[33] A first account of their synthesis and reactivity is given in this work.

RESULTS AND DISCUSSION

Preparation and Structural Characterization of [Cp*M(N_{xyl}N)($NNPh_2$)(dmap)] (M = Zr, 3a; M = Hf, 3b). The dichlorido complexes [Cp*M(NxylN)Cl_2] (M = Zr, **1a**; M = Hf, **1b**) were prepared from Cp*MCl_3 by a modified procedure based on work by Sita and co-workers.[34] Cp*MCl_3 was reacted with MeLi in order to generate a monomethyl complex in situ, which was then reacted with the protio ligand HN_{xyl}N, giving **1a**,**b** in 89% and 93% yields, respectively (Scheme 1).

Addition of $LiNHNPh_2$ then resulted in the formation of the monohydrazido(1−) complexes [Cp*M(N_{xyl}N)($NHNPh_2$)Cl] (**2a**,**b**). As compound **2a** was thermally unstable, it was directly reacted in situ with LiHMDS in the presence of dmap.[21,22,35] The corresponding hydrazinediido complex [Cp*Zr(N_{xyl}N)-($NNPh_2$)dmap] (**3a**) was obtained in 84% yield as a yellow-ocher powder. ^{1}H, ^{13}C, and ^{15}N NMR spectra indicated a mixture of two isomers in a ratio of 2:1; in particular, the ^{15}N NMR spectrum displayed two signals in the characteristic

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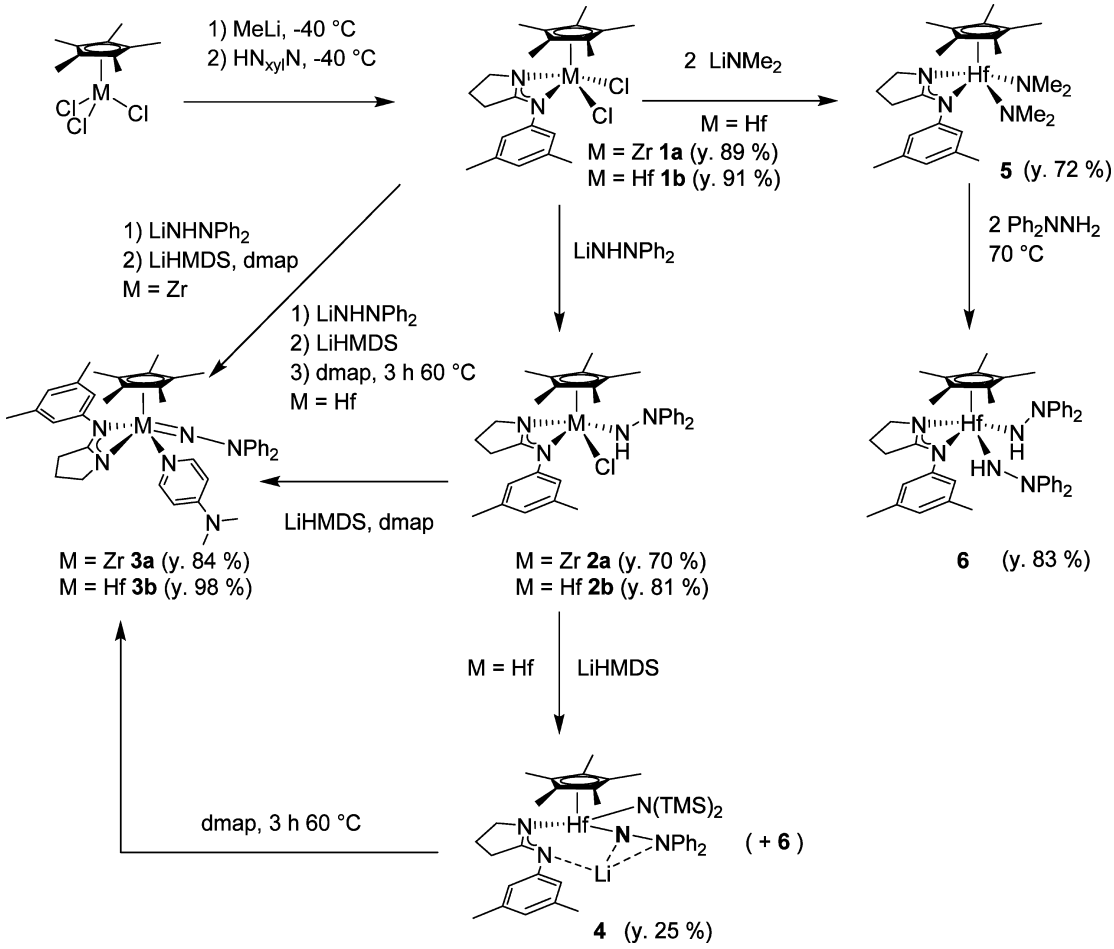
Scheme 1. Synthesis of the Hydrazinediido Complexes 3a,b



region for Zr*N*NR$_2$ (286 and 281 ppm). The ^{1}H NOESY NMR spectrum revealed cross relaxation between *o*-dmap and *o*-xylyl protons for the minor isomer but not for the major isomer. The isomers could thus be assigned to the diastereomers shown in Figure 1.

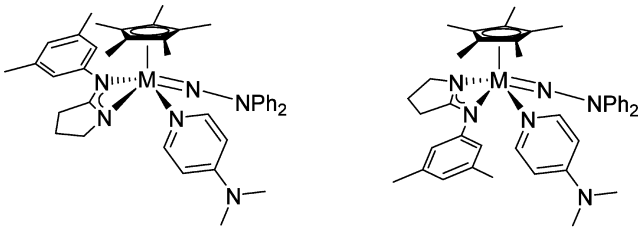


Figure 1. Diastereomers of **3a** (M = Zr) and **3b** (M = Hf).

However, this procedure was not successful for the preparative conversion of the Hf complex **2b** to the corresponding hydrazinediide. When **2b** was reacted with LiHMDS without addition of dmap, a mixture of the hafnium {LiHMDS} hydrazinediido complex **4** and hafnium bis(hydrazido) complex **6** was obtained. The mixture of **4** and **6** was then heated to 60 °C for 3 h in the presence of dmap, which yielded the hafnium hydrazinediido complex **3b** as a mixture of the two diastereomers depicted in Figure 1 in a ratio of 3:1. While thermal treatment of **6** in the presence of dmap and LiHMDS also resulted in the formation of **3b**, no reaction was observed upon heating **6** in the presence of dmap without LiHMDS. Compound **6** could also be isolated by employing a different route via the bis(dimethylamido) complex **5**, which was obtained by reacting **1b** with 2 equiv of LiNMe$_2$ and was then treated with 2 equiv of diphenylhydrazine.

Single crystals suitable for X-ray diffraction were obtained for hydrazinediides **3a,b**. Their crystal and molecular structures are very similar (Table 1). There are two independent molecules in the asymmetric unit which both correspond to the main diastereomer (Figure 1), with only a minor difference in the orientation of one of the phenyl groups (Figure 2).

Both M(1)−N(3) and N(3)−N(4) bond lengths (mean values for **3a**, Zr(1)−N(3) 1.875 Å and N(3)−N(4) 1.379 Å, mean values for **3b**, Hf(1)−N(3) 1.856 Å and N(3)−N(4) 1.389 Å, respectively) are in good agreement with those of previously reported zirconium hydrazinediido complexes, as is the slight deviation from linearity for the M(1)−N(3)−N(4) units (mean values Zr(1)−N(3)−N(4) 171.7° and Hf(1)−N(3)−N(4) 171.3°, respectively).[21−25,32] In both cases, the 2-(*N*-xylylamino)pyrrolinato ligand is bound in a κ^2 mode similarly to the analogous titanium complex, while the Zr(1)−N(1)/N(2) distances (mean values 2.306 and 2.293 Å) as well as the Hf(1)−N(1)/N(2) distances (2.272 and 2.270 Å) are—as expected—longer than those for comparable titanium complexes (mean values 2.273 and 2.265 Å).[7]

Preparation and Structural Characterization of [Cp*Hf(N$_{xyl}$N)(NNPh$_2$){N(SiMe$_3$)$_2$}Li] (4). As mentioned

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for 3a (M = Zr) and 3b (M = Hf)[a]

	Zr	Hf		Zr	Hf
M(1)−N(1)	2.3019(9) [2.3092(9)]	2.272(3) [2.273(3)]	M(1)−N(5)	2.3361(9) [2.3364(9)]	2.303(3) [2.306(3)]
M(1)−N(2)	2.3012(10) [2.2856(10)]	2.270(3) [2.260(3)]	N(1)−C(4)	1.327(2) [1.330(2)]	1.327(5) [1.322(5)]
M(1)−N(3)	1.8745(9) [1.8746(10)]	1.860(3) [1.852(3)]	N(2)−C(4)	1.323(2) [1.322(1)]	1.318(4) [1.320(4)]
N(3)−N(4)	1.380(1) [1.378(1)]	1.385(4) [1.393(4)]			
M(1)−N(3)−N(4)	171.67(8) [171.75(8)]	171.0(2) [171.6(2)]	N(1)−C(4)−N(2)	114.9(1) [115.7(1)]	114.3(3) [114.9(3)]
N(1)−M(1)−N(2)	58.06(4) [58.50(3)]	58.6(1) [58.9(1)]			

[a]Values in brackets refer to the second molecule.

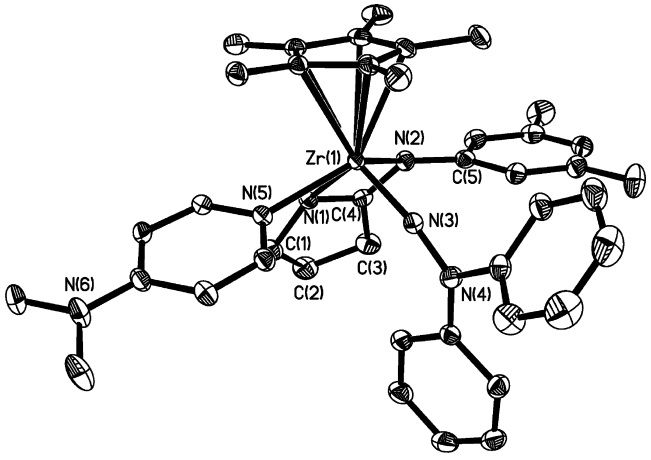

Figure 2. Molecular structure of **3a**. Only one of the two independent molecules is shown. Hydrogen atoms are omitted for clarity, and ellipsoids are drawn at the 50% probability level. For selected bond lengths (Å) and angles (deg) for **3a,b**, see Table 1.

above, reaction of **2b** with 1 equiv of LiHMDS afforded a mixture of bis(hydrazido) complex **6** and [Cp*Hf(N_{xyl}N)-($NNPh_2$){$N(SiMe_3)_2$}Li] (**4**). Compound **4** could also be obtained selectively by reacting **2b** with 2 equiv of LiHMDS.

The ^{15}N NMR spectrum displays a resonance at 263 ppm, which could be assigned unambiguously to the metal-bonded N_α atom by ^{15}N labeling, and a second resonance assigned to the hydrazinediido unit at 147 ppm for N_β. The chemical shift values for ^{15}N hydrazide resonances lie between the respective shifts for hafnium hydrazinediido complex **3b** (280 and 172 ppm) and those observed for the hydrazides(1−) **2b** (211 and 91 ppm) and **6** (206 and 119 ppm). This may indicate that the electronic structure is intermediate between that of a hydrazinediido(2−) and hydrazido(1−) complex. For the N_α signal of **4** significant line broadening was observed in comparison to that of **6** under the same conditions ($\Delta\nu_{1/2}$ = 14.7 Hz for **4** vs 1.5 Hz for **6**), indicating a Li−N bonding interaction and thus unresolved coupling of ^{15}N to ^{7}Li ($I = {}^3/_2$) and ^{6}Li (I = 1). For $^{15}N_\alpha$-labeled **4**, splitting of the Li signal was observed in both the ^{7}Li and ^{6}Li NMR spectra (Figure 3).

The coupling constants were determined to be $^1J(^{15}N,^7Li)$ = 5.1(2) Hz and $^1J(^{15}N,^6Li)$ = 2.0(1) Hz. We note that the $^1J(^{15}N,^7Li)$ value is somewhat smaller than coupling constants previously reported for lithium amido compounds (8.1−13.1 Hz).[36] The $^1J(^{15}N,^6Li)$ coupling constant lies in the typical range for lithium amide compounds (1.6−6.6 Hz).[37] In order to determine whether **4** existed in solution as a monomeric or an oligomeric species, a ^{1}H DOSY NMR experiment was carried out for a mixture of **4** and **6**. The ratio D(**4**)/D(**6**) = 1.1

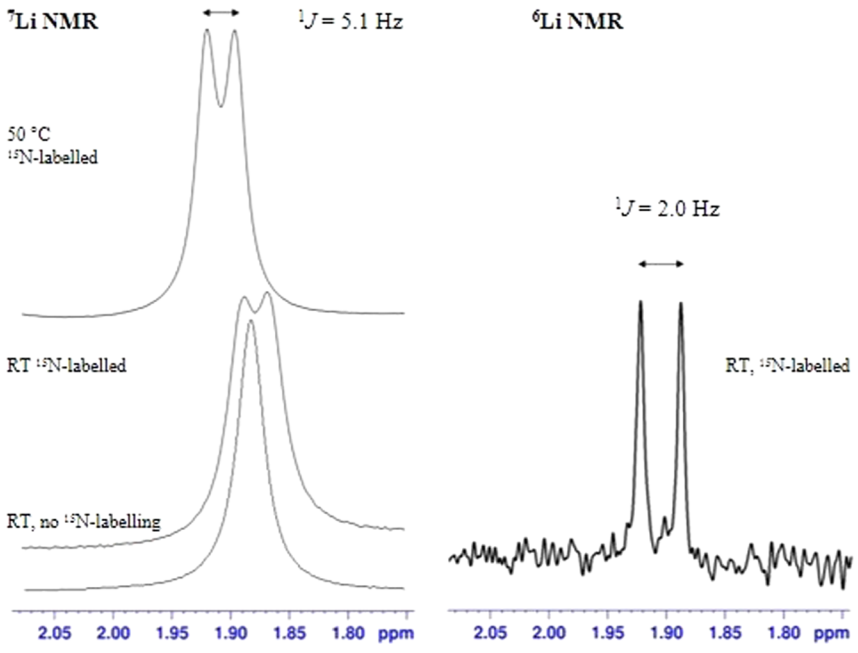

Figure 3. (left) ^{7}Li NMR spectrum for non-isotope-labeled (bottom) and ^{15}N-labeled **4** at room temperature (middle) and 50 °C (top). (right) ^{6}Li NMR spectrum for ^{15}N-labeled **4** at room temperature.

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for the diffusion constants was found, which is consistent with **4** being a monomeric species.

Single crystals of complex **4** suitable for X-ray diffraction were obtained from a concentrated hexane solution at −40 °C. In the molecular structure the Li atom is bound to the NC*N*xyl, N_α, and N_β atoms, while the aminopyrrolinato ligand is coordinated in a κ^1 mode to Hf via the *N*CNxyl atom (Figure 4). The Hf−N_α distance (1.878 Å) lies between those found for

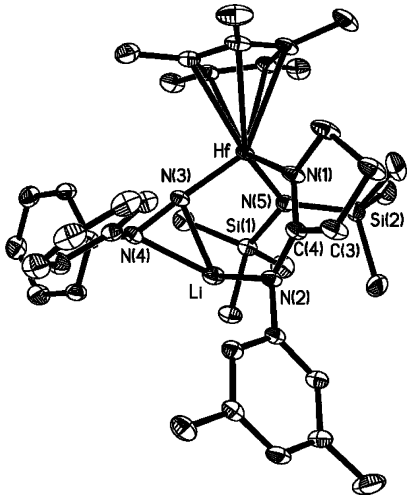

Figure 4. Molecular structure of **4**. Hydrogen atoms are omitted for clarity, and ellipsoids are drawn at the 50% probability level. Minor conformational disorder in the C_5N ring is not shown. Selected bond lengths (Å) and angles (deg): Hf−N(1) 2.204(1), Hf−N(3) 1.878(1), N(3)−N(4) 1.412(1), N(2)−Li 1.928(2), N(3)−Li 1.947(2), N(4)−Li 2.082(3), Hf−N(5) 2.149(1); Hf−N(3)−N(4) 172.30(8), N(1)−Hf−N(3) 96.18(4), N(1)−C(4)−N(2) 124.6(1).

the hydrazinediido compound **3b** and zirconium hydrazido(1−) complexes (2.080−2.123 Å).[21,35] This structural feature is similar to that for the lithium zirconimidate complexes reported by Bergman and co-workers which were obtained by the reaction of imido complexes with methyllithium or of [Cp*$_2$ZrClMe] with LiNHR.[38]

A comparison of the Mulliken charge distributions calculated for compounds **3b** and **4** by DFT (B3PW91),[39,40] using a pseudopotential for Hf (SDD)[41−45] and a 6-31G(d) basis set for all other atoms,[46] shows a significantly higher negative charge at both the N_α atom (−0.561 and −0.649 au, respectively) and the N_β atom (−0.444 and −0.560 au, respectively) of the hydrazinediido unit for complex **4** (Figure 5). This indicates partial negative charges at these two atoms rather than a localized negative charge at the N_α atom. These

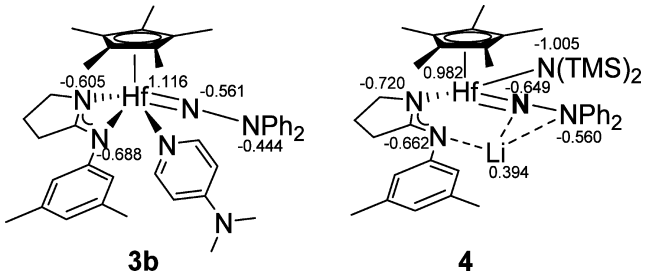

Figure 5. Comparison of the calculated Mulliken charge distributions for compounds **3b** and **4**.

findings are consistent with the bonding situation in a hydrazinediido complex coordinated by Li, rather than an N_α-lithiated hydrazide(1−). This corrobates the interpretation of the ^{15}N NMR data as well as the structural data from the X-ray diffraction study referred to above.

Cycloadditions to the Zr═N Bond and Related in the Hydrazinediido Complex 3a. We recently showed that reaction of carbodiimides with the analogous titanium hydrazinediido complex leads to four-membered titanacycles.[16] However, upon reaction of **3a** with ^{i}PrNCN^{i}Pr we observed the formation of a mixture of two different reaction products, the six-membered zirconacycle **8** and a rearranged four-membered zirconacycle **7** (Scheme 2).

Single crystals suitable for X-ray diffraction of compound **7** were obtained from a concentrated diethyl ether/hexane solution. The structure features a symmetric *N*-aminoguanidinato ligand coordinated in a κ^2 mode to zirconium (Figure 6). The three bonds to C(13) (C(13)−N(3) 1.413 Å, C(13)−N(4) 1.354 Å, C(13)−N(5) 1.325 Å) within the planar (RMSD of CN_3 0.0007 Å) aminoguanidinate lie between typical distances for single and double bonds. We note that the C(13)−N(5) distance (1.325 Å) is the shortest of the three C−N bonds, which is consistent with an exocyclic double bond. Both Zr−N bonds within the metallacycle (Zr−N(3) 2.124 Å, Zr−N(4) 2.248 Å) have lengths consistent with (amido type) single bonds and are indicative of slightly asymmetric bonding of the aminoguanidinate to Zr. The aminopyrrolinato ligand is also coordinated in a κ^2 mode; both Zr−N bond lengths (Zr−N(1) 2.313 Å, Zr−N(2) 2.290 Å) are slightly longer then those for the aminoguanidinato ligand, which can be attributed to the formally dianionic nature of the latter.

Upon addition of 2 equiv of diisopropylcarbodiimide, the six-membered zirconacycle **8** was obtained selectively. The NMR spectra are consistent with the structure shown in Scheme 2. The ^{1}H NMR spectrum featured eight doublets and three septets (one consisting of two overlapping signals) corresponding to four diastereotopic isopropyl groups. In the ^{1}H−^{13}C HMBC NMR spectrum, two signals in the ^{13}C NMR spectrum with shifts characteristic[14,16] for imino group carbon atoms (147.7 and 145.5 ppm) featured long-range coupling to the C*H*Me$_2$ protons of two isopropyl groups. The ^{15}N NMR spectrum displays eight resonances, which were assigned using ^{1}H−^{15}N HMBC NMR spectroscopy (Figure 7).

In addition, the molecular structures for both possible isomers featuring different orientations of the 2-aminopyrrolinato ligand, similar to the isomers found for **3a** (see Figure 1), were computationally modeled using DFT methods (B3PW91, SDD+f for Zr and 6-31G(d) for all other atoms; see Figure 8).[39−45] The isomer with increased steric interaction between the xylyl group of the aminopyrrolinate and the NPh$_2$ group was found to be higher in energy by 41.2 kJ/mol. We then calculated the ^{13}C and ^{15}N NMR shifts for both isomers by the GIAO method,[47−49] using a pseudopotential for Zr (SDD+f) and a 6311++G(2d,2p) basis set for all other atoms. The chemical shifts found for the isomer lower in energy gave good agreement with the experimental data (see Figure 9).

The groups of Odom and Mountford previously postulated a sequence of [2 + 2] cycloaddition of an alkyne and Ti−N insertion of a isonitrile or nitrile, respectively, for the formation of six-membered titanacycles[10,17] in analogy to a similar reaction of a titanium imido complex,[50] and an analogous pathway was proposed for the reaction with carbon dioxide[11] and the reaction of a *tert*-butoxyimido complex with 2 equiv of

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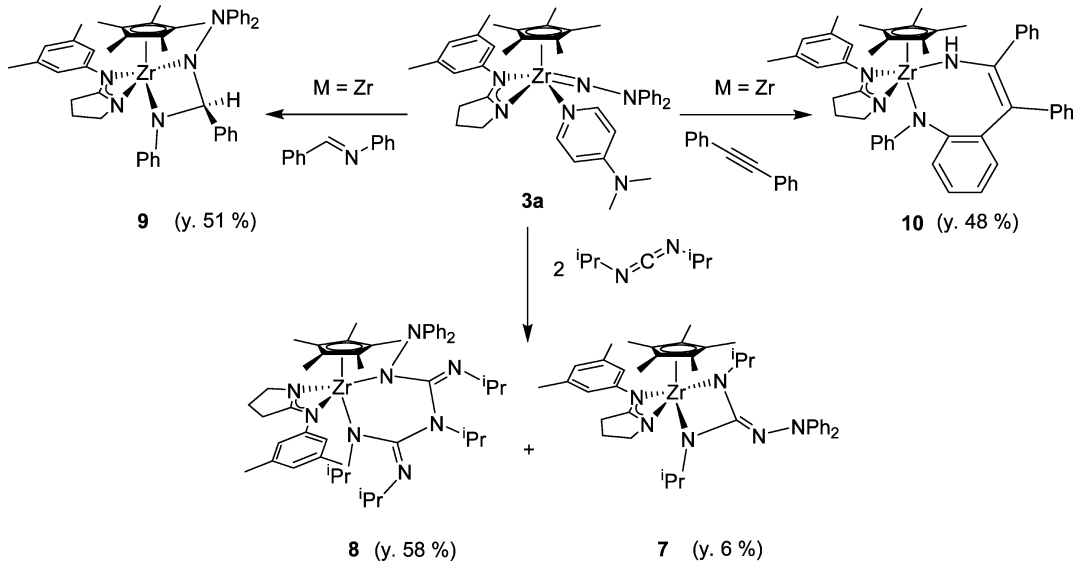
Scheme 2. Stoichiometric Reactions of 3a To Give 7, 8a,b, 9, and 10



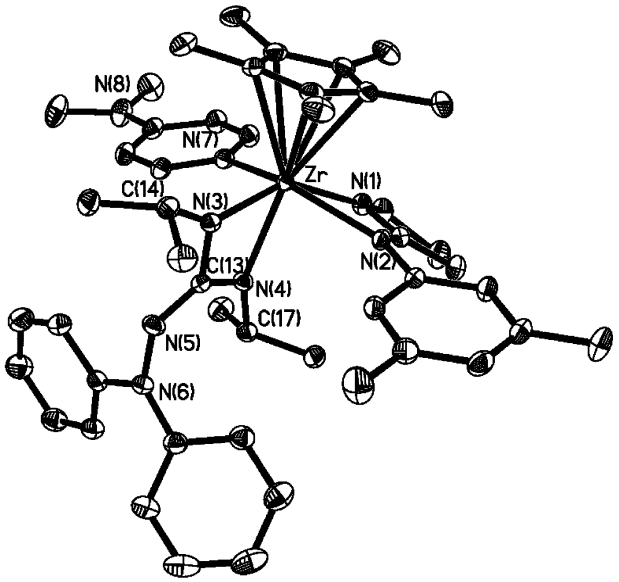


Figure 6. Molecular structure of 7. Hydrogen atoms are omitted for clarity, and ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Zr–N(1) 2.3134(9), Zr–N(2) 2.2904(9), Zr–N(3) 2.1243(9), Zr–N(4) 2.2482(9), N(3)–C(13) 1.413(1), N(4)–C(13) 1.354(1), C(13)–N(5) 1.325(1), N(5)–N(6) 1.428(1), Zr–N(7) 2.3244(9); N(1)–Zr–N(2) 58.11(3), N(3)–Zr–N(4) 61.06(3), N(3)–C(13)–N(4) 107.00(9), C(13)–N(5)–N(6) 117.67(9).

TolNCO.[51] In order to determine whether a similar mechanism leads to the formation of **7** and **8**, we monitored the reaction of **3a** with 0.5 equiv of diisopropylcarbodiimide by ^{1}H NMR spectroscopy (Scheme 3).

We observed initial formation of an intermediate product, which was then rapidly converted to **8**. Although it could not be fully characterized due to its highly reactive nature, the ^{1}H NMR signals detected for this intermediate were found to be consistent with a four-membered zirconacycle formed by [2 + 2] cycloaddition of the carbodiimide to **3a**. This suggests initial formation of a [2 + 2] cycloaddition product, which then either reacts with another 1 equiv of carbodiimide to give **8** or rearranges to **7**.

Another indication for the presence of the cycloaddition product is that the corresponding aminoguanidine was isolated in 99% yield when **3a** was employed as catalyst (5 mol %) in the hydrohydrazination of diisopropylcarbodiimide with diphenylhydrazine. The analogous titanium cycloaddition product was previously found to be an intermediate in the corresponding catalytic cycle (Scheme 4).[16]

While the reaction of zirconium imido complexes with imines has been studied in some detail by the groups of Bergman[52] and Mountford,[53] to the best of our knowledge, this reaction has not been reported for group 4 hydrazinediido complexes to date. When **3a** was reacted with *N*-phenylbenzimine, the four-membered metallacycle **9** was formed by [2 + 2] cycloaddition (see Scheme 2). The NMR spectra are consistent with the structure shown in Scheme 2. Moreover, in the ^{1}H NMR spectrum a singlet signal for the C*H*Ph proton is observed. In the ^{1}H–^{15}N HMBC NMR spectrum, coupling to the *N*NPh$_2$ (335 ppm) and the *N*Ph atom (149 ppm, additional coupling to ortho–N*Ph* protons) was detected.

Previously reported zirconium hydrazinediido complexes reacted with alkynes under N–N bond scission to yield seven-membered zirconacycles.[20,23,32] Complex **3a** exhibited the same behavior and reacted with diphenylacetylene to give the metallacyclic species **10**. The NMR spectra are consistent with the structure shown in Scheme 2. The *N*H and *N*Ph ^{15}N NMR signals at 200 and 214 ppm, respectively, could be assigned via ^{1}H–^{15}N HMBC NMR and are in good agreement with shifts for similar complexes.[23,32] Of the two possible isomers for **10**, only the isomer shown in Scheme 2 is formed. The structural assignment is based on the observed cross relaxation between the CH_2N protons and the phenylene-5 proton in the ^{1}H NOESY NMR spectrum.

Structural Characterization of Cycloadducts of [Zr(N$_2^{TBS}$N$_{py}$)(NNPh$_2$)py] (11) with ^{i}PrNC^{i}Pr and PhCH═NPh. Since we were not successful in obtaining single crystals of **8** and **9** that were suitable for an X-ray diffraction study, we chose to investigate the corresponding transformations with the zirconium complex **11**, which had been previously studied in our group (Scheme 5).[21−23,26−28,30−32]

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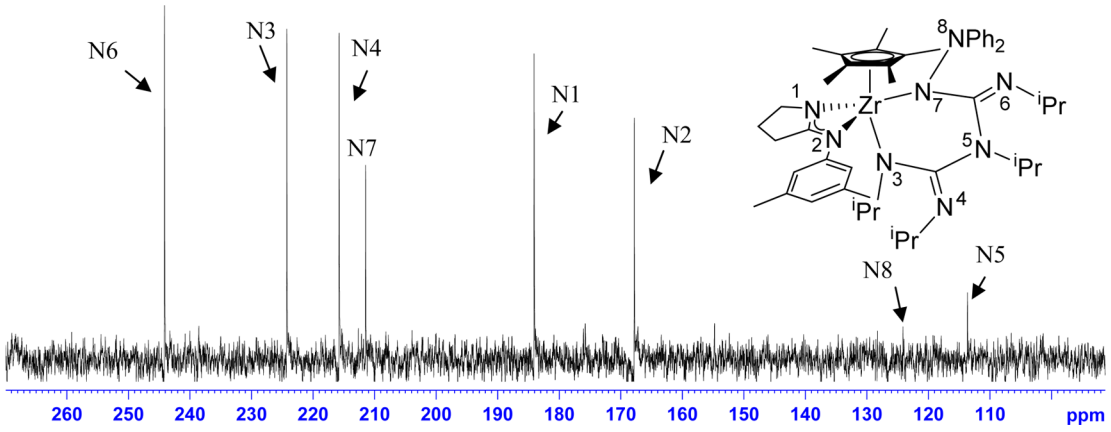
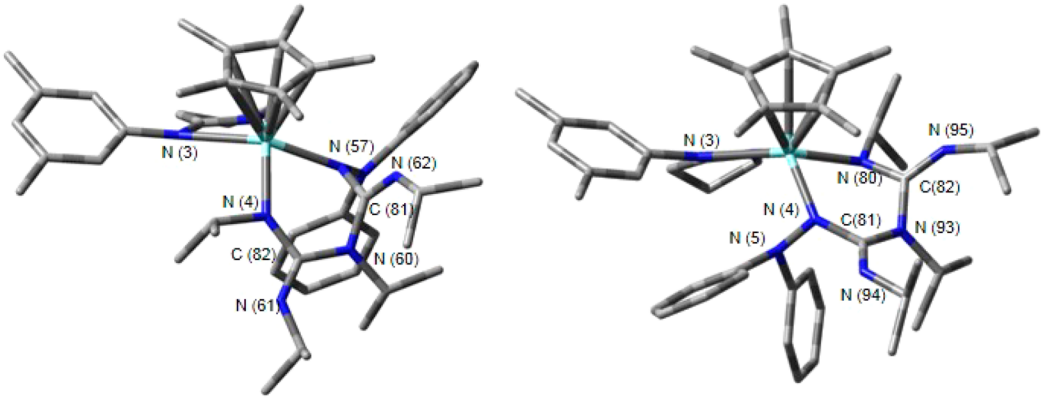


Figure 7. ^{15}N NMR spectrum for **8** along with the assignment of the resonances.



	diastereomer 1		diastereomer 2	
ΔE	0		41.2	kJ/mol
ΔG	0		48.2	kJ/mol
δ (^{13}C)		**δ (^{13}C) exp**		
C (81)	151.9	**147.7**	148.8	ppm
C (82)	145.5	**145.5**	149.5	ppm

Figure 8. DFT-optimized structures of the two possible isomers of **8** and calculated and experimental ^{13}C shifts for both imino group carbon atoms.

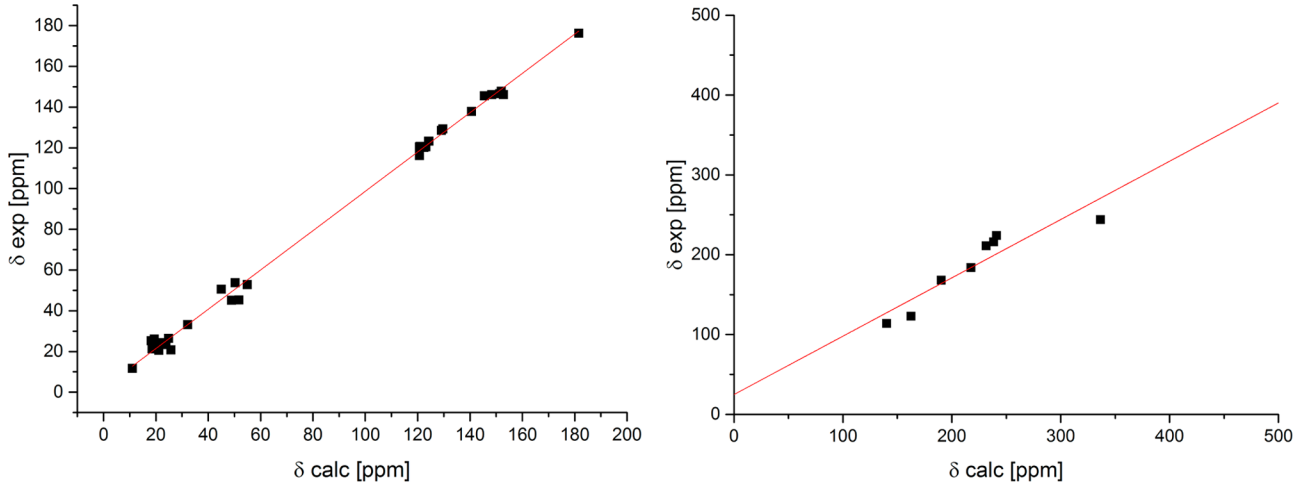


Figure 9. Correlation of calculated and experimental ^{13}C and ^{15}N NMR shifts for **8**.

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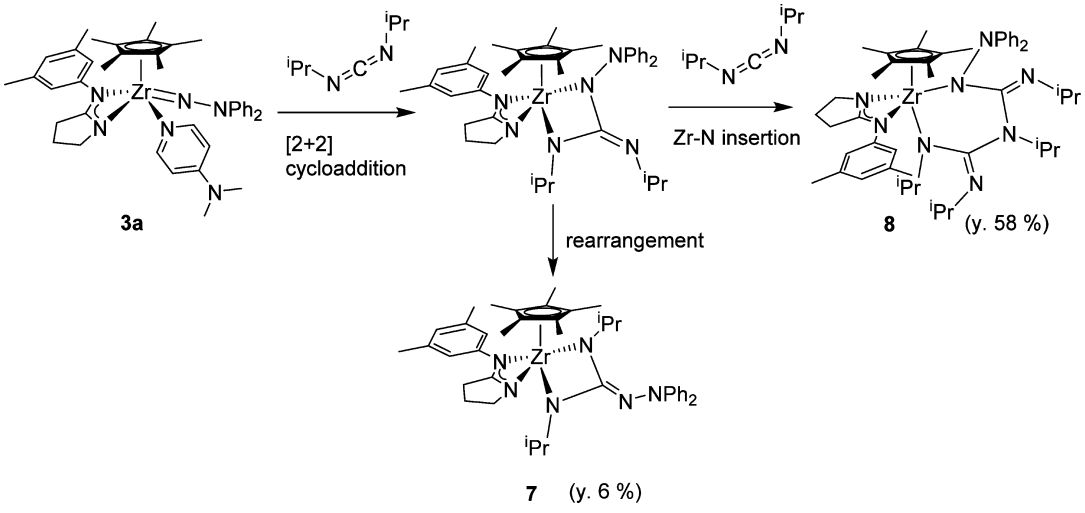
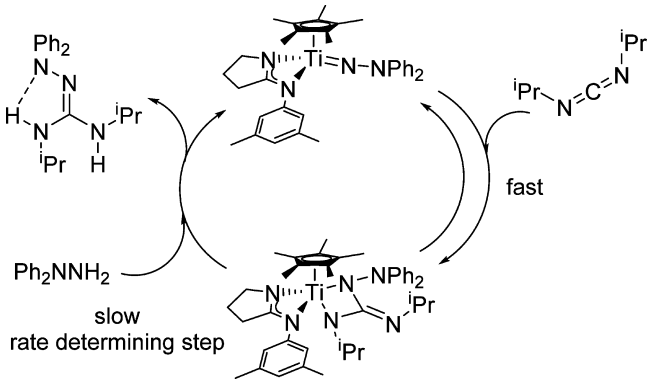
Scheme 3. Possible Formation of 7 and 8 from 3a via a [2 + 2] Cycloaddition Product

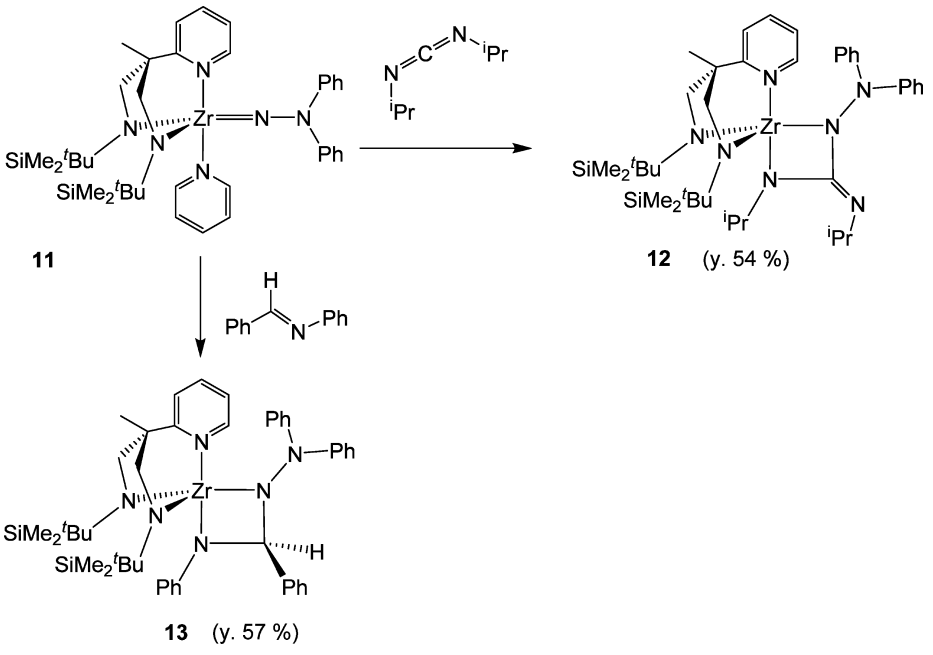


Scheme 4. Mechanism for the Ti-Catalyzed Hydrohydrazination of Carbodiimides via [2 + 2] Cycloaddition[16]



Even in the presence of a large excess of ^{i}PrNCN^{i}Pr compound **11** only formed the four-membered zirconacyclic species **12**, as inferred from the NMR spectra of the isolated product: in the ^{1}H NMR spectrum, two doublets and two septets at 1.78 and 1.19 ppm corresponding to two isopropyl groups (ZrNCHMe_2 and C═NCHMe_2) were detected, indicating C_s symmetry. On the basis of a ^{1}H ^{13}C HMBC experiment, a signal at 153.7 ppm in the characteristic ^{13}C NMR chemical shift region for imino group carbon atoms and comparable to a similar titanium complex[16] could be assigned to C═NCHMe_2. Twinned single crystals of **12** were obtained from a concentrated solution in toluene, and an X-ray diffraction study revealed two independent molecules in the asymmetric unit which only show differences in the rotational orientation of the phenyl and silyl groups (the latter being partially disordered). One of the conformers is depicted in Figure 10. While the exocyclic CN bond length is consistent with a double bond (C(72)−N(57) 1.275 Å), both endocyclic

Scheme 5. Stoichiometric Reactions of 11 To Give 12 and 13



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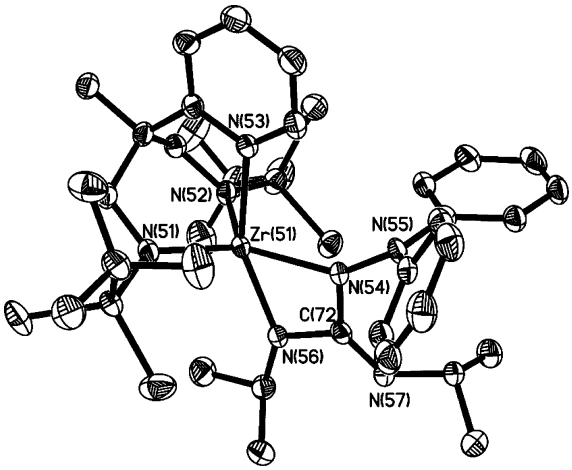

Figure 10. Molecular structure of **12**. Only one of the two independent molecules is shown. Hydrogen atoms are omitted for clarity, and ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) (values in brackets refer to the second molecule): Zr(51)−N(51) 2.042(3) [2.047(3)], Zr(51)−N(52) 2.050(3) [2.050(3)], Zr(51)−N(53) 2.327(3) [2.314(3)], Zr(51)−N(54) 2.181(3) [2.188(3)], Zr(51)−N(56) 2.092(3) [2.096(4)], N(54)−N(55) 1.405(4) [1.407(4)], N(54)−C(72) 1.421(5) [1.409(5)], N(56)−C(72) 1.399 [1.406(5)], C(72)−N(57) 1.275(5) [1.279(6)].

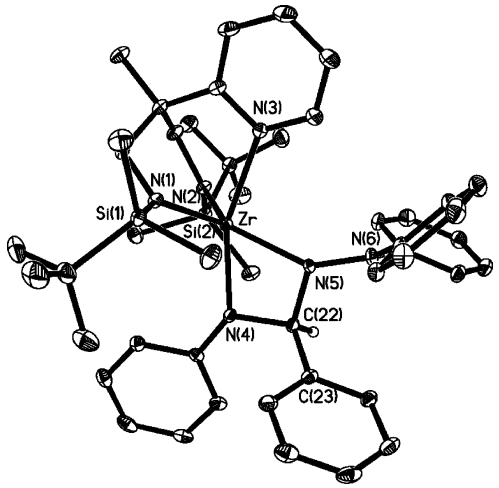

Figure 11. Molecular structure of **13**. All hydrogen atoms but H(22) are omitted for clarity, and ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Zr−N(1) 2.062(2), Zr−N(2) 2.051(2), Zr−N(3) 2.329(2), Zr−N(4) 2.108(2), Zr−N(5) 2.146(2), N(4)−C(22) 1.460(2), N(5)−C(22) 1.495(2), N(5)−N(6) 1.412(2); N(4)−Zr−N(5) 63.76(6), N(4)−C(22)−N(5) 99.0(1).

CN bonds feature interatomic distances typical for single bonds (1.421 and 1.399 Å). These parameters are very similar to those of the corresponding titanium *N*-aminoguanidinato complex,[16] and all other parameters are in good agreement with those of other previously reported cycloaddition products of **11**.[27,30]

Upon reaction of **11** with *N*-phenylbenzimine, formation of the zirconacycle **13** was observed (Scheme 5). The NMR spectra are consistent with the structure shown in Scheme 5. Again, a singlet corresponding to the C*H*Ph proton was observed in the ^{1}H NMR spectrum. The signals for the *N*NPh$_2$ and *N*Ph atoms were detected at 335 and 183 ppm, which are similar to the corresponding shifts found for the half-sandwich complex **9** (335 and 149 ppm). Single crystals of **13** were obtained from a concentrated toluene solution, and the molecular structure determined by X-ray diffraction confirms the structural assignment based on NMR spectroscopic methods (Figure 11). Both the *N*(Ph)−CHPh and the *N*(NPh$_2$)−CHPh bond lengths (1.460 and 1.495 Å) are typical for CN single bonds, and the other bond lengths and angles are in good agreement with those found in related cycloaddition products reported previously.[27,30]

■ CONCLUSIONS

In this work we reported the synthesis and reactivity of the first zirconium and hafnium half-sandwich hydrazinediido complexes. In addition, we were able to isolate a LiHMDS adduct of an anionic hafnium hydrazinediido complex, which can be regarded as an intermediate structure between deprotonated hydrazido and Li-coordinated hydrazinediido complexes. The reactivity of the hydrazinediido complexes with unsaturated substrates displayed similarities but also interesting differences in comparison to the case for analogous titanium and zirconium complexes, illustrating the importance of the choice of ancillary ligand.

■ EXPERIMENTAL SECTION

All manipulations of air- and moisture-sensitive species were carried out under an atmosphere of argon (Argon 5.0) using standard Schlenk and glovebox techniques (glovebox: M. Braun Unilab 2000). Solvents were predried over molecular sieves and dried over Na/K alloy (pentane, diethyl ether), K (THF, hexane, toluene), or CaH_2 (dichloromethane), distilled, or dried over activated alumina columns using a solvent purification system (M. Braun SPS 800) and stored over potassium mirrors (except for dichloromethane) or sodium mirror (THF) in Teflon valve ampules. The deuterated solvent benzene-d_6 was purchased from Deutero GmbH, dried over K, vacuum-distilled, and stored under argon in Teflon valve ampules. Ph_2NNH_2 was prepared from the hydrochloride salt purchased from Acros and purified by column chromatography (over silica, dichloromethane) prior to use. $LiNHNPh_2$ was prepared according to a modified literature procedure,[54] using toluene instead of benzene, and the precipitated product was purified by filtration. $Li^{15}NHNPh_2$ was prepared the same way from $Ph_2N^{15}NH_2$, which was prepared according to literature procedures for the unlabeled compound.[55] The 2-iminopyrrole $HN_{xyl}N$ was also prepared according to the literature,[33] as was $Zr(N_2^{TBS}N_{py})(NNPh_2)py$ (**11**).[21] All other chemicals were purchased from commercial sources (Acros/Thermo Fisher, ABCR/Strem, and Sigma-Aldrich). Diisopropylcarbodiimide was degassed and stored in a glovebox. Samples for NMR spectroscopy of moisture-sensitive compounds were prepared under argon in 5 mm Wilmad tubes equipped with J. Young Teflon valves. NMR spectra were recorded with Bruker Avance II 400 and Bruker Avance III 600 (with QNP-CryoProbe) NMR spectrometers. NMR spectra are quoted in ppm and were referenced internally relative to the residual protio solvent (^{1}H) or solvent (^{13}C) resonances or externally to $^{15}NH_3$ (^{15}N), ^{7}LiCl (aqueous ^{7}Li), and $^{29}SiMe_4$ (^{29}Si). Where necessary, NMR assignments were confirmed by the use of two-dimensional ^{1}H−^{1}H and ^{1}H−^{13}C correlation experiments. ^{13}C spectra were recorded with ^{1}H broad-band decoupling; the multiplicity of the resonances was determined using DEPT-135 experiments. ^{15}N data were obtained by two-dimensional ^{1}H correlated experiments or by direct detection using a cryogenically cooled direct-detection NMR probe (QNP CryoProbe). Microanalyses were performed by the microanalytical service of the chemistry department of the Universität Heidelberg on a Vario MIKRO Cube (Elementar) or a Vario EL (Elementar) CHN analyzer. Mass spectra were recorded by the Institute of Organic Chemistry of the Universität Heidelberg on a JMS 700 magnetic sector (JEOL) spectrometer in FAB (NBA or NPOE as matrix) and EI (70

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eV) modes. IR spectra were recorded on a Varian 3100 Exalibur FT-IR spectrometer as KBr plates. Infrared data are quoted in wavenumbers (cm^{-1}).

[Cp*Zr(N_{xyl}N)Cl_2] (1a). A 1.000 g portion of Cp*$ZrCl_3$ (3.005 mmol) was suspended in 20 mL of toluene in an oven-dried Schlenk flask, and the solution was cooled to −40 °C. A 1.88 mL portion of methyllithium (1.6 mol/L in diethyl ether, 3.005 mmol) was slowly added dropwise. The solution was warmed to −30 °C over 2 h and then cooled to −40 °C again. A 0.566 g portion of $HN_{xyl}N$ (3.005 mmol) was dissolved in 30 mL of toluene under sonification and the solution slowly added dropwise at −40 °C. The reaction mixture was warmed to room temperature under static vacuum and stirred for 3 h and then centrifuged and filtered. The supernatant was evaporated under reduced pressure to yield 1.302 g (2.687 mmol, 89%) of a brown solid. ^{1}H NMR (benzene-d_6, 600.1 MHz, 295 K): δ 6.99 (s, 2 H, *p*-$C_6H_3Me_2$), 6.62 (s, 1 H, *o*-$C_6H_3Me_2$), 3.39 (t, 2 H, $^3J_{H-H}$ = 6.9 Hz, NCH_2), 2.21 (s, 6 H, $C_6H_3Me_2$), 2.01 (s, 15 H, C_5Me_5), 1.89 (t, 2 H, $^3J_{H-H}$ = 7.9 Hz, CH_2CNN) 1.21 (qin, 2 H, $^3J_{H-H}$ = 7.0 Hz, CH_2CH_2CNN) ppm. ^{13}C NMR (benzene-d_6, 150.9 MHz, 295 K): δ 147.2 (s, NCN), 138.2 (s, N-$C_6H_3Me_2$), 125.8 (s, *m*-$C_6H_3Me_2$), 125.4 (d, *p*-$C_6H_3Me_2$), 125.0 (s, C_5Me_5), 121.5 (d, *o*-$C_6H_3Me_2$), 53.3 (t, NCH_2), 29.2 (t, CH_2CNN), 22.9 (t, CH_2CH_2CNN), 21.3 (q, $C_6H_3Me_2$), 12.2 (q, C_5Me_5) ppm. ^{15}N NMR (benzene-d_6, 60.81 MHz, 295 K): δ 192.3 (NCNXyl), 177.0 (*N*CNXyl) ppm. IR (KBr, cm^{-1}): ν 2963 (w), 2909 (w), 1670 (s), 1597 (s), 1507 (m), 1466 (m), 1378 (m), 1262 (s), 1099 (s), 1023 (s), 801 (s). HR-MS (HR-EI+): calcd 482.0833 u, 484.0804 u ($C_{22}H_{30}Cl_2N_2Zr$), found: 482.0813 u (Δ = −2.0 mmu), 484.0807 u (Δ = +0.3 mmu). Anal. Calcd: C, 54.52; H, 6.24; N, 5.78. Found: C, 54.82; H, 6.22; N, 5.36.

[Cp*Hf(N_{xyl}N)Cl_2] (1b). A 500 mg portion (1.190 mmol) of Cp*$HfCl_3$ was suspended in 10 mL of toluene. A 0.74 mL portion of MeLi (1.6 mol/L in diethyl ether, 1.190 mmol) was slowly added at −45 °C. The purple reaction mixture was warmed to −30 °C over 2 h, turning colorless. A 224 mg portion (1.190 mmol) of $HN_{xyl}N$ was then dissolved in toluene and slowly added at −40 °C. A slight static vacuum was applied, and the reaction mixture was warmed to room temperature, stirred for 2 h, centrifuged (13 min at 2000 rpm), and filtered. The solvent was removed under reduced pressure to yield 611 mg (1.068 mmol, 90%) of a light brown solid. ^{1}H NMR (benzene-d_6, 600.1 MHz, 295 K): δ 6.99 (s, 2 H, *o*-$C_6H_3Me_2$), 6.62 (s, 1 H, *p*-$C_6H_3Me_2$), 3.34 (t, 2 H, $^3J_{H-H}$ = 7.0 Hz, CH_2N), 2.21 (s, 6 H, $C_6H_3Me_2$), 2.07 (s, 15 H, C_5Me_5), 1.89 (t, 2 H, $^3J_{H-H}$ = 7.8 Hz, CH_2CNN), 1.19 (qin, 2 H, $^3J_{H-H}$ = 7.4 Hz, CH_2CH_2CNN) ppm. ^{13}C NMR (benzene-d_6, 150.9 MHz, 295 K): δ 177.5 (s, NCN), 147.1 (s, ipso-$C_6H_3Me_2$), 138.4 (s, *m*-$C_6H_3Me_2$), 125.7 (d, *o*-$C_6H_3Me_2$), 123.5 (s, C_5Me_5), 121.8 (d, *p*-$C_6H_3Me_2$), 52.9 (t, CH_2N), 29.6 (t, CH_2CNN), 23.5 (t, CH_2CH_2CNN), 21.6 (q, $C_6H_3Me_2$), 12.1 (q, C_5Me_5) ppm. ^{15}N NMR (benzene-d_6, 60.81 MHz, 295 K): δ 190 (NCNxyl), 174 (*N*CNxyl) ppm. IR (KBr): ν 2913 (m), 2864 (m), 1653 (s), 1595 (m), 1507 (s), 1465 (m), 1379 (m), 1294 (m), 1190 (m), 1107 (m), 1026 (m), 850 (m), 803 (m), 731 (w), 682 (w) cm^{-1}. Mass spectrometry (HR-EI+): calcd 572.1234 u, 570.1222 u, 571.1227 ($C_{22}H_{30}Cl_2N_2Hf$); found 572.1215 u (Δ = 2.1 mmu), 570.1218 u (Δ = −0.5 mmu), 571.1191 u (Δ = 0.3 mmu). Anal. Calcd: C, 46.20; H, 5.29; N, 4.90. Found: C, 45.98; H, 5.17; N, 4.40.

[Cp*Zr(N_{xyl}N)($NHNPh_2$)Cl] (2a). A 500 mg portion (1.032 mmol) of Cp*Zr(N_{Xyl}N)Cl_2 (**6**) was dissolved in 10 mL of THF in an oven-dried Schlenk-flask and cooled to −78 °C. A 196 mg portion of $LiNHNPh_2$ (1.032 mmol) was dissolved in 20 mL of THF and slowly added dropwise at this temperature. The reaction mixture was then warmed to room temperature and stirred for 24 h. The solvent was evaporated under reduced pressure, the residue was redissolved in 40 mL of toluene, and this solution was centrifuged and filtered. Toluene was evaporated under reduced pressure, and the residue was washed with pentane to yield 457 mg (0.723 mmol, 70%) of a violet-brown solid. ^{1}H NMR (benzene-d_6, 600.1 MHz, 295 K): δ 7.19 (d, 4 H, $^3J_{H-H}$ = 7.9 Hz, *o*-ZrNHN(C_6H_5)$_2$), 6.98 (t, 4 H, $^3J_{H-H}$ = 7.5 Hz, *m*-ZrNHN(C_6H_5)$_2$), 6.98 (s, 2 H, *o*-$C_6H_3Me_2$), 6.81 (t, 2 H, $^3J_{H-H}$ = 7.4 Hz, *p*-ZrNHN(C_6H_5)$_2$), 6.63 (s, 1 H, *p*-$C_6H_3Me_2$), 6.07 (s, 1 H, ZrN*H*NPh_2), 3.64−3.55 (broad m, 1 H, NCH_2-a), 3.15−3.06 (broad m, 1 H, NCH_2-b), 2.25 (s, 6 H, $C_6H_3Me_2$), 2.01 (s, 15 H, C_5Me_5), 1.34−1.26 (broad m, 1 H, CH_2CH_2CNN-a), 1.07−0.99 (broad m, 1 H, CH_2CH_2CNN-b); CH_2CNN *not observed* ppm. ^{13}C NMR (benzene-d_6, 150.9 MHz, 295 K): δ 178.9 (s, NCN), 153.1 (s, ipso-ZrNHN(C_6H_5)$_2$), 137.6 (s, *m*-$C_6H_3Me_2$), 128.5 (d, *m*-ZrNHN-(C_6H_5)$_2$), 124.8 (d, *p*-ZrNHN(C_6H_5)$_2$), 123.0 (d, *p*-$C_6H_3Me_2$), 121.9 (d, *o*-ZrNHN(C_6H_5)$_2$), 120.4 (s, C_5Me_5), 51.8 (t, NCH_2), 30.3 (t, CH_2CNN), 23.2 (t, CH_2CH_2CNN), 21.7 (q, $C_6H_3Me_2$), 11.9 (q, C_5Me_5) ppm. ^{15}N NMR (benzene-d_6, 60.81 MHz, 295 K): δ 216 (d, $^1J_{N-H}$ = 74 Hz, Zr*N*HNPh_2), 94 (ZrN*N*Ph_2) ppm; *N*CNxyl, NC*N*xyl *not observed*. IR (KBr, cm^{-1}): ν 3297 (w, *NH*), 2963 (m), 2908 (m), 2858 (m), 1590 (s), 1522 (m), 1491 (s), 1291 (m), 1262 (s), 1181 (m), 1098 (s), 1026 (s), 804 (s), 750 (s), 693 (s), 612 (m). Due to the compound's instability, no elemental analysis could be performed.

[Cp*Hf(N_{xyl}N)($NHNPh_2$)Cl] (2b). A 500 mg portion (0.874 mmol) of Cp*Hf(N_{xyl}N)Cl_2 was dissolved in 15 mL of toluene and cooled to −78 °C. A 166 mg portion (0.874 mmol) of $LiNHNPh_2$ was dissolved in 10 mL of toluene and slowly added dropwise to the reaction solution at this temperature. The reaction mixture was stirred at room temperature for 40 h and then centrifuged (10 min at 2000 rpm) and filtered. The solvent was removed from the supernatant under reduced pressure to yield 510 mg (0.709 mmol, 81%) of a light brown solid. For labeling experiments, a batch of this compound which had been ^{15}N-labeled in the N_α position was synthesized the same way using $Li^{15}NHNPh_2$. ^{1}H NMR (benzene-d_6, 600.1 MHz, 295 K): δ 7.19 (d, 4 H, $^3J_{H-H}$ = 8.3 Hz, *o*-HfNHN(C_6H_5)$_2$), 7.00 (t, 4 H, $^3J_{H-H}$ = 8.3 Hz, *m*-HfNHN(C_6H_5)$_2$), 6.96 (s, 2 H, *o*-$C_6H_3Me_2$), 6.81 (t, 2 H, $^3J_{H-H}$ = 7.4 Hz, *p*-HfNHN(C_6H_5)$_2$), 6.62 (s, 1 H, *p*-$C_6H_3Me_2$), 6.38 (s, 1 H, HfN*H*N(C_6H_5)$_2$), 3.07 (broad m, 1 H, CH_2N-a), [CH_2CNN-a and b overlaid, but observed in HSQC: 2.25, 2.15 ppm], 2.24 (s, 6 H, $C_6H_3Me_2$), 2.05 (s, 15 H, C_5Me_5), 1.29 (broad s, 1 H, CH_2CH_2CNN-a), 1.04 (broad s, 1 H, CH_2CH_2CNN-a) ppm. ^{13}C NMR (benzene-d_6, 150.9 MHz, 295 K): δ 178.6 (s, NCN), 153.3 (s, ipso-HfNHN-(C_6H_5)$_2$), 137.6 (s, *m*-$C_6H_3Me_2$), 129.2 (d, *m*-HfNHN(C_6H_5)$_2$), 124.6 (d, *p*-$C_6H_3Me_2$), 123.0 (d, *p*-HfNHN(C_6H_5)$_2$), 121.9 (d, *o*-$C_6H_3Me_2$), 119.8 (d, *o*-HfNHN(C_6H_5)$_2$), 118.7 (s, C_5Me_5), 51.7 (t, CH_2N), 30.5 (t, CH_2CNN), 23.5 (t, CH_2CH_2CNN), 21.7 (q, $C_6H_3Me_2$), 11.7 (q, C_5Me_5) ppm. ^{15}N NMR (benzene-d_6, 60.81 MHz, 295 K): δ 211 (d, $^1J_{N-H}$ = 74 Hz, Hf*N*HNPh_2), 183 (NC*N*xyl), 168 (*N*CNxyl), 91 (HfNH*N*Ph_2) ppm. IR (KBr): ν 3328 (w, *NH*), 2962 (m), 2908 (m), 1589 (s), 1522 (s), 1490 (s), 1291 (m), 1184 (m), 1101 (m), 1026 (m), 749 (m), 693 (m), 612 (w) cm^{-1}. Anal. Calcd: C, 56.74; H, 5.74; N, 7.79. Found: C, 56.27; H, 5.71; N, 7.45.

[Cp*Zr(N_{xyl}N)($NNPh_2$)DMAP] (3a). A 300 mg portion (0.619 mmol) of Cp*Zr(N_{Xyl}N)Cl_2 (**6**) was dissolved in 20 mL of THF and cooled to −78 °C. A 118 mg portion (0.619 mmol) of $LiNHNPh_2$ was dissolved in 10 mL of THF and slowly added dropwise at this temperature. The reaction mixture was warmed to room temperature and stirred for 27 h. Then 84 mg (0.619 mmol) of DMAP was added, and 104 mg (0.619 mmol) LiHMDS was dissolved in THF and slowly added dropwise at −78 °C. The reaction mixture was slowly warmed to room temperature and stirred for 23 h, the solvent was subsequently evaporated under reduced pressure, the residue was taken up in toluene, and this solution was filtered. Toluene was evaporated under reduced pressure, and the resulting foam was washed with pentane, yielding 620 mg (0.863 mmol, 84%) of a bronze-colored solid (major:minor 2:1). Crystals of the major isomer suitable for X-ray diffraction could be obtained from a concentrated solution in hexane at room temperature. *Data for the major component are as follows.* ^{1}H NMR (benzene-d_6, 600.1 MHz, 295 K): δ 8.57 (d, 2 H, $^3J_{H-H}$ = 6.6 Hz, *o*-$NMe_2C_5H_4N$), 7.69 (d, 4 H, $^3J_{H-H}$ = 8.4 Hz, *o*-ZrNN(C_6H_5)$_2$), 7.20 (t, 6 H, $^3J_{H-H}$ = 7.1 Hz, *m*-ZrNN(C_6H_5)$_2$ *and o*- and *p*-$C_6H_3Me_2$), 6.81 (t, 2 H, $^3J_{H-H}$ = 7.2 Hz, *p*-ZrNN(C_6H_5)$_2$), 6.62 (s, 1 H, *p*-$C_6H_3Me_2$), 5.78 (d, 2 H, $^3J_{H-H}$ = 6.6 Hz, *m*-$NMe_2C_5H_4N$), 3.63 (dt, 1 H, $^2J_{H-H}$ = 11.1 Hz, $^3J_{H-H}$ = 6.9 Hz, NCH_2-a), 3.22 (m, 1 H, NCH_2-b), 2.61 (m, 1 H, CH_2CNN-a), 2.26 (s, 6 H, $C_6H_3Me_2$), 2.07 (s, 15 H, C_5Me_5), 2.02 (s, 6 H, $NMe_2C_5H_4N$), 1.70 (broad m, 2 H, CH_2CH_2CNN-a and -b) ppm. ^{13}C NMR (benzene-d_6, 150.9 MHz, 295 K): δ 175.6 (s, NCN), 154.3 (s, ipso-$C_6H_3Me_2$), 152.5 (d, *o*-

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$NMe_2C_5H_4N$), 149.1 (s, ipso-ZrNN(C_6H_5)$_2$), 137.7 (s, *m*-$C_6H_3Me_2$), 128.8 (d, *m*-ZrNN(C_6H_5)$_2$), 123.8 (d, *p*-$C_6H_3Me_2$), 122.8 (d, *o*-$C_6H_3Me_2$), 120.1 (d, *p*-ZrNN(C_6H_5)$_2$), 119.5 (d, *o*-ZrNN(C_6H_5)$_2$), 116.4 (s, C_5Me_5), 105.9 (d, *m*-$NMe_2C_5H_4N$), 53.0 (t, NCH_2), 38.2 (q, $C_6H_3Me_2$), 29.9 (t, CH_2CNN), 23.9 (t, CH_2CH_2CNN), 21.7 (q, $C_6H_3Me_2$), 11.8 (q, C_5Me_5) ppm. ^{15}N NMR (benzene-d_6, 60.81 MHz, 295 K): δ 286 ($ZrNNPh_2$), 238 ($NMe_2C_5H_4N$), 177 ($ZrNNPh_2$), 175 (*N*CNxyl) 173 (NC*N*xyl), 62 ($Me_2NC_5H_4N$) ppm. *Data for the minor component are as follows.* ^{1}H NMR (benzene-d_6, 600.1 MHz, 295 K): δ 8.29 (d, 2 H, $^3J_{H-H}$ = 6.7 Hz, *o*-$NMe_2C_5H_4N$), 7.70 (d, 4 H, $^3J_{H-H}$ = 8.6 Hz, *o*-ZrNN(C_6H_5)$_2$), 7.27 (t, 4 H, $^3J_{H-H}$ = 7.7 Hz, *m*-ZrNN(C_6H_5)$_2$), 6.88 (t, 2 H, $^3J_{H-H}$ = 7.2 Hz, *p*-ZrNN(C_6H_5)$_2$), 6.57 (s, 1 H, *p*-$C_6H_3Me_2$), 6.43 (s, 2 H, *o*-$C_6H_3Me_2$), 5.58 (d, 2 H, $^3J_{H-H}$ = 6.5 Hz, *m*-$NMe_2C_5H_4N$), 3.92 (m, 1 H, NCH_2-a), 3.71 (dt, 1 H, $^2J_{H-H}$ = 11.3 Hz, $^3J_{H-H}$ = 7.4 Hz, NCH_2-b), 2.10 (s, 6 H, $C_6H_3Me_2$), 2.09 (s, 15 H, C_5Me_5), 1.95 (s, 6 H, $NMe_2C_5H_4N$); CH_2CNN and CH_2CH_2N *not observed directly* ppm. ^{13}C NMR (benzene-d_6, 150.9 MHz, 295 K): δ 175.8 (s, NCN), 154.1 (s, ipso-$C_6H_3Me_2$), 152.6 (d, *o*-$NMe_2C_5H_4N$), 149.1 (s, ipso-ZrNN(C_6H_5)$_2$), 137.4 (s, *m*-$C_6H_3Me_2$), 124.1 (d, *o*-$C_6H_3Me_2$), 123.8 (d, *p*-$C_6H_3Me_2$), 120.0 (d, *p*-ZrNN(C_6H_5)$_2$), 119.7 (d, *o*-ZrNN(C_6H_5)$_2$), 116.1 (s, C_5Me_5), 105.5 (d, *m*-$NMe_2C_5H_4N$), 55.3 (t, NCH_2), 38.0 (q, $NMe_2C_5H_4N$), 29.9 (t, CH_2CNN), 23.8 (t, CH_2CH_2CNN), 21.5 (q, $C_6H_3Me_2$), 11.8 (q, C_5Me_5) ppm; *m*-ZrNN(C_6H_5)$_2$ could not be assigned. ^{15}N NMR (benzene-d_6, 60.81 MHz, 295 K): δ 281 ($ZrNNPh_2$), 236 ($Me_2NC_5H_4N$), 171 ($ZrNNPh_2$), 59 ($Me_2NC_5H_4N$) ppm; *N*CNxyl, NC*N*xyl *not observed.* IR (KBr, cm^{-1}): ν 3054 (w), 3023 (w), 2962 (m), 2906 (m), 20855 (m), 1605 (s), 1523 (s), 1487 (s), 1378 (m), 1289 (m), 1226 (m), 1095 (m), 1010 (m), 805 (m), 748 (m), 693 (m), 624 (w), 534 (w), 500 (w). Anal. Calcd: C, 68.58; H, 7.02; N, 11.70. Found: C, 67.99; H, 7.33; N, 10.78.

[Cp*Hf(N_{xyl}N)($NNPh_2$)DMAP] (3b). A 500 mg portion (0.695 mmol) of Cp*Hf(N_{Xyl}N)Cl($NHNPh_2$) was dissolved in 40 mL of toluene. A 120 mg portion (0.695 mmol) of LiHMDS was dissolved in 10 mL of toluene and slowly added dropwise at −78 °C. The reaction mixture was slowly warmed to room temperature over 7 h and stirred at room temperature overnight. An 85 mg portion (0.695 mmol) of dmap was added, and the reaction mixture was then heated to 60 °C for 3 h and subsequently filtered. The solvent was removed from the filtrate under reduced pressure to yield 560 mg (0.695 mmol, 98%) of a brown solid, composed of of two isomers (3:1). Single crystals suitable for X-ray diffraction were obtained from a concentrated hexane solution. *Data for the major component are as follows.* ^{1}H NMR (benzene-d_6, 600.1 MHz, 295 K): δ 8.60 (d, 2 H, $^3J_{H-H}$ = 6.5 Hz, *o*-$NMe_2C_5H_4N$), 7.77 (dd, 4 H, $^3J_{H-H}$ = 8.5 Hz, $^4J_{H-H}$ = 1.1 Hz, *o*-HfNN(C_6H_5)$_2$), 7.25 (s, 2 H, *o*-$C_6H_3Me_2$), 7.21 (t, 4 H, $^3J_{H-H}$ = 8.5 Hz, *m*-HfNN(C_6H_5)$_2$), 6.80 (t, 2 H, $^3J_{H-H}$ = 7.8 Hz, *p*-HfNN-(C_6H_5)$_2$), 6.63 (s, 1 H, *p*-$C_6H_3Me_2$), 5.74 (d, 2 H, $^3J_{H-H}$ = 6.8 Hz, *m*-$NMe_2C_5H_4N$), 3.56 (dt, 1 H, $^2J_{H-H}$ = 11.2 Hz, $^3J_{H-H}$ = 7.1 Hz, CH_2N-a), 3.17 (m, 1 H, CH_2N-b), 2.58 (dt, 1 H, $^2J_{H-H}$ = 8.5 Hz, $^3J_{H-H}$ = 16.3 Hz, CH_2CNN-a), 2.26 (s, 6 H, $C_6H_3Me_2$), 2.22−2.17 (m, 1 H, CH_2CNN-b), 2.09 (s, 15 H, C_5Me_5), 1.98 (s, 6 H, $NMe_2C_5H_4N$), 1.97 (broad m, 1 H, CH_2CH_2CNN-a), 1.14 (broad m, 1 H, CH_2CH_2CNN-b) ppm. ^{13}C NMR (benzene-d_6, 150.9 MHz, 295 K): δ 175.2 (s, NCN), 152.6 (d, *o*-$NMe_2C_5H_4N$), 151.1 (s, ipso-$C_6H_3Me_2$), 149.7 (s, ipso-HfNN(C_6H_5)$_2$), 137.8 (s, *m*-$C_6H_3Me_2$), 128.7 (d, *m*-HfNN-(C_6H_5)$_2$), 124.0 (d, *p*-$C_6H_3Me_2$), 122.9 (d, *o*-$C_6H_3Me_2$), 119.8 (d, *p*-HfNN(C_6H_5)$_2$), 119.5 (d, *o*-HfNN(C_6H_5)$_2$), 115.7 (s, C_5Me_5), 105.8 (d, *m*-$NMe_2C_5H_4N$), 52.7 (t, CH_2N), 38.1 (q, $NMe_2C_5H_4N$), 29.9 (t, CH_2CNN), 24.1 (t, CH_2CH_2CNN), 21.7 (q, $C_6H_3Me_2$), 11.8 (q, C_5Me_5) ppm. ^{15}N NMR (benzene-d_6, 60.81 MHz, 295 K): δ 280 ($HfNNPh_2$), 237 ($NMe_2C_5H_4N$), 172 ($HfNNPh_2$), 62 ($NMe_2C_5H_4N$) ppm. *Data for the minor component are as follows.* ^{1}H NMR (benzene-d_6, 600.1 MHz, 295 K): δ 8.35 (d, 2 H, $^3J_{H-H}$ = 7.1 Hz, *o*-$NMe_2C_5H_4N$), 7.72 (d, 4 H, $^3J_{H-H}$ = 8.2 Hz, *o*-HfNN(C_6H_5)$_2$), 7.30 (t, 4 H, $^3J_{H-H}$ = 7.8 Hz, *m*-HfNN(C_6H_5)$_2$), 6.88 (t, 2 H, $^3J_{H-H}$ = 7.2 Hz, *m*-HfNN(C_6H_5)$_2$), 6.68 (s, 1 H, *p*-$C_6H_3Me_2$), 5.56 (d, 2 H, $^3J_{H-H}$ = 7.2 Hz, *m*-$NMe_2C_5H_4N$), 3.86 (m, 1 H, CH_2N-a), 3.70 (dt, 1 H, $^2J_{H-H}$ = 11.1 Hz, $^3J_{H-H}$ = 7.2 Hz, CH_2N-b), 2.10 (s, 6 H, $C_6H_3Me_2$), 1.93 (s, 15 H, C_5Me_5) ppm; CH_2CNN, CH_2CH_2CNN not observed. ^{13}C NMR (benzene-d_6, 150.9 MHz, 295 K): δ 179.1 (s, NCN), 152.7 (d, *o*-$NMe_2C_5H_4N$), 151.3 (s, ipso-$C_6H_3Me_2$), 149.8 (s, ipso-HfNN(C_6H_5)$_2$), 137.5 (s, *m*-$C_6H_3Me_2$), 128.7 (d, *m*-HfNN-(C_6H_5)$_2$),124.2 (d, *p*-$C_6H_3Me_2$), 123.3 (d, *o*-$C_6H_3Me_2$), 115.4 (s, C_5Me_5), 105.5 (d, *m*-$NMe_2C_5H_4N$), 52.3 (t, CH_2N), 38.0 (q, $NMe_2C_5H_4N$), 30.0 (t, CH_2CNN), 24.0 (t, CH_2CH_2CNN), 21.5 (q, $C_6H_3Me_2$), 11.7 (q, C_5Me_5) ppm. IR (KBr): ν 3023 (w), 2908 (m), 2857 (m), 1601 (s), 1523 (s), 1489 (s), 1444 (m), 1377 (m), 1290 (m), 1262 (m), 1227 (m), 1185 (m), 1100 (m), 1065 (m), 1012 (m), 994 (m), 950 (w), 877 (w), 805 (m), 749 (m), 693 (m), 623 (w), 534 (w), 499 (w) cm^{-1}. Anal. Calcd: C, 61.14; H, 6.26; N, 10.44. Found: C, 60.68; H, 6.49; N, 9.82.

[Cp*Hf(N_{xyl}N)($NNPh_2$){N($SiMe_3$)$_2$}Li] (4). A 169 mg portion (0.236 mmol) of Cp*Hf(N_{Xyl}N)Cl($NHNPh_2$) was dissolved in 10 mL of toluene, and 81 mg (0.472 mmol, 2 equiv) of LiHMDS was added. After it was stirred overnight, the reaction mixture was filtered, and the filtrate was evaporated to dryness under reduced pressure and washed with hexane to yield 41 mg (0.060 mmol, 25%) of a crystalline yellow solid. Crystals suitable for X-ray diffraction were grown from a concentrated solution in hexane at −40 °C. ^{1}H NMR (benzene-d_6, 600.1 MHz, 295 K): δ 7.32 (d, 4 H, $^3J_{H-H}$ = 8.1 Hz, *o-Ph*), 7.15 (t, 4 H, $^3J_{H-H}$ = 7.9 Hz, *m-Ph*), 6.89 (t, 2 H, $^3J_{H-H}$ = 7.4 Hz, *p-Ph*), 6.56 (s, 1 H, *p*-$C_6H_3Me_2$), 6.36 (s, 2 H, *o*-$C_6H_3Me_2$), 3.82−3.76 (m, 2 H, CH_2N), 2.13 (CH_2CNN, *only observed in H,H-Cosy and HSQC*), 2.11 (s, 6 H, $C_6H_3Me_2$), 2.10 (s, 15 H, C_5Me_5), 1.66−1.57 (m, 2 H, CH_2CH_2CNN), 0.25 (broad s, 18 H, N($SiMe_3$)$_2$) ppm. ^{13}C NMR (benzene-d_6, 150.9 MHz, 295 K): δ 179.5 (NCN), 153.1 (*m*-$C_6H_3Me_2$), 151.2 (ipso-*Ph*), 138.9 (ipso-$C_6H_3Me_2$), 128.6 (*m*-Ph), 124.9 (*p*-$C_6H_3Me_2$), 121.6 (*o*-$C_6H_3Me_2$), 121.1 (*p-Ph*), 120.3 (*o-Ph*), 118.2 (C_5Me_5), 55.4 (CH_2N), 30.9 (CH_2CNN), 25.6 (CH_2CH_2CNN), 21.4 ($C_6H_3Me_2$), 12.8 (C_5Me_5), 6.7 ($SiMe_3$) ppm. ^{15}N NMR (benzene-d_6, 60.81 MHz, 295 K): δ 263 ($NNPh_2$), 196 (NCNxyl), 147 ($NNPh_2$) ppm; NCNxyl, *N*($SiMe_3$)$_2$ *not observed.* ^{29}Si NMR (benzene-d_6, 79.45 MHz, 295 K): δ −22 ppm. ^{7}Li NMR (benzene-d_6, 155.4 MHz, 295 K): δ 1.89 ppm. A ^{15}N-labeled version of **4** was generated in situ by dissolving 20 mg of ^{15}N-**2b** in 0.5 mL of benzene-d_6 in a J. Young NMR tube and adding 9.6 mg of LiHMDS. After 2 h, spectra were recorded on a 600 MHz (^{15}N) or a 400 MHz (^{6}Li, ^{7}Li). ^{7}Li NMR (benzene-d_6, 155.4 MHz, 323 K): δ 1.92 (d, $^1J_{7Li,15N}$ = 5.1 Hz) ppm. ^{6}Li NMR (benzene-d_6, 58.8 MHz, 295 K): δ 1.91 ppm (d, $^1J_{6Li,15N}$ = 2.0 Hz) ppm. IR (KBr): ν 3061 (w), 2954 (m), 2901 (m9, 2861 (m), 1588 (m), 1560 (s), 1489 (s), 1449 (m), 1372 (m), 1260 (s), 1189 (w), 1164 (m), 1136 (m), 1076 (w), 1025 (w), 996 (w), 916 (s), 853 (s), 784 (m), 751 (m), 669 (m), 620 (w), 576 (w), 538 (w) cm^{-1}. Mass spectrometry (HR-FAB): calcd 684.2718 u, 682.2690 u, 681.2685 u ($C_{34}H_{40}N_4Hf$); found 684.2721 u (Δ = 0.2 mmu), 682.2685 u (Δ = −0.5 mmu), 681.2709 u (Δ = 2.2 mmu). Anal. Calcd: C, 56.49; H, 6.87; N, 8.23. Found: C, 56.59; H, 6.95; N, 8.14.

[Cp*Hf(N_{xyl}N)(NMe_2)$_2$] (5). A 200 mg portion (0.350 mmol) of Cp*Hf(N_{xyl}N)Cl_2 (**2b**) was dissolved in 10 mL of toluene, 36 mg (0.699 mmol, 2 equiv) of $LiNMe_2$ was added, and the mixture was stirred for 41 h and then centrifuged (10 min at 2000 rpm) and filtered. The filtrate was evaporated under reduced pressure to yield 148 mg (0.251 mmol, 72%) of a brown solid. ^{1}H NMR (benzene-d_6, 600.1 MHz, 295 K): δ 6.59 (s, 1 H, *p*-$C_6H_3Me_2$), 6.51 (s, 2 H, *o*-$C_6H_3Me_2$), 3.41 (t, 2 H, $^3J_{H-H}$ = 6.8 Hz, CH_2N), 3.09 (s, 12 H, NMe_2), 2.30 (s, 6 H, $C_6H_3Me_2$), 2.30−2.27 (m, 2 H, CH_2CNN), 2.03 (C_5Me_5), 1.47 (quin, 2 H, $^3J_{H-H}$ = 7.2 Hz, CH_2CH_2CNN) ppm. ^{13}C NMR (benzene-d_6, 150.9 MHz, 295 K): δ 176.9 (NCN), 148.0 (ipso-$C_6H_3Me_2$), 137.8 (*m*-$C_6H_3Me_2$), 122.5 (*p*-$C_6H_3Me_2$), 119.8 (*o*-$C_6H_3Me_2$), 117.4 (C_5Me_5), 51.7 (CH_2N), 43.6 (NMe_2), 31.6 (CH_2CNN), 24.2 (CH_2CH_2CNN), 21.9 ($C_6H_3Me_2$), 11.3 (C_5Me_5) ppm. ^{15}N NMR (benzene-d_6, 60.81 MHz, 295 K): δ 184 (NCNxyl), 167 (NCNxyl) ppm. IR (KBr): ν 2964 (w), 2908 (w), 2860 (w), 2757 (w), 1638 (w), 1592 (m), 1521 (m), 1455 (m), 1375 (w), 1322 (w), 1294 (m), 1262 (m), 1187 (m), 1097 (s), 1021 (s), 957 (m), 928 (m), 867 (m), 799 (s), 686 (m), 524 (m) cm^{-1}. Mass spectrometry (HR-EI): calcd 590.2879 u, 589.2873 u, 588.2851 u, 587.2843 u ($C_{26}H_{42}N_4Hf$); found 590.2891 u (Δ = 1.6 mmu), 589.2911 u (Δ =

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4.3 mmu), 588.2891 u (Δ = 4.4 mmu), 587.2844 u (Δ = 0.2 mmu). Anal. Calcd: C, 53.01; H, 7.19; N, 9.51. Found: C, 53.50; H, 6.53; N, 9.09.

[Cp*Hf(N_{xyl}N)($NHNPh_2$)$_2$] (6). A 170 mg portion (0.289 mmol) of Cp*Hf(N_{xyl}N)(NMe_2)$_2$ (**19**) and 106 mg (0.577 mmol, 2 equiv) of Ph_2NNH_2 were dissolved in 10 mL of toluene and heated to 70 °C for 14 h. Subsequently the reaction mixture was filtered, and the solvent was removed under reduced pressure to yield 218 mg (0.240 mmol, 83%) of a brown oil. ^{1}H NMR (benzene-d_6, 600.1 MHz, 295 K): δ 7.20 (d, 4 H, $^3J_{H-H}$ = 8.2 Hz, *o-Ph*), 7.1 (t, 4 H, $^3J_{H-H}$ = 7.7 Hz, *m-Ph*), 6.78 (t, 2 H, $^3J_{H-H}$ = 7.3 Hz, *p-Ph*), 6.69 (s, 2 H, *o*-$C_6H_3Me_2$), 6.55 (s, 2 H, *p*-$C_6H_3Me_2$), 5.90 (s, 2 H, N*H*NPh$_2$), 3.31 (t, 2 H, $^3J_{H-H}$ = 6.8 Hz, CH_2N), 2.12 (s, 6 H, $C_6H_3Me_2$), 1.98 (CH_2CNN, *only observed in H,H−COSY and HSQC*), 1.93 (s, 15 H, C_5Me_5), 1.15 (quin, 2 H, $^3J_{H-H}$ = 7.2 Hz, CH_2CH$_2$CNN) ppm. ^{13}C NMR (benzene-d_6, 150.9 MHz, 295 K): δ 179.1 (NCN), 150.7 (ipso-*Ph*), 148.3 (*m*-$C_6H_3Me_2$), 137.9 (ipso-$C_6H_3Me_2$), 128.6 (*m*-Ph), 124.9 (*p*-$C_6H_3Me_2$), 123.3 (*o*-$C_6H_3Me_2$), 122.4 (*p-Ph*), 121.8 (*o-Ph*), 118.5 (C_5Me_5), 52.3 (CH$_2$N), 30.5 (CH$_2$CNN), 23.2 (CH$_2$CH$_2$CNN), 21.4 ($C_6H_3Me_2$), 11.4 (C_5Me_5) ppm. ^{15}N NMR (benzene-d_6, 60.81 MHz, 295 K): δ 206 (d, $^1J_{N-H}$ = 66 Hz, *N*HNPh$_2$), 169 (NC*N*xyl), 119 (NH*N*Ph$_2$) ppm. IR (KBr): ν 3342 (w), 3057 (w), 2963 (w), 2910 (w), 2859 (w), 2859 (w), 1587 (m), 1522 (m), 1490 (m), 1457 (m), 1376 (m), 1319 (m), 1262 (m), 1184 (m), 1154 (m), 1099 (m), 1072 (m), 1027 (m), 954 (w), 800 (m), 749 (s), 693 (s), 619 (m), 567 (w) cm^{-1}. Anal. Calcd: C, 60.73; H, 5.76; N, 9.24 (for **6**-LiCl). Found: C, 61.29; H, 6.11; N, 9.36.

[Cp*Zr(N_{xyl}N){κ^2-N^{i}PrC($NNPh_2$)N^{i}Pr}] (7). A 300 mg portion (0.418 mmol) of Cp*Zr(N_{xyl}N)($NNPh_2$)dmap (**3a**) was dissolved in toluene (10 mL), and 52 μL (0.334 mmol, 0.8 equiv) of ^{i}PrNCN^{i}Pr was added. After the mixture was stirred for 30 min at room temperature, the solvent was removed under reduced pressure and the residue washed with hexane. The residue was then dissolved in diethyl ether (5 mL) and this solution was layered with hexane (10 mL), which resulted in precipitation of a solid. After 30 min, the suspension was filtered, the filtrate was cooled to −30 °C for 2 days, the solution was again filtered, and the filtrate was evaporated to dryness under reduced pressure and washed with hexane to yield 20 mg (0.024 mmol, 6%) of a brown solid. Single crystals of the DMAP adduct suitable for X-ray diffraction were obtained from a concentrated solution in diethyl ether/hexane. *Data for the major component are as follows.* ^{1}H NMR (benzene-d_6, 600.1 MHz, 295 K): δ 7.44 (d, 4 H, $^3J_{H-H}$ = 7.8 Hz, *o-Ph*), 7.31 (s, 2 H, *o*-$C_6H_3Me_2$), 7.20 (t, 4 H, $^3J_{H-H}$ = 8.0 Hz, *m-Ph*), 6.87−6.82 (m, 2 H, *p-Ph*), 6.61 (s, 1 H, *p*-$C_6H_3Me_2$), 3.84−3.78 (m, 1 H, C*H*Me$_2$-a), 3.77−3.71 (m, 1 H, CH_2N-a), 3.62−3.55 (m, CH_2N-b), 3.45−3.38 (m, 1 H, C*H*Me$_2$-b), 2.86−2.80 (m, 1 H, CH_2CNN-a), 2.34 (s, 6 H, $C_6H_3Me_2$), 2.31−2.29 (m, 1 H, CH_2CNN-b), 1.86 (s, 15 H, C_5Me_5), 1.72−1.66 (m, 2 H, CH_2CH$_2$CNN), 1.54 (d, 3 H, $^3J_{H-H}$ = 6.6 Hz, CH*Me*$_2$-a), 1.07 (d, 3 H, $^3J_{H-H}$ = 6.3 Hz, CH*Me*$_2$-a), 0.53 (d, 3 H, $^3J_{H-H}$ = 6.2 Hz, CH*Me*$_2$-b), 0.50 (d, 3 H, $^3J_{H-H}$ = 6.0 Hz, CH*Me*$_2$-a) ppm. ^{13}C NMR (benzene-d_6, 150.9 MHz, 295 K): δ 173.7 (NCN), 165.9 (C=NNPh$_2$), 159.3 (*m*-$C_6H_3Me_2$), 150.4 129.1 (*m-Ph*), 123.9 (C_5Me_5), 123.3 (*p*-$C_6H_3Me_2$), 122.1 (*p-Ph*), 121.3 (*o*-$C_6H_3Me_2$), 121.0 (*o-Ph*), 52.7 (CH$_2$N), 47.5 (C*H*Me$_2$-a), 45.7 (C*H*Me$_2$-b), 31.6 (CH$_2$CNN), 24.2 (CH*Me*$_2$-a), 24.1 (CH*Me*$_2$-b), 23.9 (CH*Me*$_2$-a), 23.7 (CH*Me*$_2$-b), 22.9 (CH$_2$CH$_2$CNN), 21.9 ($C_6H_3Me_2$), 12.1 (C_5Me_5) ppm. *Data for the minor component are as follows.* ^{1}H NMR (benzene-d_6, 600.1 MHz, 295 K): δ 7.61 (d, 4 H, $^3J_{H-H}$ = 8.5 Hz, *o-Ph*), 7.26 (t, 4 H, $^3J_{H-H}$ = 8.3 Hz, *m-Ph*), 6.78 (s, 2 H, *o*-$C_6H_3Me_2$), 6.77−6.74 (m, 2 H, *p-Ph*), 6.60 (s, 1 H, *p*-$C_6H_3Me_2$), 3.94 (sep, 1 H, $^3J_{H-H}$ = 6.6 Hz, C*H*Me$_2$-a), 3.77−3.71 (m, 1 H, CH_2N-a), 3.68−3.63 (m, 1 H, CH_2N-b), 3.62−3.55 (m, C*H*Me$_2$-b), 2.35 (s, 6 H, $C_6H_3Me_2$), 1.89 (s, 15 H, C_5Me_5), 1.49 (d, 3 H, $^3J_{H-H}$ = 5.9 Hz, CH*Me*$_2$-a), 1.05 (d, 3 H, $^3J_{H-H}$ = 6.5 Hz, CH*Me*$_2$-a), 0.73 (d, 3 H, $^3J_{H-H}$ = 6.3 Hz, CH*Me*$_2$-b), 0.65 (d, 3 H, $^3J_{H-H}$ = 6.1 Hz, CH*Me*$_2$-b) ppm. ^{13}C NMR (benzene-d_6, 150.9 MHz, 295 K): δ 143.8 (ipso-*Ph*), 129.0 (*m-Ph*), 123.7 (C_5Me_5), 129.9 (*o*-$C_6H_3Me_2$), 121.9 (*p-Ph*), 119.2 (*o-Ph*), 53.1 (CH$_2$N), 47.8 (C*H*Me$_2$-a), 46.4 (CHMe$_2$-b), 32.0 (CH$_2$CNN), 23.1 (CH$_2$CH$_2$CNN), 21.7 ($C_6H_3Me_2$), 12.1 (C_5Me_5) ppm; NCN, *C*=NNPh$_2$, ipso-, *m-* and *p*-$C_6H_3Me_2$, CHMe$_2$ *not observed.* IR (KBr): ν 2964 (m), 2912 (m), 2860 (m), 1595 (s), 1560 (m), 1541 (m), 1522 (m), 1490 (s), 1383 (m), 1319 (w), 1292 (w), 1229 (w), 1262 (m), 1099 (m), 1026 (m), 885 (s), 749 (m), 693 (m), 617 (w) cm^{-1}. Despite numerous attempts, we have not been able to obtain an elemental analysis, probably due to the instability of the compound.

[Cp*Zr(N_{xyl}N){κ^2-N(NPh_2)C(N^{i}Pr)N^{iPr}C(N^{i}Pr)N^{iPr}}] (8). A 300 mg portion (0.418 mmol) of Cp*Zr(N_{xyl}N)($NNPh_2$)dmap (**3a**) was dissolved in toluene (10 mL), and 130 μL (0.836 mmol) of ^{i}PrNCN^{i}Pr was added. After the mixture was stirred for 30 min at room temperature, the solvent was removed under reduced pressure, and the residue was washed with hexane to yield 234 mg (0.241 mmol, 58%) of a dark brown solid. ^{1}H NMR (benzene-d_6, 600.1 MHz, 295 K): δ 7.52 (d, 4 H, $^3J_{H-H}$ = 8.0 Hz, *o-Ph*), 7.30 (t, 2 H, $^3J_{H-H}$ = 7.8 Hz, *m-Ph*-a), 7.22 (t, 2 H, $^3J_{H-H}$ = 7.9 Hz, *m-Ph*-b), 6.88 (t, 1 H, $^3J_{H-H}$ = 7.3 Hz, *p-Ph*-b), 6.84 (s, 2 H, *o*-$C_6H_3Me_2$), 6.84 (m, 1 H, *p-Ph*-a), 6.59 (s, 1 H, *p*-$C_6H_3Me_2$), 5.32 (sep, 1 H, $^3J_{H-H}$ = 5.9 Hz, ZrN(NPh$_2$)C=NC*H*Me$_2$), 4.65 (sep, 1 H, $^3J_{H-H}$ = 6.5 Hz, ZrN^{iPr}C(N^{i}Pr)NC*H*Me$_2$), 4.39−4.31 (sep, sep, ZrN^{iPr}C=NC*H*Me$_2$ and ZrNC*H*Me$_2$), 3.64−3.54 (m, 2 H, CH_2N), 2.74−2.67 (m, 1 H, CH_2CNN-a), 2.32 (s, 6 H, $C_6H_3Me_2$), 2.30−2.24 (m, 1 H, CH_2CNN-b), 2.12 (d, 3 H, $^3J_{H-H}$ = 6.8 Hz, ZrN^{iPr}C=NCH*Me*$_2$-a), 1.95 (d, 3 H, $^3J_{H-H}$ = 6.5 Hz, ZrN^{iPr}C=NCH*Me*$_2$-b), 1.66 (s, 15 H, C_5Me_5), 1.64−1.60 (m, 1 H, CH_2CH$_2$CNN-a), 1.58−1.54 (m, 1 H, CH_2CH$_2$CNN-b), 1.31 (d, 3 H, $^3J_{H-H}$ = 6.7 Hz, ZrN^{iPr}C(N^{i}Pr)NCH*Me*$_2$-a), 1.29 (d, 3 H, $^3J_{H-H}$ = 6.1 Hz, ZrN(NPh$_2$)C=NCH*Me*$_2$-a), 1.17 (d, 3 H, $^3J_{H-H}$ = 6.0 Hz, ZrNCH*Me*$_2$-a), 1.08 (d, d, 6 H, $^3J_{H-H}$ = 6.1 and 5.5 Hz, ZrN^{iPr}C(N^{i}Pr)NCH*Me*$_2$-b and ZrN(NPh$_2$)C=NCH*Me*$_2$-b), 0.57 (d, 3 H, $^3J_{H-H}$ = 6.0 Hz, ZrNCH*Me*$_2$-b) ppm. ^{13}C NMR (benzene-d_6, 150.9 MHz, 295 K): δ 176.3 (NCN$_{xyl}$), 147.7 (ZrN^{iPr}*C*=N^{i}Pr), 146.6 (ipso-$C_6H_3Me_2$), 146.1 (ipso-*Ph*), 145.5 (ZrN(NPh$_2$)*C*=N^{i}Pr), 137.9 (*m*-$C_6H_3Me_2$), 129.2 (*m-Ph*-a), 128.5 (*m-Ph*-b), 123.3 (*p*-$C_6H_3Me_2$), 123.2 (C_5Me_5), 120.7 (*p-Ph*-b), 120.5 (*o*-$C_6H_3Me_2$), 120.4 (*p-Ph*-a), 120.2 (*o-Ph*-a), 116.2 (*o-Ph*-b), 53.7 (CH$_2$N), 52.8 (ZrN^{iPr}C=NCHMe$_2$), 50.6 (ZrN^{iPr}C(N^{iPr})NCHMe$_2$), 45.3 (ZrNCHMe$_2$), 45.2 (ZrN(NPh$_2$)C=NCHMe$_2$), 33.1 (CH$_2$CNN), 26.4 (ZrN(NPh$_2$)C=NCH*Me*$_2$-a), 26.1 (ZrNCH*Me*$_2$-a), 25.2 (ZrNCH*Me*$_2$-b), 24.3 (ZrN^{iPr}C=NCH*Me*$_2$-a), 24.0 (ZrN^{iPr}C=NCH*Me*$_2$-b), 23.4 (CH$_2$CH$_2$CNN), 21.6 ($C_6H_3Me_2$), 21.3 (ZrN(NPh$_2$)C=NCH*Me*$_2$-b), 20.8 (ZrN^{iPr}C(N^{iPr})NCH*Me*$_2$-a), 20.5 (ZrN^{iPr}C(N^{iPr})NCH*Me*$_2$-b), 11.7 (C_5Me_5) ppm. ^{15}N NMR (benzene-d_6, 60.81 MHz, 295 K): δ 114 (ZrN^{iPr}C(N^{iPr})*N*^{i}Pr), 123 (*N*NPh$_2$), 168 (NC*N*xyl), 184 (*N*CNxyl), 211 (*N*NPh$_2$), 216 (ZrN^{iPr}C=*N*^{i}Pr), 224 (ZrN^{i}Pr), 244 (Zr(NNPh$_2$)-C=*N*^{i}Pr) ppm. IR (KBr): ν 2962 (m), 2911 (m), 2859 (m), 1662 (s), 1602 (s), 1521 (s), 1490 (s), 1446 (m), 1375 (m), 1319 (m), 1292 (m), 1228 (m), 1191 (m), 1098 (m), 1011 (m), 951 (w), 887 (w), 804 (m), 746 (m), 693 (m), 534 (w) cm^{-1}. Anal. Calcd: C, 67.96; H, 8.08; N, 13.21. Found: C, 67.95; H, 7.39; N, 13.64.

[Cp*Zr(N_{xyl}N){κ^2-N(NPh_2)CHPhNPh}] (9). A 300 mg portion (0.418 mmol) of Cp*Zr(N_{xyl}N)($NNPh_2$)dmap (**3a**) was dissolved in 10 mL of toluene, and 68 mg (0.376 mmol) of *N*-phenylbenzimine was added. After the mixture was stirred for 2 days, the solvent was removed under reduced pressure and the residue washed with hexane to yield 193 mg (0.215 mmol, 51%) of a brown solid. ^{1}H NMR (benzene-d_6, 600.1 MHz, 295 K): δ 7.53 (d, 2 H, $^3J_{H-H}$ = 7.1 Hz, *o*-CH*Ph*), 7.24 (t, 2 H, $^3J_{H-H}$ = 7.4 Hz, *m*-NN*Ph*), 7.22 (s, 1 H, C*H*Ph), 7.14−7.07 (m, H, C*H*-Ar, *o-* and *m*-ZrN*Ph*, *p*-$C_6H_3Me_2$), 7.06−7.02 (m, H, CH-Ar,), 6.96−6.91 (m, H, C*H*-Ar, *p*-NN*Ph*), 6.77 (d, 2 H, $^3J_{H-H}$ = 7.3 Hz, *o*-N*Ph*), 6.69 (s, 2 H, *o*-$C_6H_3Me_2$), 6.61 (d, 2 H, $^3J_{H-H}$ = 7.8 Hz, *o-Ph*), 3.63−3.55 (m, 1 H, CH_2N-a), 3.47−3.41 (m, 1 H, CH_2N-b), 2.37 (m, 1 H, CH_2CNN-a), 2.05 (m, 1 H, CH_2CNN-b), 2.04 (s, 6 H, $C_6H_3Me_2$), 1.94 (s, 15 H, C_5Me_5), 1.47 (m, 1 H, CH_2CH$_2$CNN-a), 1.36 (m, 1 H, CH_2CH$_2$CNN-b) ppm. ^{13}C NMR (benzene-d_6, 150.9 MHz, 295 K): δ 175.2 (NCN), 148.1 (ipso-$C_6H_3Me_2$), 145.1 (ipso-*Ph*), 144.2 (ipso-*Ph*), 138.5 (*m*-$C_6H_3Me_2$), 136.8 (ipso-*Ph*), 135.7, 130.1 (CH Ar), 128.8 (CH Ar), 126.7 (*o*-CH*Ph*), 126.1 (*o-Ph*-b), 124.7 (*p*-$C_6H_3Me_2$), 123.0 (*o*-$C_6H_3Me_2$), 122.9 (C_5Me_5), 117.9 (*o*-NN*Ph*$_2$), 116.9 (*o-Ph*-c), 66.7 (C*H*Ph), 54.4 (CH_2N), 29.8 (CH$_2$CNN), 23.7 (CH$_2$CH$_2$CNN), 21.3 ($C_6H_3Me_2$), 11.3 (C_5Me_5) ppm. ^{15}N NMR (benzene-d_6, 60.81 MHz, 295 K): δ 335

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(Zr*N*NPh$_2$), 196 (ZrN*N*Ph$_2$), 173 (NC*N*xyl), 149 (Zr*N*Ph) ppm. IR (KBr): ν 3025 (w), 2908 (m), 2857 (m), 1602 (s), 1560 (m), 1522 (s), 1490 (s), 1376 (m), 1289 (m), 1263 (m), 1229 (m), 1176 (w), 1095 (m), 1063 (w), 1025 (w), 1009 (w), 950 (w), 874 (w), 805 (m), 751 (m), 693 (m), 657 (w) cm^{-1}. Anal. Calcd: C, 72.64; H, 6.61; N, 9.01. Found: C, 72.31; H, 6.88; N, 8.20.

[Cp*Zr(N$_{Xyl}$N){κ^2-N(Ph)-*o*-phenylene-C(Ph)=C(Ph)NH}] (10). A 200 mg portion (0.279 mmol) of Cp*Zr(N$_{Xyl}$N)(NNPh$_2$)dmap (**3a**) was dissolved in 10 mL of toluene, 50 mg (0.279 mmol) of diphenylacetylene was added, and the solution was stirred for 3 days at room temperature. The solvent was subsequently removed under reduced pressure, and 5 mL of pentane was added and removed under reduced pressure to yield 135 mg (0.133 mmol, 48%) of the DMAP adduct as a brown solid. ^{1}H NMR (benzene-d_6, 600.1 MHz, 295 K): δ 7.45 (d, 1 H, $^3J_{H-H}$ = 7.9 Hz, ZrN(Ph)*phenylene*-5), 7.30 (td, 1 H, $^3J_{H-H}$ = 7.1 Hz, $^4J_{H-H}$ = 2.2 Hz, ZrN(Ph)*phenylene*-2), 7.27 (t, 2 H, $^3J_{H-H}$ = 7.8 Hz, *m*-N*Ph*), 7.22 (d, 2 H, $^3J_{H-H}$ = 7.2 Hz, *o*-*Ph*-b), 7.08 (d, 2 H, $^3J_{H-H}$ = 7.9 Hz, *o*-N*Ph*), 6.91 (t, 1 H, *p*-N*Ph*), 6.90 (d, 2 H, $^3J_{H-H}$ = 7.5 Hz, *o*-*Ph*-a), 6.87 (t, 2 H, $^3J_{H-H}$ = 7.3 Hz, *m*-*Ph*), 6.82 (d, 2 H, $^3J_{H-H}$ = 7.1 Hz, *m*-*Ph*), 6.81−6.75 (m, 4 H, C*H* ar), 6.69 (s, 2 H, *o*-C$_6H_3$Me$_2$), 6.68 (s, 1 H, *p*-C$_6H_3$Me$_2$), 6.12 (s, 1 H, N*H*), 3.48−3.39 (m, 2 H, C*H*$_2$N), 2.38 (s, 6 H, C$_6$H$_3$*Me*$_2$), 1.90 (s, 15 H, C$_5$*Me*$_5$) ppm. ^{13}C NMR (benzene-d_6, 150.9 MHz, 295 K): δ 174.3 (NCN), 154.4 (ipso-*Ph*), 154.1 (NHC(Ph)=CPh), 153.0 (ipso-N*Ph*), 151.6 (ZrN-(Ph)*phenylene*-1), 149.6 (ipso-C$_6$H$_3$Me$_2$), 148.2 (ipso-ZrNHC(Ph)=C(*Ph*)), 147.4 (ipso-*Ph*), 140.8 (ipso-NHC(*Ph*)=CPh), 137.6 (*m*-C$_6$H$_3$Me$_2$), 135.2 (CH ar), 134.4 (C ar), 133.1 (*o*- and *p*-*Ph*), 129.3 (C ar), 128.5, 128.4 (*m*-*Ph* and *p*-*Ph*), 127.5 (CH ar), 126.3 (*o*-*Ph*), 124.8 (*p*-C$_6$H$_3$Me$_2$), 124.5 (*C*H ar), 124.0 (*C*H ar), 122.8 (*o*-*Ph*), 122.7 (*o*-C$_6$H$_3$Me$_2$), 122.3 (CH ar), 120.4 (C$_5$Me$_5$), 111.8 (NHC(Ph)=*C*Ph), 52.3 (CH$_2$N), 29.4 (CH$_2$CNN), 24.3 (CH$_2$CH$_2$CNN), 21.8 (C$_6$H$_3$*Me*$_2$), 11.9 (C$_5$*Me*$_5$) ppm. ^{15}N NMR (benzene-d_6, 60.81 MHz, 295 K): δ 214 (Zr*N*Ph), 200 (d, $^1J_{N-H}$ = 65 Hz, Zr*N*H), 177 (NC*N*$_{xyl}$) ppm. IR (KBr, cm^{-1}): ν 3386 (w), 3023 (w), 2963 (m), 2908 (m), 2857 (m), 1594 (s), 1521 (s), 1492 (s), 1446 (s), 1375 (m), 1315 (m), 1289 (m), 1262 (m), 1228 (m), 1182 (w), 1097 (m), 1069 (m), 950 (w), 875 (w), 804 (m), 748 (s), 694 (s), 619 (w), 535 (w). Anal. Calcd: C, 74.47; H, 6.51; N, 7.24. Found: C, 74.34; H, 6.91; N, 6.96.

[Zr(N$_2^{TBS}$N$_{py}$){κ^2-N(NPh$_2$)C(N^{i}Pr)N^{i}Pr}] (12). A 300 mg portion (0.400 mmol) of Zr(N$_2^{TBS}$N$_{py}$)(NNPh$_2$)py (**11**) was dissolved in toluene, and 62 μL (0.400 mmol) of ^{i}PrNCN^{i}Pr was added. After the mixture was stirred at room temperature for 30 min, the solvent was removed under reduced pressure and the residue washed with pentane to yield 185 mg (0.234 mmol, 54%) of a yellow solid. The product contained two isomers in a 5:1 ratio. Crystals suitable for X-ray diffraction were grown from a concentrated toluene solution. *Data for the major component are as follows.* ^{1}H NMR (benzene-d_6, 600.1 MHz, 295 K): δ 9.02 (d, 1 H, $^3J_{H-H}$ = 5.6 Hz, Py-H6), 7.67 (d, 4 H, $^3J_{H-H}$ = 7.9 Hz, *o*-*Ph*), 7.22 (t, 4 H, $^3J_{H-H}$ = 7.6 Hz, *m*-*Ph*), 6.94 (t, 1 H, $^3J_{H-H}$ = 7.6 Hz, Py-H4), 6.80 (t, 2 H, $^3J_{H-H}$ = 7.1 Hz, *p*-*Ph*), 6.75 (d, 1 H, $^3J_{H-H}$ = 7.9 Hz, Py-H3), 6.38 (t, 1 H, $^3J_{H-H}$ = 6.5 Hz, Py-H5), 4.72 (sep, 1 H, $^3J_{H-H}$ = 5.8 Hz, C=NC*H*Me$_2$), 4.40 (sep, 1 H, $^3J_{H-H}$ = 6.2 Hz, ZrNC*H*Me$_2$), 3.90 (d, 2 H, $^2J_{H-H}$ = 12.4 Hz, C*H*$_2$-a), 3.26 (d, 2 H, $^2J_{H-H}$ = 12.4 Hz, C*H*$_2$-b), 1.78 (d, 6 H, $^3J_{H-H}$ = 6.2 Hz, ZrNCHMe$_2$), 1.19 (d, 6 H, $^3J_{H-H}$ = 5.8 Hz, C=NCH*Me*$_2$), 0.97 (s, 3 H, C*H*$_3$), 0.78 (s, 18 H, SiMe$_2$C*Me*$_3$), 0.39 (s, 6 H, Si*Me*$_2$CMe$_3$-a), −0.02 (s, 6 H, Si*Me*$_2$CMe$_3$-b) ppm. ^{13}C NMR (benzene-d_6, 150.9 MHz, 295 K): δ 160.6 (Py-*C*2), 153.7 (*C*=N^{i}Pr), 148.3 (ipso-*Ph*), 147.2 (Py-*C*6), 140.4 (Py-*C*4), 129.0 (*m*-*Ph*), 122.6 (Py-*C*5), 121.2 (Py-*C*3), 120.9 (*p*-*Ph*), 119.4 (*o*-*Ph*), 62.5 (CH$_2$), 48.4 (Py-C1), 48.0 (ZrNCHMe$_2$), 44.7 (C=NCHMe$_2$), 27.9 (SiC*Me*$_3$), 27.6 (C=NCH*Me*$_2$), 26.8 (*C*H$_3$), 25.2 (ZrNCH*Me*$_2$), 19.8 (SiCMe$_3$), −3.3 (Si*Me*$_3$), −4.4 (Si*Me*$_3$) ppm. ^{15}N NMR (benzene-d_6, 60.81 MHz, 295 K): δ 277 (Py-*N*), 214 (Zr*N*^{i}Pr), 203 (C=*N*^{i}Pr), 64 (TBS-*N*Zr) ppm. *Data for the minor component are as follows.* ^{1}H NMR (benzene-d_6, 600.1 MHz, 295 K): δ 8.48 (d, 1 H, $^3J_{H-H}$ = 5.6 Hz, Py-H6), 7.42 (d, 4 H, $^3J_{H-H}$ = 7.9 Hz, *o*-*Ph*), 7.18 (m, *overlaid by benzene-d$_6$*, *m*-Ph), 7.12 (m, 1 H, Py-*H*3), 6.87 (t, 2 H, $^3J_{H-H}$ = 7.3 Hz, *p*-*Ph*), 6.60 (t, 1 H, $^3J_{H-H}$ = 6.0 Hz, Py-*H*5), 4.26 (m, 1 H, C=NC*H*Me$_2$), 3.31 (d, $^2J_{H-H}$ = 12.3 Hz, C*H*$_2$-a), 3.30 (d, $^2J_{H-H}$ = 12.3 Hz, C*H*$_2$-b), 3.11 (d, $^2J_{H-H}$ = 12.2 Hz, C*H*$_2$-a), 3.09 (d, $^2J_{H-H}$ = 12.2 Hz, C*H*$_2$-b), 2.81 (m, 1 H, ZrNC*H*Me$_2$), 1.34 (s, 3 H, C*H*$_3$), 1.10 (d, 6 H, $^3J_{H-H}$ = 6.4 Hz, C=NCH*Me*$_2$), 0.92 (s, 18 H, SiC*Me*$_3$), 0.68 (d, 6 H, $^3J_{H-H}$ = 6.0 Hz, ZrNCH*Me*$_2$), 0.01 (Si*Me*), 0.00 (Si*Me*) ppm; *Py-H3 not observed.* ^{13}C NMR (benzene-d_6, 150.9 MHz, 295 K): δ 166.3 (Py-*C*2), 159.2 (*C*=NCHMe$_2$), 150.3 (ipso-*Ph*), 149.1 (Py-*C*6), 135.7 (Py-*C*4), 129.0 (*m*-*Ph*), 122.0 (*p*-*Ph*), 121.8 (Py-*C*5), 121.0 (*o*-*Ph*), 51.2 (CH$_2$), 48.5 (Py-C1), 43.8 (C=NCHMe$_2$), 42.7 (ZrNCHMe$_2$), 26.8 (SiC*Me*$_3$), 21.1 (*C*H$_3$), 18.7 (SiCMe$_3$), −4.7 (Si*Me*), −4.8 (Si*Me*) ppm. IR (KBr): ν 3064 (w), 2955 (m), 2927 (m), 2882 (m), 2854 (m), 1592 (s), 1491 (s), 1472 (m), 1387 (m), 1310 (w), 1246 (m), 1175 (m), 1044 (m), 1020 (m), 908 (w), 851 (m), 830 (s), 774 (m), 748 (m), 691 (m), 669 (m), 593 (w), 511 (w) cm^{-1}. Anal. Calcd: C, 60.71; H, 8.28; N, 12.39. Found: C, 60.37; H, 7.87; N, 12.27.

[Zr(N$_2^{TBS}$N$_{py}$){κ^2-N(NPh$_2$)CHPhNPh}] (13). A 350 mg portion (0.470 mmol) of Zr(N$_2^{TBS}$N$_{py}$)(NNPh$_2$)py (**11**) was dissolved in 10 mL of toluene, and 85 mg (0.470 mmol) of *N*-phenylbenzimine (*N*-benzylideneaniline) was added. After the mixture was stirred for 3 h, the solvent was removed under removed pressure and the residue washed with hexane to yield 228 mg (0.269 mmol, 57%) of a yellow solid. Crystals suitable for X-ray diffraction were grown from a concentrated solution in toluene. ^{1}H NMR (benzene-d_6, 600.1 MHz, 295 K): δ 9.05 (d, 1 H, $^3J_{H-H}$ = 5.2 Hz, Py-H6), 7.80 (d, 2 H, $^3J_{H-H}$ = 7.5 Hz, *o*-CH*Ph*), 7.24−7.17 (m, 8 H, *m*-CH*Ph*, *o*-N*Ph*, *o*-NN*Ph*$_2$), 7.08 (t, 1 H, $^3J_{H-H}$ = 7.3 Hz, *p*-CH*Ph*), 6.98 (t, 1 H, $^3J_{H-H}$ = 7.7 Hz, *p*-N*Ph*), 6.94−6.76 (broad m, 2 H, NN*Ph*$_2$), 6.83 (t, 1 H, $^3J_{H-H}$ = 7.7 Hz, Py-*H*4), 6.72 (d, 1 H, $^3J_{H-H}$ = 8.1 Hz, Py-*H*3), 6.70−6.64 (m, 3 H, *m*-N*Ph* and NN*Ph*$_2$), 6.35 (s, 1 H, C*H*Ph), 6.31 (t, 1 H, $^3J_{H-H}$ = 6.5 Hz, Py-*H*5), 4.15 (d, 1 H, $^2J_{H-H}$ = 12.5 Hz, C*H*$_2$-a), 4.08 (d, 1 H, $^2J_{H-H}$ = 12.2 Hz, C*H*$_2$-b), 3.39 (d, 1 H, $^2J_{H-H}$ = 11.9 Hz, C*H*$_2$-b), 3.37 (d, 1 H, $^2J_{H-H}$ = 12.1 Hz, C*H*$_2$-a), 1.02 (s, 3 H, C*H*$_3$), 0.87 (s, 9 H, C*Me*$_3$-a), 0.80 (s, 9 H, C*Me*$_3$-b), 0.46 (s, 3 H, Si*Me*-b), 0.23 (s, 3 H, Si*Me*-b), 0.19 (s, 3 H, Si*Me*-a), −0.27 (s, 3 H, Si*Me*-a) ppm. ^{13}C NMR (benzene-d_6, 150.9 MHz, 295 K): δ 160.9 (Py-*C*2), 151.9 (ipso-CH*Ph*), 147.0 (Py-*C*6), 142.3 (ipso-N*Ph*), 140.3 (Py-*C*4), 129.1 (*o*-CH*Ph*), 129.0 (*C*H Ar), 127.3 (*C*H Ar), 126.1 (*C*H Ar), 123.5 (*C*H Ar), 122.6 (Py-*C*5), 121.3 (*C*H Ar), 121.0 (Py-*C*3), 116.8 (*m*-N*Ph*), 74.6 (CHPh), 63.0 (CH$_2$-a), 62.8 (*C*H$_2$-b), 48.5 (Py-C1), 28.2 (*C*Me$_3$-a), 27.8 (*C*Me$_3$-b), 25.5 (*C*H$_3$), 19.6, 19.5 (*C*Me$_3$-a *and* b), −2.4 (Si*Me*-b), −3.0 (Si*Me*-b), −3.6 (Si*Me*-a), −5.1 (Si*Me*-a) ppm. ^{15}N NMR (benzene-d_6, 60.81 MHz, 295 K): δ 335 (Zr*N*NPh$_2$), 301 (*N*Si^{t}BuMe$_2$-b), 299 (*N*Si^{t}BuMe$_2$-a), 278 (Py*N*), 183 (Zr*N*Ph) ppm; NNPh$_2$ *not observed.* IR (KBr): ν 3061 (w), 3025 (w), 2952 (w), 2926 (w), 2853 (w), 1588 (m), 1489 (m), 1385 (w), 1316 (m), 1257 (m), 1109 (m), 1085 (m), 1039 (m), 995 (m), 909 (m), 849 (s), 830 (s), 775 (s), 750 (s), 693 (s), 669 (m), 636 (w), 611 (w), 587 (m) cm^{-1}. Anal. Calcd; C, 65.27; H, 7.38; N, 9.93. Found: C, 65.82; H, 7.45; N, 9.50.

General Procedure for Catalytic *N*-Aminoguanidine Synthesis. A 0.05 mmol portion of catalyst **3a** was dissolved in 1 mL of toluene. A 1.0 mmol portion of diisopropylcarbodiimide and 1.1 mmol of diphenylhydrazine were dissolved in 1 mL of toluene, and the solutions were combined and heated to 105 °C for 24 h. The reaction mixture was then diluted with 120 mL of diethyl ether and filtered through a pad of alumina, the solvent was removed under reduced pressure, and the crude product was purified by column chromatography (DCM with 5% MeOH, 0.5% NEt$_3$, 80 g of silica). A 309 mg amount (0.99 mmol, 99%) of a yellow solid was obtained. NMR spectra were in good agreement with those found in the literature.[56]

Computational Studies. All molecular structures were optimized using the B3PW91 hybrid functional[39,40] with a 631G(d) basis set[46] for C, H, N, Li, and Si and a pseudopotential for Zr (SDD+f) and Hf (SDD)[41−45] using the Gaussian09 program package.[57] Energy minima were verified by frequency analysis. The coordinates of the minimum structures are provided in the Supporting Information.

The modeling of the NMR chemical shifts has been carried out, utilizing the DFT-optimized structures, with the GIAO method[47−49] employing the B3PW91 hybrid functional with a 6311++G(2d,2p) basis set for C, H, and N and a pseudopotential (SDD+f) for Zr.

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X-ray Crystal Structure Determinations. Crystal data and details of the structure determinations are given in the Supporting Information. Full shells of intensity data were collected at low temperature (complex **13**, 100 K; all others, 110 K) with a Bruker AXS Smart 1000 CCD diffractometer (Mo Kα radiation, sealed tube, graphite monochromator) (complex **13**) or a Agilent Technologies Supernova-E CCD diffractometer (Mo or Cu Kα radiation, microfocus tube, multilayer mirror optics). Data were corrected for air and detector absorption, Lorentz, and polarization effects;[58,59] absorption by the crystal was treated with a semiempirical multiscan method (complexes **3a**, **12**, and **13**)[60−62] or was treated analytically (complex **7**)[59,63] or numerically (Gaussian grid) (complexes **3b** and **4**).[59] The structures were solved by the charge flip procedure[64] and refined by full-matrix least-squares methods based on F^2 against all unique reflections.[65] All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were generally input at calculated positions and refined with a riding model. When justified by the quality of the data, the positions of some hydrogen atoms were taken from difference Fourier syntheses and refined. When found necessary, disordered groups and/or solvent molecules were subjected to suitable geometry and adp restraints. Crystals of **12** were twinned; after detwinning (approximately twin fractions 0.52:0.48) refinement was carried out against all singles and composites involving both domains.

■ ASSOCIATED CONTENT

Supporting Information

Tables, text, figures, and CIF, .mol, and .xyz files giving crystallographic data for **3a**,**b**, **4**, **7**, **12**, and **13**, all computed molecule Cartesian coordinates in a format for convenient visualization, and details on the computational studies. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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