

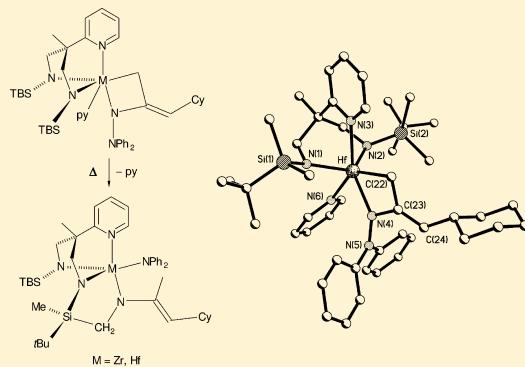
[2 + 2] Cycloaddition Products of Zirconium and Hafnium Hydrazinediides with Allenes and Heteroallenes and Their Thermally Induced Rearrangements

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Supporting Information

ABSTRACT: Reactions of the hydrazinediido complexes $[M(N_2^{TBS}N_{py})-(NNPh_2)(py)]$ ($M = Zr$ (**1a**), Hf (**1b**)) with (hetero)allenes result in a variety of [2 + 2] cycloaddition products of the general type $[M(N_2^{TBS}N_{py})(\kappa^2 N,E-(E= \text{CH}_2, S; E' = \text{CH}, N; R = \text{alkyl, aryl}))NNPh_2(py)]$ ($E = \text{CH}_2, S; E' = \text{CH}, N; R = \text{alkyl, aryl}$). The reaction of $[Zr(N_2^{TBS}N_{py})(NNPh_2)(py)]$ (**1a**) with 1 molar equiv of phenyl or mesityl isothiocyanate at room temperature yields $[Zr(N_2^{TBS}N_{py})(\kappa^2 N,S-\text{SC}(=\text{NAr})NNPh_2)(py)]$ ($\text{Ar} = \text{phenyl}$ (**2a**), mesityl (**2b**)). Reacting the hydrazinediides $[M(N_2^{TBS}N_{py})-(NNPh_2)(py)]$ ($M = Zr$ (**1a**), Hf (**1b**)) with allenes results in the formation of the metallazacyclobutanes $[M(N_2^{TBS}N_{py})(\kappa^2 N,C-N(NPh_2)-\text{CH}_2\text{C}=\text{CH}(R))(py)]$ ($M = Zr, R = \text{Ph}$ (**4a**), cyclohexyl (**5a**), methyl (**6**); $M = Hf, R = \text{phenyl}$ (**4b**), cyclohexyl (**5b**)). Subsequent heating of the cycloaddition products revealed different reactivity patterns: the complex $[Zr(N_2^{TBS}N_{py})(\kappa^2 N,S-\text{SC}(=\text{NAr})NNPh_2)(py)]$ (**2a**) forms the isomerization product $[Zr(N_2^{TBS}N_{py})(\kappa^2 N,S-\text{SC}(=\text{NNPh}_2))-\text{NPh}]$ (**3**), retaining the N–N bond of the hydrazide. In contrast, the metallacyclobutanes **4a,b** and **5a,b** show a tendency toward N–N bond cleavage, resulting in the formation of the C–N- and C–C-coupled product complexes $[M(\kappa^4 N,N,N,N-\text{N}_2^{TBS}N_{py}\text{NC(Me)}=\text{CHCy})(NPh_2)]$ ($M = Zr$ (**7a**), Hf (**7b**)), $[Zr(N_2^{TBS}N_{py})(\kappa^2 N,C-(\text{Ph})\text{NC}_6\text{H}_4\text{C}(\text{Me})=\text{C}(\text{Ph})\text{NH})]$ (**8**) and $[Zr(\kappa^4 N,N,N,N-\text{N}_2^{TBS}N_{py}\text{NC(Me)}=\text{CHPh})(NPh_2)]$ (**9**).



INTRODUCTION

Azametallacycles of the group 4 elements are key intermediates in a range of stoichiometric and catalytic C–N and C–C coupling reactions mediated by these metals.^{1,2} The most intensely studied catalytic transformation involving such species is the hydroamination of alkynes.^{3–8}

In contrast, after early pioneering work from Bergman's group,⁹ [2 + 2] cycloadditions of group 4 metal hydrazinediido complexes have only been looked into systematically in recent years.¹⁰ The reactions of titanium and zirconium hydrazinediido complexes with alkynes which lead to hydrohydrazination¹¹ or N–N bond cleavage products¹² have been studied and modeled in detail, whereas much less is known about the reactivity toward allenes. In general, reactions of hydrazinediido titanium complexes with allenes or heteroallenes give stable [2 + 2] cycloaddition products, they may lead to double substrate insertion into the Ti–hydrazido double bond, or tend to undergo metathesis to give N-aminoisothiocyanates.^{10b,c} However, all these reactions occur with retention of the hydrazido N–N double bond. In contrast, a zirconium hydrazinediido/phenyl allene adduct was found to react under N–N bond scission upon heating.^{12d} With this pattern of reactivity in mind and given the lack of investigations focusing on the heavier group 4 metal hydrazinediido reactivity, we began systematic studies in this field.¹³ Here we report the isolation and characterization of [2 + 2] cycloaddition products

of zirconium and hafnium hydrazinediido complexes with several allenes and heteroallenes, as well as some pathways of their thermal rearrangement and fragmentation.

RESULTS AND DISCUSSION

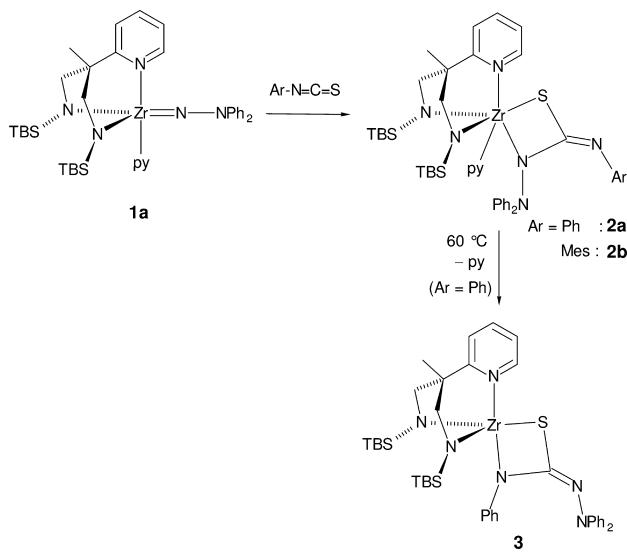
Synthesis and Structural Characterization of [2 + 2] Cycloadducts of a Zirconium Hydrazinediido Complex with Isothiocyanates and Their Thermal Rearrangement. Reaction of the hydrazinediido zirconium complex $[Zr(N_2^{TBS}N_{py})(NNPh_2)(py)]$ (**1a**; $[N_2^{TBS}N_{py}]^{2-} = [C_5H_4NC(CH_3)(CH_2NSi^tBuMe_2)]^{2-}$) with 1 molar equiv of phenyl or mesityl isothiocyanate yielded the [2 + 2] cycloaddition products $[Zr(N_2^{TBS}N_{py})(\kappa^2 N,S-\text{SC}(=\text{NPh})NNPh_2)(py)]$ (**2a**) and $[Zr(N_2^{TBS}N_{py})(\kappa^2 N,S-\text{SC}(=\text{NMes})NNPh_2)(py)]$ (**2b**), respectively (Scheme 1).

Addition of isothiocyanates to titanium hydrazinediides has been described in the literature,¹⁰ whereas these reactions are unprecedented for zirconium. Cycloaddition products **2a,b** are both formed selectively and are stable at room temperature. Their ^1H and ^{13}C NMR spectra are consistent with the formation of complexes with C_s symmetry. Furthermore, it is evident that both complexes contain one pyridine donor ligand

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Scheme 1. Reaction of the Hydrazinediido Zirconium Complex **1a** with Isothiocyanates To Give [2 + 2] Cycloaddition Products



coordinated to the metal center. The ^{15}N NMR shifts in the metallacycle are in good accordance with those observed for the related compound $[\text{Cp}^*\text{Ti}(\text{N}^{xy}\text{N})(\kappa^2\text{N},\text{S}-\text{SC}(=\text{NPh})-\text{NNPh}_2)]^{11\text{g}}$ (**2a**, δ 129.8 (NPh₂), 209.5 (Zr-N), 244.6 (CN-Ph); $[\text{Cp}^*\text{Ti}(\text{N}^{xy}\text{N})(\kappa^2\text{N},\text{S}-\text{SC}(=\text{NPh})\text{NNPh}_2)]$, δ 126.9 (NPh₂), 266.2 (Ti-N), 245.1 (CN-Ph)).

On the basis of these similarities the structure with $\kappa^2\text{N},\text{S}$ ligation as shown in Scheme 1 was suggested and subsequently confirmed by single-crystal X-ray structure analyses of complexes **2a,b**. The molecular structures of both complexes are shown in Figure 1; selected bond lengths and angles are given in Table 1.

The molecular geometry in complexes **2a,b** cannot be readily described by reference to classic coordination polyhedra. The structures are related to those found for [2 + 2] cycloaddition products of complex **1a** with other unsaturated substrates.^{10d} The N_a atom of the former hydrazinediido ligand is coupled to the isothiocyanate carbon atom and lies beneath a virtual plane defined by N1, N2, and the metal atom. The four-membered metallacycles are essentially planar (rms deviation from the

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complexes **2a,b**

	2a	2b
Zr-N(1)	2.076(4)	2.0740(13)
Zr-N(3)	2.386(4)	2.3777(13)
Zr-N(4)	2.218(4)	2.2039(15)
Zr-S	2.544(1)	2.5680(8)
C(22)-S	1.773(5)	1.779(1)
C(22)-N(4)	1.374(7)	1.376(2)
C(22)-N(6)	1.289(6)	1.277(2)
N(4)-N(5)	1.428(5)	1.415(2)
Zr-N(4)-C(22)	107.0(3)	107.64(8)
Zr-S-C(22)	83.4(2)	82.63(6)
N(4)-C(22)-N(6)	126.2(5)	126.3(1)
N(4)-C(22)-S	106.0(3)	106.10(9)
N(6)-C(22)-S	127.8(4)	127.62(11)

mean plane 0.01 Å for both complexes). The planar environment of C(22) ($\sum \angle \text{C}22 = 360.0^\circ$) and the exocyclic C(22)-N(6) distance (1.289(6) Å (**2a**) and 1.277(2) Å (**2b**)) are consistent with a C=N double bond.¹⁴

When **2b** is heated, nonselective degradation is observed, whereas for **2a** the single isomerization product [$\text{Zr}(\text{N}_2^{\text{TBS}}\text{N}_{\text{py}})(\kappa^2\text{N},\text{S}-\text{SC}(=\text{NPh}_2)\text{NPh}_2)$] (**3**) is detected (Scheme 1). The analytical data as well as the ^1H , ^{13}C , and ^{15}N NMR spectroscopic data are consistent with the depicted structure. The neutral pyridine ligand is no longer coordinated, and the signal sets for the remaining groups are similar to those observed for complexes **2a,b**. The N-N bond of the hydrazide has remained intact, as is indicated by the marginal shift of the $^{15}\text{N}_\beta$ NMR signals (**2a**, δ 129.8; **3**, δ 129.9). The occurrence of a $\kappa^2\text{N},\text{N}'$ -coordinated ligand as found in titanium^{10c,11g} and scandium¹⁵ complexes can be excluded, since the ^{13}C NMR signal of C22 is only slightly shifted downfield (δ 159.4 in **2a**, δ 168.1 in **3**). In contrast, for a $\kappa^2\text{N},\text{N}'$ -coordinated form the ^{13}C NMR resonance of a hypothetical C=S unit would be expected around 200 ppm (δ 198.1 in $[\text{Cp}^*\text{Ti}(\text{N}^{xy}\text{N})(\kappa^2\text{N},\text{N}'-\text{PhNC}(=\text{S})\text{NNPh}_2)]$).^{11g} The ^{15}N NMR resonance of the N4 atom in complex **3** is also consistent with the formation of an exocyclic C=NNPh₂ moiety: the observed shift of δ 271.2 lies in the typical range for hydrazones.¹⁶ Such

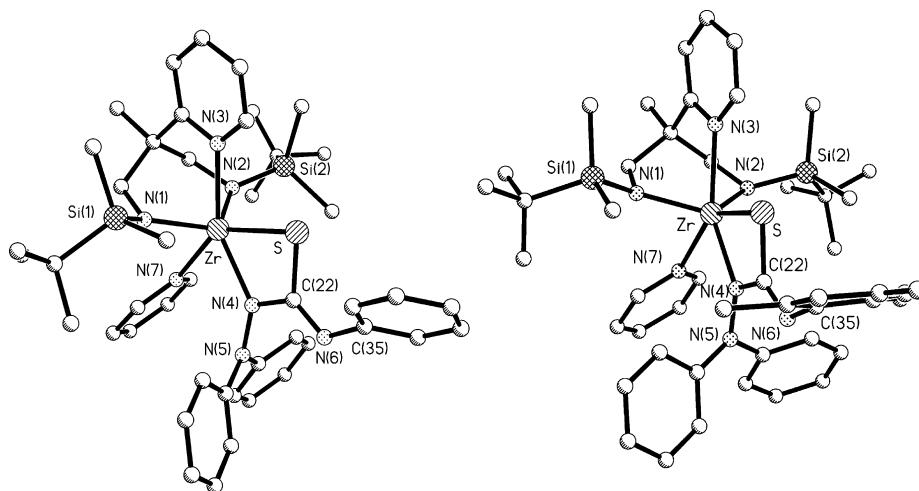
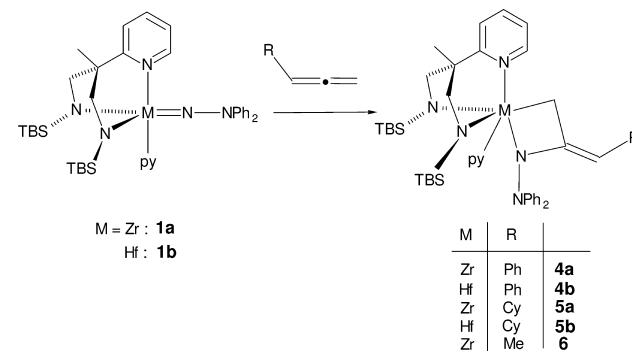


Figure 1. Molecular structures of the [2 + 2] cycloaddition products **2a** (left) and **2b** (right). H atoms are omitted for clarity.

an isomer can be regarded as an intermediate in the formation of a zirconium sulfido complex upon release of *N*-amino-carbodiimide, as reported recently by Mountford et al.^{10c}

Synthesis and Structural Characterization of [2 + 2] Cycloadducts with Allenes. Reactions of hydrazinido complexes $[M(N_2^{TBS}N_{py})(NNPh_2)(py)]$ ($M = Zr$ (**1a**), Hf (**1b**)) with phenyl allene, cyclohexyl allene, and methyl allene yields the metallaazacyclobutanes $[Zr(N_2^{TBS}N_{py})(\kappa^2 N, C-N-(NPh_2)CH_2C=CH(Ph))(py)]$ (**4a**), $[Zr(N_2^{TBS}N_{py})(\kappa^2 N, C-N-(NPh_2)CH_2C=CH(Cy))(py)]$ (**5a**), and $[Zr(N_2^{TBS}N_{py})(\kappa^2 N, C-N-(NPh_2)CH_2C=CH(Me))(py)]$ (**6**) by [2 + 2] cycloaddition reactions with Markovnikov regioselectivity. For the hafnium complex **1b** only the phenyl derivative $[Hf(N_2^{TBS}N_{py})(\kappa^2 N, C-N(NPh_2)CH_2C=CH(Ph))(py)]$ (**4b**) and cyclohexyl derivative $[Zr(N_2^{TBS}N_{py})(\kappa^2 N, C-N(NPh_2)CH_2C=CH(Cy))(py)]$ (**5b**) were isolated (Scheme 2).

Scheme 2. Formal [2 + 2] Cycloadditions of Complexes **1a,b with Allenes Yielding the Metallacycles **4a,b**, **5a,b**, and **6****



All five complexes were isolated and characterized spectroscopically and analytically. Single-crystal X-ray structure analyses established the regioselectivity of the cycloaddition product for the zirconium phenyl derivative **4a** and the hafnium cyclohexyl compound **5b**. Their molecular structures, which are depicted in Figures 2 and 3, respectively, are related to those of the isothiocyanate cycloaddition products **2a,b**. Here again, the usual deltahedral coordination geometries for 6-fold coordination do not apply, and the molecular geometries are best described as being derived from a triangulated dodecahedron (coordination number 8) with two of its vertices removed.

Thermally Induced N–N Bond Cleavage and Rearrangement Reactions. Heating the [2 + 2] cycloaddition product **5a** at 80 °C in toluene led to its conversion to one main reaction product, $[Zr(\kappa^4-N,N,N,N-TBSN_{py}NC(Me)=CHCy)(NPh_2)]$ (**7a**; 95% yield) (Scheme 3).

Likewise, heating the hafnium compound **5b** also gave the corresponding rearrangement product $[Hf(\kappa^4-N,N,N,N-TBSN_{py}NC(Me)=CHCy)(NPh_2)]$ (**7b**), albeit in lower yield (50%). The analytical and spectroscopic data of **7a,b** indicate the absence of mirror symmetry for both species. A detailed ¹H and ¹⁵N NMR HMBC NMR study led to the structural assignment of the C–H activation products, as shown in Figure 4 for **7b**.

Correlation of the protons of a newly formed methylene group with both the ¹⁵N(4) and ¹⁵N(2) nuclei as observed in the ¹H ¹⁵N NMR spectrum provided direct evidence for the insertion of the N_α atom (N4) into one of the methyl C–H bonds of the *tert*-butyldimethylsilyl substituents on the tripodal diamido-pyridyl ligand. The resonance of the ¹⁵N_β

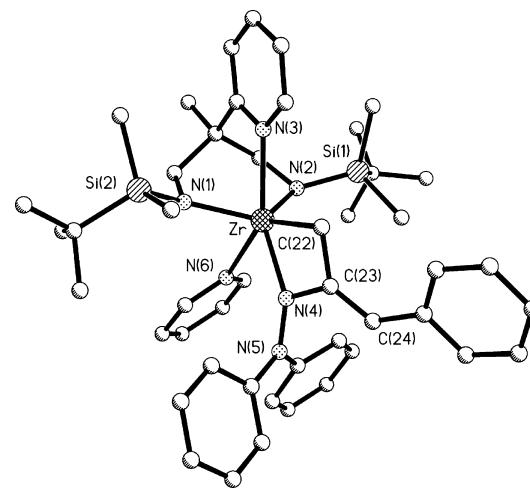


Figure 2. Molecular structure of the [2 + 2] cycloaddition product **4a.** H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr–N(4) = 2.183(1), Zr–C(22) = 2.334(1), N(4)–N(5) = 1.415(2), C(22)–C(23) = 1.495(2), C(23)–N(4) = 1.395(2), C(23)–C(24) = 1.361(2); Zr–C(22)–C(23) = 91.91(8), Zr–N(4)–N(5) = 139.55(8), C(24)–C(23)–N(4) = 124.5(1), N3(1)–Zr–N(6) = 140.93(4).

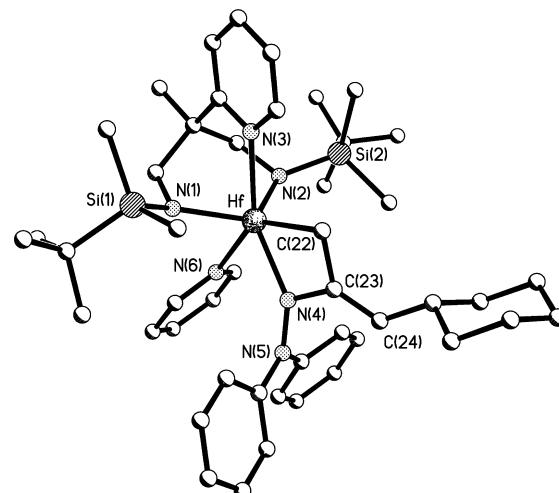
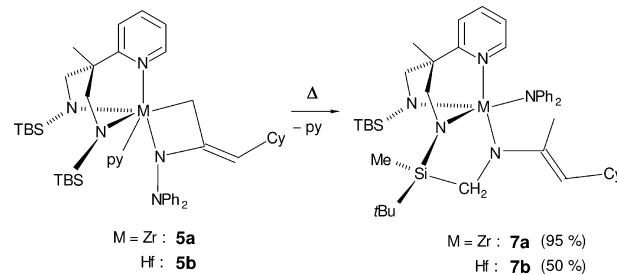


Figure 3. Molecular structure of the [2 + 2] cycloaddition product **5b.** H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Hf–N(4) = 2.160(2), Hf–C(22) = 2.290(2), N(4)–N(5) = 1.420(3), C(22)–C(23) = 1.507(3), C(23)–N(4) = 1.406(3), C(23)–C(24) = 1.346(3); Hf–C(22)–C(23) = 92.9(1), Hf–N(4)–N(5) = 141.0(1), C(24)–C(23)–N(4) = 128.4(2), N(3)–Hf–N(6) = 141.78(7).

Scheme 3. Thermolysis of the [2 + 2] Cycloaddition Products **5a,b**



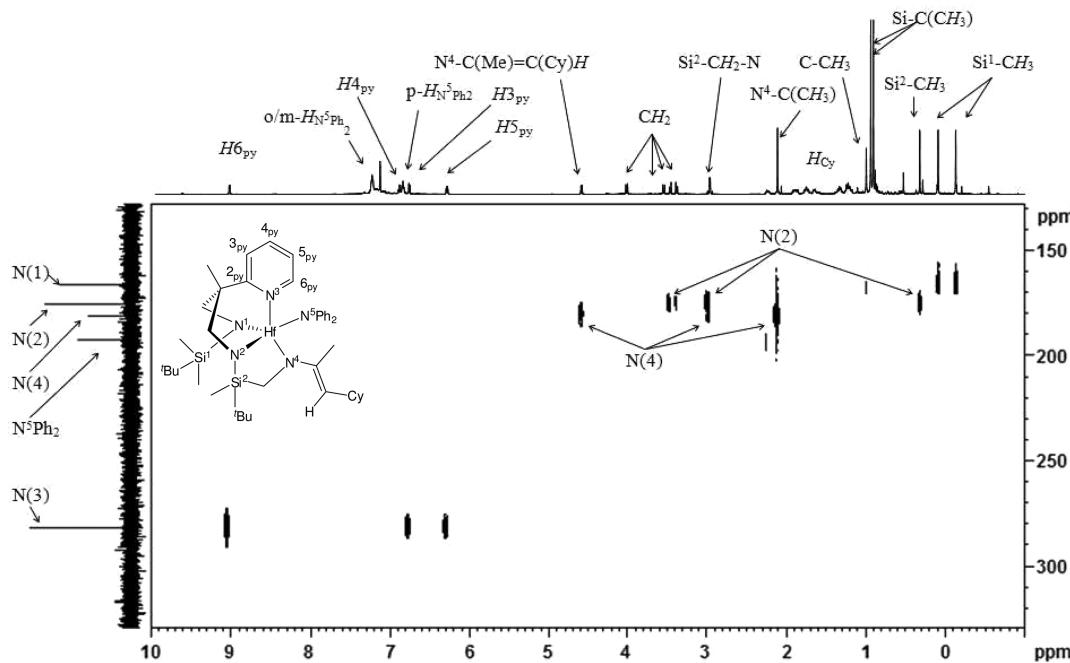


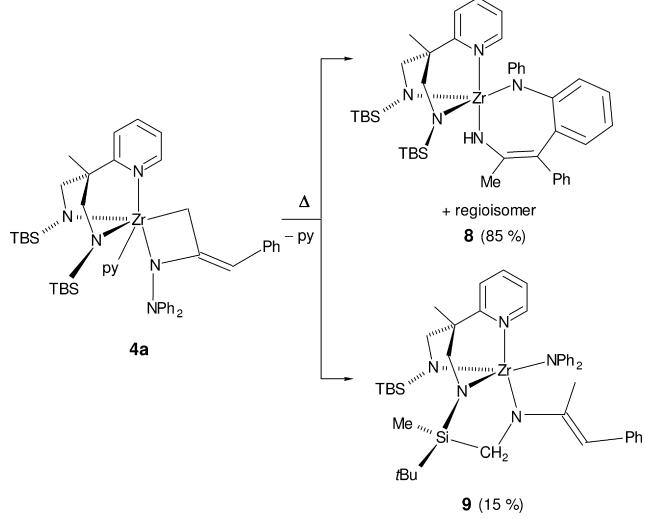
Figure 4. $^{15}\text{N}-^1\text{H}$ correlated NMR spectrum of complex **7b**.

nucleus (N^5Ph_2) ($\delta_{\text{N}(5)}$ 192.7 ppm) is shifted downfield compared to those of the corresponding complex **5b** ($\delta_{\text{N}(5)}(\text{Sb})$ 123.1 ppm), which is consistent with the cleavage of the $\text{N}_{\alpha}-\text{N}_{\beta}$ bond and coordination of the N^5Ph_2 fragment on the central atom, as also found in previous studies.¹³

Finally, thermolysis of complex **4a** also yields two products, namely $[\text{Zr}(\text{N}_2^{\text{TBS}}\text{N}_{\text{py}})(\kappa^2\text{N},\text{C}-(\text{Ph})\text{NC}_6\text{H}_4\text{C}(\text{Me})=\text{C}(\text{Ph})-\text{NH})]$ (**8**) and $[\text{Zr}(\kappa^4\text{N},\text{N},\text{N},\text{N}-\text{N}_2^{\text{TBS}}\text{N}_{\text{py}})\text{NC}(\text{Me})=\text{CHPh}-(\text{NPh}_2)]$ (**9**) (Scheme 4). The formation of the diazazircona-

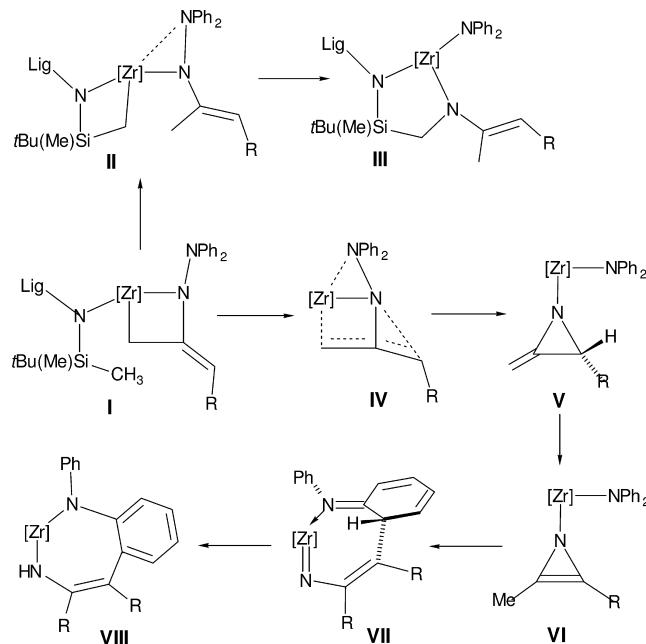
Given the lack of selectivity in the transformations of complexes **4a** and **5a,b** to the metallacyclic species represented in Schemes 3 and 4, a systematic investigation of the underlying mechanism was not possible. However, in view of the related transformations of the zirconium hydrazinediides with alkynes, which we studied in detail previously,^{12d,e} we propose the reaction sequences depicted in Scheme 5. The intramolecular attack and coupling of the N–silyl unit, as observed in complexes **7a,b** and **9** (represented in Scheme 5 as **III**) is

Scheme 4. Thermolysis of the Metallacyclic Complex **4a**



cycloheptenyl complexes **8** and **8'** (both regiosomers) was established by comparison of the analytical and NMR spectroscopic data with those of a sample synthesized previously by a different route.^{12d} The minor component **9** could not be isolated, but the NMR spectra were consistent with the formation of a complex with a $\text{Si}-\text{CH}_3$ activated ligand as found in **7a,b**.

Scheme 5. Proposed Mechanistic Scheme for the Thermal Transformation of the [2 + 2] Hydrazinediide/Allene Cycloaddition Products (**I**) to the Two Types of Metallacyclic Compounds **III** and **VIII**



thought to be initiated by rupture of the Zr–C bond in the metallocycle I (the [2 + 2] cycloaddition product of hydrazide + allene), H atom abstraction from the silyl group results in the formation of the cyclic intermediate II, which in turn undergoes N–N bond cleavage and C–N coupling to give the metallocycle III.^{12d} On the other hand, the rupture of the Zr–C bond may be associated with transfer of the NPh₂ to the metal and C–N coupling (IV) to give the aziridinato–Zr species V, which undergoes a 1,3-sigmatropic H shift to give the metalated azirinate VI. In a detailed computational study of the Zr catalytic indole formation published recently by us,^{12e} this species has been invoked as a key intermediate leading to the type VIII metallocycles.

CONCLUSIONS

In this work we reported the syntheses and structural characterization of [2 + 2] cycloaddition products derived from hydrazinediido complexes of the heavier group 4 metals and allenes or heteroallenes. Thermolysis of these compounds led to rearrangement and a variety of C–H activation and C–C and C–N coupling products. In particular, the formation of complexes such as 7a,b and 9 is unprecedented. This and the observation that the reactivity differs significantly from that of the related titanium systems justifies further investigation into the reactivity of zirconium and hafnium hydrazido complexes.

EXPERIMENTAL SECTION

All manipulations of air- and moisture-sensitive materials were performed under an inert atmosphere of dry argon using standard Schlenk techniques or by working in a glovebox (Unilab-2000, M. Braun). Argon was dried over phosphorus pentoxide (Sicapent, Merck Chemicals). Solvents were dried over sodium (toluene, methyl cyclohexane), potassium (hexane), or sodium/potassium alloy (pentane), distilled, and degassed prior to use. Deuterated solvents were dried over potassium (C₆D₆, THF-d₈), vacuum-distilled, and stored in Teflon valve ampules under argon. The hydrazinediido complexes [Zr(N₂TBSN_{py})(NNPh₂)(py)] (1a) and [Hf(N₂TBSN_{py})(NNPh₂)(py)] (1b) were prepared according to published procedures.^{13,17} All other reagents were obtained from commercial sources and used as received unless explicitly stated otherwise. All liquid reagents were degassed prior to use.

Preparation of [Zr(N₂TBSN_{py})(κ²N,S-SC(=NPh)NNPh₂)(py)] (2a). To a stirred solution of [Zr(N₂TBSN_{py})(NNPh₂)(py)] (1a; 800 mg, 1.08 mmol) in toluene (20 mL) was added a solution of phenyl isothiocyanate (140 mg, 0.93 mmol) in toluene (1 mL). The reaction mixture was stirred overnight at room temperature and filtered, and the volatiles were removed under reduced pressure. The crude product was washed with pentane (3 × 5 mL) and dried in vacuo to yield 800 mg (85%) of 2a as a yellow solid. Single crystals for X-ray diffraction were grown from a saturated toluene solution at room temperature. ¹H NMR (600.13 MHz, THF-d₈, 296 K): δ –0.70, 0.33 (s, 6 H, Si(CH₃)₂), 0.65 (s, 18 H, Si-C(CH₃)₃), 1.34 (CH₃), 3.35, (bs, 2 H, CHH), 3.46 (d, ²J_{HH} = 13.5 Hz, 2 H, CHH), 6.67–6.73 (m, 6 H, p-H_{Ph}, p-H_{PhNCS}), 6.98 (t, ³J(m-H_{PhNCS}/o-H_{PhNCS}/p-H_{PhNCS}) = 7.7 Hz, 2 H, m-H_{PhNCS}), 7.00–7.20 (m, 10 H, o-H_{Ph}, m-H_{Ph}, o-H_{PhNCS}), 7.24 (bs, 2 H, m-H_{py}), 7.42 (t, ³J(H_{5py}H_{6py}/H_{4py}) = 6.4 Hz, 1 H, H_{5py}), 7.64 (d, ³J(H_{3py}H_{4py}) = 8.0 Hz, 1 H, H_{3py}), 7.74 (bs, 1 H, p-H_{py}), 7.96 (dt, ³J(H_{4py}H_{3py}/H_{5py}) = 7.9 Hz, ⁴J(H_{4py}H_{6py}) = 1.5 Hz, 1 H, H_{4py}), 8.74 (bs, 2 H, o-H_{py}), 9.30 (d, ³J(H_{6py}H_{5py}) = 5.5 Hz, 1 H, H_{6py}). ¹³C{¹H} NMR (150.90 MHz, THF-d₈, 296 K): δ –4.7, –1.5 (Si(CH₃)₂), 21.9 (Si-C(CH₃)₃), 26.1 (C-CH₃), 28.8 (Si-C(CH₃)₃), 48.5 (C-CH₃), 65.4 (CH₂), 121.0–123.9 (C_{Ar}), 124.0 (C_{Spy}), 124.4 (C_{3py}), 125.2 (m-C_{py}), 128.1–130.3 (C_{Ar}), 140.7 (C_{4py}), 149.0 (i-C_{Ph-NCS}), 149.5 (C_{6py}), 151.9 (o-C_{py}), 152.5 (i-C_{NPh}), 159.4 (NCS), 162.0 (C_{2py}). ²⁹Si{¹H} NMR (79.45 MHz, THF-d₈, 296 K): δ 1.88 (Si(CH₃)₂Bu). ¹⁵N NMR (60.82 MHz, THF-d₈, 296 K): δ 129.8 (NPh₂), 189.9 (N-Si(CH₃)₂Bu), 209.5 (Zr-NCS), 244.6 (Ph-NCS),

289.1 (L-N_{py}), not observed (N_{py}). IR (Nujol, NaCl): ν 1586 s, 1491 sh, 1465 s, 1378 m, 1308 w, 1246 s, 1143 s, 1085 w, 1059 w, 1031 s, 997 w, 937 s, 907 w, 856 s, 787 m, 770 m, 747 s, 720 m, 693 m, 671 w cm⁻¹. Anal. Calcd for C₄₅H₆₁N₇SSi₂Zr: C, 61.46; H, 6.99; N, 11.15. Found: C, 61.54; H, 6.99; N, 11.11.

Preparation of [Zr(N₂TBSN_{py})(κ²N,S-SC(=NMes)NNPh₂)(py)] (2b). To a stirred solution of [Zr(N₂TBSN_{py})(NNPh₂)(py)] (1a; 800 mg, 1.08 mmol) in toluene (20 mL) was added a solution of mesityl isothiocyanate (136 mg, 1.08 mmol) in toluene (1 mL). The reaction mixture was stirred overnight at room temperature and filtered, and the volatiles were removed under reduced pressure. The crude product was washed with pentane (3 × 5 mL) and dried in vacuo to yield 920 mg (93%) of yellow 2b. Single crystals for X-ray diffraction were grown from a saturated toluene solution at room temperature. ¹H NMR (600.13 MHz, THF-d₈, 296 K): δ –0.76, 0.38 (s, 6 H, Si(CH₃)₂), 0.71 (s, 18 H, Si-C(CH₃)₃), 1.43 (CH₃), 1.82 (s, 6 H, o-Mes-CH₃), 2.13 (s, 3 H, p-Mes-CH₃), 3.41 (bs, 2 H, CHH), 3.50 (d, ²J_{HH} = 12.6 Hz, 2 H, CHH), 6.56 (s, 2 H, m-H_{Mes}), 6.73 (t, ³J(p-H_{Ph}m-H_{Ph}) = 7.2 Hz, 2 H, p-H_{Ph}), 7.06 (bs, 4 H, m-H_{Ph}), 7.16–7.37 (m, 6 H, o-H_{Ph}m-H_{Ph}), 7.41 (t, ³J(H_{5py}H_{6py}/H_{4py}) = 6.4 Hz, 1 H, H_{5py}), 7.66 (d, ³J(H_{3py}H_{4py}) = 8.0 Hz, 1 H, H_{3py}), 7.75 (bs, 1 H, p-H_{py}), 7.97 (dt, ³J(H_{4py}H_{3py}/H_{5py}) = 7.9 Hz, 1 H, H_{4py}), 8.79 (bs, 2 H, o-H_{py}), 9.23 (d, ³J(H_{6py}H_{5py}) = 5.0 Hz, 1 H, H_{6py}). ¹³C{¹H} NMR (150.90 MHz, THF-d₈, 296 K): δ –5.0, –1.4 (Si(CH₃)₂), 19.8 (o-CH₃-Mes), 21.2 (p-CH₃-Mes), 21.6 (Si-C(CH₃)₃), 25.6 (C-CH₃), 28.5 (Si-C(CH₃)₃), 48.1 (C-CH₃), 65.1 (CH₂), 120.8 (p-C_{Ph}), 121.1 (m-C_{py}), 123.5 (C_{Spy}), 124.0 (C_{3py}), 124.8 (p-C_{py}), 128.4 (m-C_{Mes}), 128.6 (m-C_{Ph}), 129.3 (p-C_{Mes}), 130.3 (o-C_{Mes}), 140.0 (C_{4py}), 147.5 (i-C_{Mes}), 149.2 (C_{6py}), 149.2 (i-C_{NPh}), 151.5 (o-C_{py}), 157.9 (NCS), 161.6 (C_{2py}). ²⁹Si{¹H} NMR (79.45 MHz, THF-d₈, 296 K): δ 1.48 (Si(CH₃)₂Bu). ¹⁵N NMR (60.82 MHz, THF-d₈, 296 K): δ 121.5 (NPh₂), 188.5 (N-Si(CH₃)₂Bu), 209.1 (Zr-NCS), 245.2 (Mes-NCS), 289.3 (L-N_{py}), not observed (N_{py}). IR (Nujol, NaCl): ν 1579 s, 1463 s, 1377 s, 1303 w, 1260 s, 1169 m, 1146 m, 1095 m, 1022 s, 932 w, 832 m, 800 s, 722 w, 691 cm⁻¹. Anal. Calcd for C₆₈H₆₇N₇SSi₂Zr·0.75C₇H₈: C, 64.56; H, 7.43; N, 9.90. Found: C, 64.59; H, 7.41; N, 9.58.

Preparation of [Zr(N₂TBSN_{py})(κ²N,S-SC(=NNPh₂)NPh)] (3). To a stirred solution of [Zr(N₂TBSN_{py})(NNPh₂)(py)] (1a; 700 mg, 0.94 mmol) in toluene (20 mL) was added a solution of phenyl isothiocyanate (123 mg, 0.94 mmol) in toluene (1 mL). The reaction mixture was stirred overnight at room temperature and then heated to 60 °C for 5 h. After it was cooled, the reaction mixture was filtered and the volatiles were removed under reduced pressure. The crude product was washed with pentane (3 × 5 mL), recrystallized from cold (–78 °C) pentane, and dried in vacuo to yield 620 mg (70%) of 3 as a yellow solid. ¹H NMR (600.13 MHz, THF-d₈, 296 K): δ –0.25, 0.14 (s, 6 H, Si(CH₃)₂), 0.60 (s, 18 H, Si-C(CH₃)₃), 1.57 (CH₃), 3.30, (d, ²J_{HH} = 13.0 Hz, 2 H, CHH), 4.05 (d, ²J_{HH} = 13.0 Hz, 2 H, CHH), 6.70 (tt, ³J(p-H_{Ph}m-H_{Ph}) = 7.3 Hz, ⁴J(p-H_{Ph}o-H_{Ph}) = 1.2 Hz, 2 H, p-H_{Ph}), 6.86 (tt, ³J(p-H_{Ph}NCSm-H_{Ph}NCS) = 7.4 Hz, ⁴J(p-H_{Ph}NCSo-H_{Ph}NCS) = 1.1 Hz, 1 H, p-H_{Ph}NCS), 7.07 (m, 4 H, m-H_{Ph}), 7.18 (m, 2 H, m-H_{Ph}NCS), 7.22 (dd, ³J(o-H_{Ph}m-H_{Ph}) = 7.6 Hz, ⁴J(o-H_{Ph}p-H_{Ph}) = 1.2 Hz, 4 H, o-H_{Ph}), 7.50 (dt, ³J(H_{5py}H_{6py}/H_{4py}) = 6.6 Hz, ⁴J(H_{5py}H_{3py}) = 1.0 Hz, 1 H, H_{5py}), 7.68 (d, ³J(o-H_{Ph}NCSm-H_{Ph}NCS) = 8.0 Hz, 2 H, o-H_{Ph}NCS), 7.77 (d, ³J(H_{3py}H_{4py}) = 8.0 Hz, 1 H, H_{3py}), 8.09 (dt, ³J(H_{4py}H_{3py}/H_{5py}) = 7.8 Hz, ⁴J(H_{4py}H_{6py}) = 1.7 Hz, 1 H, H_{4py}), 8.98 (d, ³J(H_{6py}H_{5py}) = 5.1 Hz, 1 H, H_{6py}). ¹³C{¹H} NMR (150.90 MHz, THF-d₈, 296 K): δ –4.7, –4.0 (Si(CH₃)₂), 20.9 (Si-C(CH₃)₃), 25.8 (C-CH₃), 27.9 (Si-C(CH₃)₃), 49.0 (C-CH₃), 63.9 (CH₂), 120.4 (p-C_{Ph}), 120.6 (o-C_{Ph}), 122.4 (p-C_{Ph}NCS), 123.3 (C_{3py}), 124.1 (C_{Spy}), 125.2 (o-C_{Ph}NCS), 128.8 (m-C_{Ph}), 129.0 (m-C_{Ph}NCS), 142.0 (C_{4py}), 149.3 (i-C_{Ph}NCS), 149.6 (i-C_{NPh}), 148.3 (C_{6py}), 161.5 (C_{2py}), 168.1 (NCS); ²⁹Si{¹H} NMR (79.45 MHz, THF-d₈, 296 K): δ 2.18 (Si(CH₃)₂Bu). ¹⁵N NMR (60.82 MHz, THF-d₈, 296 K): δ 129.9 (NPh₂), 194.0 (Ph-NCS), 203.2 (N-Si(CH₃)₂Bu), 271.2 (Zr-NCS) 280.1 (L-N_{py}). IR (Nujol, NaCl) ν 1686 m, 1464 s, 1377 s, 1306 w, 1260 m, 1215 w, 1153 w, 1087 m, 1021 s, 895 w, 850 m, 821 m, 801 m, 733 w, 722 w, 692 w, 669 w cm⁻¹. Anal. Calcd for C₄₀H₅₆N₆SSi₂Zr: C, 60.03; H, 7.05; N, 10.50. Found: C, 60.10; H, 6.79; N, 10.96.

Preparation of $[\text{Zr}(\text{N}_2^{\text{TBS}}\text{N}_{\text{py}})(\kappa^2\text{N},\text{C}-\text{N}(\text{NPh}_2)\text{CH}_2\text{C}=\text{CH}(\text{Ph}))-\text{(py)}]$ (4a). To a stirred solution of $[\text{Zr}(\text{N}_2^{\text{TBS}}\text{N}_{\text{py}})(\text{NNPh}_2)(\text{py})]$ (400 mg, 0.54 mmol) in toluene (20 mL) was added a solution of phenyl allene (62 mg, 0.54 mmol) in toluene (2 mL). The reaction mixture was stirred for 16 h at room temperature and filtered, and the volatiles were removed under reduced pressure. The resulting yellow solid was washed with hexane (3×3 mL) before drying in vacuo to yield 320 mg (95%) of $[\text{Zr}(\text{N}_2^{\text{TBS}}\text{N}_{\text{py}})(\kappa^2\text{N},\text{C}-\text{N}(\text{NPh}_2)\text{CH}_2\text{C}=\text{CH}(\text{Ph}))(\text{py})]$ (4a) as a yellow solid. Single crystals for X-ray diffraction were grown from a methylcyclohexane/toluene (1/1) solution at room temperature. ^1H NMR (600 MHz, C_6D_6 , 296 K): δ -0.73, 0.45 (s, 6 H, Si(CH_3)₂), 0.80 (s, 3 H, CH_3), 0.81 (s, 18 H, Si-C(CH_3)₃), 2.24 (s, 2 H, Zr CH_2), 3.00 (bd, ${}^2J_{\text{HH}} = 12.5$ Hz, 2 H, CHH), 3.24 (d, ${}^2J_{\text{HH}} = 12.5$ Hz, 2 H, CHH), 5.77 (s, 1 H, C=C), 6.56 (t, 3J (p-H_{py}m-H_{py}) = 6.2 Hz, 2 H, m-H_{py}), 6.61 (t, 3J (H₃pyH₄py/H₆py) = 6.4 Hz, 1 H, HS_{py}), 6.76–6.87 (m, 5 H, H₃py m-H_{py} p-H_{Ph}), 6.91 (t, 3J (p-H_{Ph}CH_m-H_{Ph}CH) = 7.2 Hz, 1 H, p-H_{Ph}CH), 7.07 (t, 3J (H₄pyH₃py/HS_{py}) = 7.8 Hz, 1 H, H₄py), 7.12–7.16 (m, 4 H, m-H_{py}), 7.25 (t, 3J (m-H_{Ph}CH_o-H_{Ph}CH/p-H_{Ph}CH) = 7.8 Hz, 2 H, m-H_{Ph}CH), 7.40 (t, 3J (o-H_{Ph}m-H_{Ph}) = 7.8 Hz, 4 H, o-H_{Ph}), 7.76 (t, 3J (o-H_{Ph}CH_m-H_{Ph}CH) = 7.8 Hz, 2 H, o-H_{Ph}CH), 8.92 (bs, 2 H, o-H_{py}), 9.09 (d, 3J (H₆pyHS_{py}) = 5.0 Hz, 1 H, H₆py). $^{13}\text{C}\{{}^1\text{H}\}$ NMR (150 MHz, C_6D_6 , 296 K): δ -5.5, -2.4 (Si(CH_3)₂), 20.9 (Si-C(CH_3)₃), 24.9 (C- CH_3), 28.0 (Si-C(CH_3)₃), 46.5 (C- CH_3), 49.2 (Zr CH_2), 63.9 (CH₂), 93.1 ((Ph)HC=C), 119.3 (o-C_{Ph}), 120.0 (p-C_{Ph}), 121.1 (p-C_{Ph}-CH), 122.0, 122.1 (C₃py, CS_{py}), 123.6 (m-C_{py}), 127.1 (o-C_{Ph}CH), 128.0 (p-C_{Ph}CH), 128.7 (m-C_{Ph}), 137.9 (p-C_{py}), 138.3 (C₄py), 143.7 (i-C_{Ph}CH), 147.1 (C₆py), 147.2 (i-C_{Ph}), 151.0 (o-C_{py}), 158.2 ((Ph)HC=C), 160.4 (C₂py). $^{29}\text{Si}\{{}^1\text{H}\}$ NMR (80 MHz, C_6D_6 , 296 K): δ 0.37 (Si(CH_3)₂'Bu). ^{15}N NMR (60 MHz, C_6D_6 , 296 K): δ 121.4 (NPh₂), 177.2 (N-Si(CH_3)₂'Bu), 223.0 (Zr-NC), 291.6 (L-N_{py}), not observed (Npy). IR (Nujol, NaCl): ν 2725 w, 2669 s, 1607 sh, 1574 s, 1556 s, 1463 s, 1328 sh, 1247 w, 1174 m, 1029 m, 953 w, 891 w, 844 s, 770 w, 722 s, 692 m cm⁻¹. Anal. Calcd for $\text{C}_{47}\text{H}_{64}\text{N}_6\text{Si}_2\text{Zr}$: C, 65.61; H, 7.50; N, 9.77. Found: C, 65.21; H, 7.40; N, 9.78.

Preparation of $[\text{Hf}(\text{N}_2^{\text{TBS}}\text{N}_{\text{py}})(\kappa^2\text{N},\text{C}-\text{N}(\text{NPh}_2)\text{CH}_2\text{C}=\text{CH}(\text{Ph}))-\text{(py)}]$ (4b). To a stirred solution of $[\text{Hf}(\text{N}_2^{\text{TBS}}\text{N}_{\text{py}})(\text{NNPh}_2)(\text{py})]$ (1b; 200 mg, 0.24 mmol) in toluene (20 mL) was added phenyl allene (27 mg, 0.24 mmol). The reaction mixture was stirred overnight at room temperature and filtered, and the volatiles were removed under reduced pressure. The resulting yellow solid was washed with pentane (2×5 mL) before drying in vacuo to yield 94 mg (41%) of $[\text{Hf}(\text{N}_2^{\text{TBS}}\text{N}_{\text{py}})(\kappa^2\text{N},\text{C}-\text{N}(\text{NPh}_2)\text{CH}_2\text{C}=\text{CH}(\text{Ph}))(\text{py})]$ (4b) as a yellow solid. ^1H NMR (C_6D_6 , 600.13 MHz, 296 K): δ -0.72 (s, 6 H, Si(CH_3)₂), 0.41 (s, 6 H, Si(CH_3)₂), 0.80 (s, 3 H, C- CH_3), 0.82 (s, 18 H, Si-C(CH_3)₃), 2.14 (s, 2 H, Hf- CH_2), 2.90–3.11 (m, 2 H, CH_aH_b), 3.40 (d, ${}^2J_{\text{HH}} = 12.8$ Hz, 2 H, CH_aH_b), 5.90 (s, 1 H, C=C), 6.56–6.60 (m, 2 H, m-H_{py}), 6.60–6.65 (m, 1 H, HS_{py}), 6.78–6.86 (m, 4 H, H₃py p-H_{py}, p-H_{Ph}), 6.93 (t, 3J (H_pH_m) = 7.2 Hz, 1 H, p-H_{Ph}), 7.00–7.12 (m, 1 H, H₄py), 7.13–7.16 (m, 4 H, m-H_{Ph}), 7.27 (t, 3J (H_pH_m) = 7.5 Hz, 2 H, m-H_{Ph}), 7.40 (d, 3J (H_oH_m) = 5.5 Hz, 4 H, o-H_{Ph}), 7.79 (d, 3J (H_oH_m) = 7.6 Hz, 2 H, o-H_{Ph}), 8.97 (s, 2 H, o-H_{py}), 9.14 (s, 1 H, H₆py). $^{13}\text{C}\{{}^1\text{H}\}$ NMR (C_6D_6 , 150.92 MHz, 296 K): δ -5.4, -2.5 (Si(CH_3)₂), 21.3 (Si-C(CH_3)₃), 24.5 (C- CH_3), 28.2 (Si-C(CH_3)₃), 45.2 (C- CH_3), 54.2 (Hf- CH_2), 63.2 (CH₂), 95.2 (C=CHPh), 119.5 (o-C_{Ph}), 120.2 (C₃py, p-C_{py}, p-C_{Ph}), 121.4 (p-C_{Ph}), 122.1 (C₃py, p-C_{py}, p-C_{Ph}), 122.4 (CS_{py}), 123.8 (m-C_{py}), 127.4 (o-C_{Ph}), 128.7 (m-C_{Ph}), 137.8 (C₃py, p-C_{py}, p-C_{Ph}), 138.2 (C₄py), 143.5 (ipso-C_{Ph}), 146.8 (C₆py), 147.4 (i-C_{Ph}), 151.0 (o-C_{py}), 160.4 (C=CHPh), 165.3 (C₂py). ^{15}N NMR (C_6D_6 , 60.84 MHz, 296 K): δ 123.4 (NPh₂), 166.9 (N-TBS), 222.2 (Hf-NC), 281.5 (N_{py}), 292.7 (N_{py}). $^{29}\text{Si}\{{}^1\text{H}\}$ NMR (C_6D_6 , 79.45 MHz, 296 K): δ 1.6 (Si(CH_3)₂'Bu)). IR (Nujol, NaCl, cm⁻¹): ν 2926 vs, 2854 vs, 1923 w, 1579 m, 1464 s, 1378 m, 1328 w, 1258 m, 1174 m, 1098 w, 1024 m, 892 w, 851 w, 799 m, 743 m, 693 m, 627 w cm⁻¹. Anal. Calcd for $\text{C}_{47}\text{H}_{64}\text{N}_6\text{Si}_2\text{Hf}$: C, 59.56; H, 6.81; N, 8.87. Found C, 59.61; H, 6.78; N, 9.31. Despite repeated recrystallizations of 4b we were unable to obtain a more accurate value for the nitrogen content.

Preparation of $[\text{Zr}(\text{N}_2^{\text{TBS}}\text{N}_{\text{py}})(\kappa^2\text{N},\text{C}-\text{N}(\text{NPh}_2)\text{CH}_2\text{C}=\text{CH}(\text{Cy}))-\text{(py)}]$ (5a). To a stirred solution of $[\text{Zr}(\text{N}_2^{\text{TBS}}\text{N}_{\text{py}})(\text{NNPh}_2)(\text{py})]$

(300 mg, 0.40 mmol) in toluene (20 mL) was added a solution of cyclohexyl allene (60 μL , 0.40 mmol) in toluene (2 mL). The reaction mixture was stirred for 16 h at room temperature and filtered, and the volatiles were removed under reduced pressure. The resulting yellow solid was washed with hexane (3×5 mL) before drying in vacuo to yield 200 mg (44%) of $[\text{Zr}(\text{N}_2^{\text{TBS}}\text{N}_{\text{py}})(\kappa^2\text{N},\text{C}-\text{N}(\text{NPh}_2)\text{CH}_2\text{C}=\text{CH}(\text{Cy}))(\text{py})]$ as a yellow solid. ^1H NMR (600 MHz, C_6D_6 , 296 K): δ -0.69, 0.52 (s, 6 H, Si(CH_3)₂), 0.82 (s, 3 H, CH_3), 0.85 (s, 18 H, Si-C(CH_3)₃), 1.14–1.24 (m, 3 H, cy- CH_2), 1.45–1.53 (m, 2 H, cy- CH_2), 1.59–1.67 (m, 1 H, cy- CH_2), 1.74–1.81 (m, 2 H, cy- CH_2), 1.88 (s, 2 H, Zr CH_2), 1.97–2.05 (m, 2 H, cy- CH_2), 2.63–2.72 (m, 1 H, cy- CH), 2.99 (bd, ${}^2J_{\text{HH}} = 12.9$ Hz, 2 H, CHH), 3.25 (d, ${}^2J_{\text{HH}} = 12.9$ Hz, 2 H, CHH), 4.35 (d, ${}^3J_{\text{HH}} = 8.5$ Hz, 1 H, C=C), 6.54–6.59 (m, 2 H, m-H_{py}), 6.65 (t, 3J (H₅pyH₄py/H₆py) = 6.2 Hz, 1 H, HS_{py}), 6.79 (t, 3J (m-H_{Ph}o-H_{Ph}/p-H_{Ph}) = 7.2 Hz, 4 H, m-H_{Ph}), 6.87 (d, 3J (H₃pyH₄py) = 7.2 Hz, 1 H, H₃py), 7.09 (t, 3J (H₄pyH₃py/HS_{py}) = 7.6 Hz, 1 H, H₄py), 7.13–7.17 (m, 4 H, m-H_{Ph}), 7.39 (t, 3J (o-H_{Ph}m-H_{Ph}) = 7.8 Hz, 4 H, o-H_{Ph}), 8.94 (bs, 2 H, o-H_{py}), 9.11 (d, 3J (H₆pyHS_{py}) = 5.3 Hz, 1 H, H₆py). $^{13}\text{C}\{{}^1\text{H}\}$ NMR (150 MHz, C_6D_6 , 296 K): δ -5.4, -2.4 (Si(CH_3)₂), 21.0 (Si-C(CH_3)₃), 25.0 (C- CH_3), 27.1 (cy- CH_2), 27.4 (cy- CH_2), 28.1 (Si-C(CH_3)₃), 36.3 (cy- CH_2 , cy- CH), 45.9 (Zr CH_2), 46.5 (C- CH_3), 63.9 (CH₂), 97.1 ((cy)HC=C), 119.2 (o-C_{Ph}), 119.5 (p-C_{Ph}), 121.7 (CS_{py}), 121.9 (C₃py), 123.5 (m-C_{py}), 128.4 (m-C_{Ph}), 137.8 (C₄py), 137.9 (p-C_{py}), 147.2 (i-C_{Ph}), 147.5 (C₆py), 149.3 ((cy)HC=C), 151.0 (o-C_{py}), 160.6 (C₂py). $^{29}\text{Si}\{{}^1\text{H}\}$ NMR (80 MHz, C_6D_6 , 296 K): δ 0.39 (Si(CH_3)₂'Bu). ^{15}N NMR (60 MHz, C_6D_6 , 296 K): δ 123.9 (NPh₂), 172.0 (N-Si(CH_3)₂'Bu), 220.6 (Zr-NC), 293.6 (L-N_{py}), not observed (Npy). IR (Nujol, NaCl): ν 1626 m, 1600 m, 1585 m, 1498 sh, 1463 s, 1377 s, 1247 m, 1161 w, 1085 w, 1036 m, 885 w, 846 s, 826 m, 771 w, 740 m, 722 w, 691 w, 659 cm⁻¹. Anal. Calcd for $\text{C}_{47}\text{H}_{64}\text{N}_6\text{Si}_2\text{Zr}$: C, 65.61; H, 7.50; N, 9.77. Found: C, 65.21; H, 7.40; N, 9.78.

Preparation of $[\text{Hf}(\text{N}_2^{\text{TBS}}\text{N}_{\text{py}})(\kappa^2\text{N},\text{C}-\text{N}(\text{NPh}_2)\text{CH}_2\text{C}=\text{CH}(\text{Cy}))-\text{(py)}]$ (5b). To a stirred solution of $[\text{Hf}(\text{N}_2^{\text{TBS}}\text{N}_{\text{py}})(\text{NNPh}_2)(\text{py})]$ (1b; 800 mg, 0.96 mmol) in toluene (60 mL) was added cyclohexyl allene (117 mg, 0.96 mmol). The reaction mixture was stirred overnight at room temperature and filtered, and the volatiles were removed under reduced pressure. The resulting yellow solid was washed with pentane (2×5 mL) before drying in vacuo to yield 610 mg (67%) of $[\text{Hf}(\text{N}_2^{\text{TBS}}\text{N}_{\text{py}})(\kappa^2\text{N},\text{C}-\text{N}(\text{NPh}_2)\text{CH}_2\text{C}=\text{CH}(\text{Cy}))(\text{py})]$ (5b) as a yellow solid. Single crystals for X-ray diffraction were grown from a hexane solution at room temperature. ^1H NMR (C_6D_6 , 600.13 MHz, 296 K): δ -0.70 (s, 6 H, Si(CH_3)₂), 0.49 (s, 6 H, Si(CH_3)₂), 0.82 (s, 3 H, C- CH_3), 0.86 (s, 18 H, Si-C(CH_3)₃), 1.24–1.28 (m, 3 H, cy- CH_2), 1.47–1.54 (m, 2 H, cy- CH_2), 1.62–1.64 (m, 1 H, cy- CH_2), 1.76–1.79 (m, 4 H, Hf- CH_2 , cy- CH_2), 2.02–2.04 (m, 2 H, cy- CH_2), 2.71–2.73 (m, 1 H, cy- CH_2), 3.00 (bd, ${}^2J_{\text{HH}} = 12.3$ Hz, 2 H, CH_aH_b), 3.40 (d, ${}^2J_{\text{HH}} = 12.7$ Hz, 2 H, CH_aH_b), 4.47 (d, 1 H, 3J (HH_c) = 7.71 Hz, C=C), 6.57–6.59 (m, 2 H, m-H_{py}), 6.63–6.66 (m, 1 H, HS_{py}), 6.78–6.86 (m, 4 H, p-H_{Ph}, p-H_{py}, H₃py), 7.08–7.10 (m, 1 H, H₄py), 7.16–7.18 (m, 4 H, m-H_{Ph}), 7.39 (d, ${}^3J_{\text{HH}} = 7.2$ Hz, 4 H, o-H_{Ph}), 8.96 (d, 2 H, 3J (o-Hm-H) = 3.8 Hz, o-H_{py}), 9.15–9.16 (m, 1 H, H₆py). $^{13}\text{C}\{{}^1\text{H}\}$ NMR (C_6D_6 , 150.92 MHz, 296 K): δ -5.3, -2.5 (Si(CH_3)₂), 21.3 (Si-C(CH_3)₃), 24.6 (C- CH_3), 27.1, 27.4 (cy- CH_2), 28.2 (Si-C(CH_3)₃), 36.3, 36.8 (cy- CH_2), 45.2 (C- CH_3), 50.8 (Hf- CH_2), 63.3 (CH₂), 99.2 (C=CCH_c), 119.4 (o-C_{Ph}), 119.6 (C₃py, p-C_{py}, p-C_{Ph}), 122.9 (C₃py, p-C_{py}, p-C_{Ph}), 122.0 (CS_{py}), 123.6 (m-C_{py}), 137.5 (C₃py, p-C_{py}, p-C_{Ph}), 137.9 (C₄py), 143.4 (ipso-C_{Ph}), 146.9 (C₆py), 147.7 (C=CCH_c), 150.9 (o-C_{py}), 160.4 (C₂py). ^{15}N NMR (C_6D_6 , 60.84 MHz, 296 K): δ 123.1 (N(SiPh)₂), 163.6 (N(1/2)-TBS), 220.4 (Hf-N(4)), 285.9 (N_{py}), 293.6 (N(3)_{py}). $^{29}\text{Si}\{{}^1\text{H}\}$ NMR (C_6D_6 , 79.45 MHz, 296 K): δ 1.5 (Si(CH_3)₂'Bu)). IR (Nujol, NaCl): ν 2924 vs, 2854 vs, 1464 s, 1377 m, 1260 m, 1091 m, 1024 m, 852 w, 798 m, 585 w, 527 w cm⁻¹. Anal. Calcd for $\text{C}_{47}\text{H}_{70}\text{N}_6\text{Si}_2\text{Hf}$: C, 59.19; H, 7.40; N, 8.81. Found: C, 59.01; H, 7.50; N, 8.66.

Preparation of $[\text{Zr}(\text{N}_2^{\text{TBS}}\text{N}_{\text{py}})(\kappa^2\text{N},\text{C}-\text{N}(\text{NPh}_2)\text{CH}_2\text{C}=\text{CH}(\text{Me}))-\text{(py)}]$ (6). Methyl allene was bubbled for 10 min through a stirred solution of $[\text{Zr}(\text{N}_2^{\text{TBS}}\text{N}_{\text{py}})(\text{NNPh}_2)(\text{py})]$ (800 mg, 1.08 mmol) in toluene (30 mL) until the solution stayed orange. The reaction mixture was stirred for an additional 2 h, and the volatiles were

Table 2. Details of the Crystal Structure Determinations of 2a,b and 4a,b

	2a·(toluene)	2b·(toluene)	4a	4b·(n-hexane)
formula	C ₅₂ H ₆₉ N ₇ SSi ₂ Zr	C ₅₅ H ₇₅ N ₇ SSi ₂ Zr	C ₄₇ H ₆₄ N ₆ Si ₂ Zr	C ₅₃ H ₈₄ HfN ₆ Si ₂
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	P2 ₁ /n	P2 ₁ /n	P2 ₁ /c	P2 ₁ /n
a/Å	11.596(3)	11.392(6)	11.140(5)	11.179(6)
b/Å	21.607(5)	21.888(11)	22.176(10)	23.599(12)
c/Å	20.596(5)	22.235(11)	19.373(8)	20.213(10)
β/deg	96.340(4)	103.007(7)	104.619(10)	91.200(9)
V/Å ³	5129(2)	5402(5)	4631(3)	5331(5)
Z	4	4	4	4
M _r	971.60	1013.68	860.44	1039.93
F ₀₀₀	2056	2152	1824	2176
d _c /Mg m ⁻³	1.258	1.246	1.234	1.296
μ/mm ⁻¹	0.343	0.329	0.327	2.041
max, min transmissn factors	0.7452, 0.6650	0.7464, 0.6789	0.7464, 0.6646	0.7464, 0.6324
θ range/deg	1.4 to 25.2	1.3 to 32.3	1.8 to 32.2	2.0 to 32.4
index ranges (indep set) h,k,l	-13 to +13, 0-25, 0-24	-17 to +16, 0-32, 0-33	-16 to +15, 0-33, 0-28	-16 to +16, 0-35, 0-29
no. of rflns				
measd	86 349	136 919	116 350	131 306
unique (<i>R</i> _{int})	9145 (0.1504)	18 314 (0.0445)	15 547 (0.0426)	18 031 (0.068)
obsd (<i>I</i> > 2σ(<i>I</i>))	5844	15 221	12 868	14 468
no. of params refined	580	619	516	572
GOF on <i>F</i> ²	1.107	1.030	1.058	1.034
<i>R</i> indices (<i>F</i> > 4σ(<i>F</i>): <i>R</i> (<i>F</i>), <i>R</i> _w (<i>F</i> ²)	0.0540, 0.1292	0.0359, 0.0837	0.0322, 0.0759	0.0325, 0.0638
<i>R</i> indices (all data): <i>R</i> (<i>F</i>), <i>R</i> _w (<i>F</i> ²)	0.1067, 0.1488	0.0485, 0.0925	0.0454, 0.0844	0.0499, 0.0708
largest residual peaks/e Å ⁻³	0.672, -0.705	0.691, -0.404	0.622, -0.385	2.802, -1.357

removed under reduced pressure. The resulting yellow solid was washed with hexane (3 × 5 mL) before drying in vacuo to yield 300 mg (35%) of [Zr(N₂^{TBS}N_{py})(κ²N,C-N(NPh₂)CH₂C=CH(Me))(py)] (**6**) as a yellow solid. ¹H NMR (600 MHz, C₆D₆, 296 K): δ -0.66, 0.50 (s, 6 H, Si(CH₃)₂), 0.84 (s, 18 H, Si-(CH₃)₃), 1.14 (s, 3 H, CH₃), 1.87 (s, 2 H, ZrCH₂), (d, ²J_{HH} = 6.3 Hz, 3 H, C=C-CH₃), 3.05 (bd, ²J_{HH} = 12.8 Hz, 2 H, CHH), 3.27 (d, = 12.8 Hz, 2 H, CHH), 4.59 (d, ³J_{HH} = 6.3 Hz, 1 H, C=CH), 6.57 (bs, 2 H, m-H_{py}), 6.65 (t, ³J(HS_{py}H4_{py}/H6_{py}) = 6.0 Hz, 1 H, HS_{py}), 6.79 (t, ³J(m-H_{ph}o-H_{ph}/p-H_{ph}) = 7.1 Hz, 4 H, m-H_{ph}), 6.81–6.87 (m, 3 H, p-H_{py}/H3_{py}), 7.08 (t, ³J(H4_{py}H3_{py}/HS_{py}) = 6.0 Hz, 1 H, H4_{py}), 7.13–7.17 (m, 4 H, m-H_{ph}), 7.42 (t, ³J(o-H_{ph}m-H_{ph}) = 7.6 Hz, 4 H, o-H_{ph}), 8.90 (bs, 2 H, o-H_{py}), 9.13 (d, ³J(H6_{py}H5_{py}) = 5.3 Hz, 1 H, H6_{py}). ¹³C{¹H} NMR (150 MHz, C₆D₆, 296 K): δ -5.6, -2.7 (Si(CH₃)₂), 12.0 (C=C-CH₃), 20.8 (Si-C(CH₃)₃), 24.8 (C-CH₃), 27.9 (Si-C(CH₃)₃), 45.3 (ZrCH₂), 46.3 (C-CH₃), 63.7 (CH₂), 82.4 ((Me)HC=C), 119.1 (o-C_{ph}), 119.4 (p-C_{ph}), 121.5 (C5_{py}), 121.8 (C3_{py}), 123.3 (m-C_{py}), 128.2 (m-C_{ph}), 137.0 (p-C_{py}), 137.7 (C4_{py}), 147.0 (C6_{py}), 147.5 (i-C_{ph}), 150.7 (o-C_{py}), 151.1 ((Me)HC=C), 160.4 (C2_{py}). ²⁹Si{¹H} NMR (80 MHz, C₆D₆, 296 K): δ 0.24 (Si(CH₃)₂'Bu). ¹⁵N NMR (60 MHz, C₆D₆, 296 K): δ 123.3 (NPh₂), 172.3 (N-Si(CH₃)₂'Bu), 222.8 (Zr-NC), 293.9 (L-N_{py}), not observed (Npy). IR (Nujol, NaCl): ν 1630 m, 1599 s, 1463 s, 1377 s, 1306 w, 1260 s, 1203 w, 1162 w, 1097 m, 1037 s, 950 w, 891 w 846 s, 825 s, 771 m, 722 s, 690 w, 658 w cm⁻¹. Anal. Calcd for C, 63.18; H, 7.83; N, 10.53. Found: C, 62.80; H, 7.62; N, 9.41. Found: C, 62.97; H, 7.94; N, 10.10.

Preparation of [Zr(κ⁴N,N,N,N-N₂^{TBS}N_{py}NC(Me)=CHCy](NPh₂) (**7a**). A solution of [Zr(N₂^{TBS}N_{py})(κ²NC-N(NPh₂)CH₂C=CH(Cy)-(py)] (**5a**; 800 mg, 1.07 mmol) in toluene (20 mL) was heated with stirring for 5 h to 80 °C. The reaction mixture was filtered, and the volatiles were removed under reduced pressure. The resulting yellow solid was washed with pentane (3 × 5 mL) before drying in vacuo to yield 600 mg (71%) of **7a** as a yellow solid. ¹H NMR (600 MHz, C₆D₆, 296 K): δ -0.16, 0.05, 0.33, (s, 3 H, Si(CH₃)₂), 0.92, 0.94 (s, 9 H, Si-C(CH₃)₃), 1.04 (s, 3 H, CH₃), 1.16–1.22 (m, 3 H, cy-CH₂), 1.30–1.38 (m, 2 H, cy-CH₂), 1.63–1.68 (m, 1 H, cy-CH₂), 1.72–1.79 (m, 2 H, cy-CH₂), 1.83–1.93 (m, 2 H, cy-CH₂), 2.13 (s, 3 H, C=C-CH₃), 2.21–2.62 (m, 1 H, cy-CH), 2.96 (d, ²J_{HH} = 14.2 Hz, 1 H,

CHH), 3.08 (d, ²J_{HH} = 14.2 Hz, 1 H, CHH), 3.28 (d, ²J_{HH} = 12.6 Hz, 1 H, CHH), 3.34 (d, ²J_{HH} = 12.8 Hz, 1 H, CHH), 3.38 (d, ²J_{HH} = 12.6 Hz, 1 H, CHH), 3.95 (d, ²J_{HH} = 12.8 Hz, 1 H, CHH), 4.68 (d, ³J_{HH} = 8.6 Hz, 1 H, C=CH), 6.31 (t, ³J(HS_{py}H4_{py}/H6_{py}) = 6.1 Hz, 1 H, HS_{py}), 6.78 (d, ³J(H3_{py}H4_{py}) = 8.0 Hz, 1 H, H3_{py}), 6.86 (t, ³J(p-H_{ph}o-mH_{ph}) = 6.7 Hz, 2 H, p-H_{ph}), 6.90 (t, ³J(H4_{py}H3_{py}/HS_{py}) = 7.5 Hz, 1 H, H4_{py}), 8.98 (d, ³J(H6_{py}H5_{py}) = 5.6 Hz, 2 H, H6_{py}). ¹³C{¹H} NMR (150 MHz, C₆D₆, 296 K): δ -5.8, -4.3, -2.6 (Si(CH₃)₂), 19.6 (C=C-CH₃), 20.1, 20.2 (Si-C(CH₃)₃), 22.7 (cy-CH₂), 23.8 (C-CH₃), 26.8 (cy-CH₂), 27.0 (Si-C(CH₃)₃), 27.6 (cy-CH₂), 28.2 (Si-C(CH₃)₃), 34.4 (cy-CH₂), 36.7 (ZrCH₂), 37.9 (cy-CH), 52.2 (C-CH₃), 61.7, 63.3 (CH₂), 109.5 ((cy)HC=C), 119.8 (C3_{py}), 120.7 (p-C_{ph}), 121.9 (C5_{py}), 130.1 (m-C_{ph}), 139.4 (C4_{py}), 147.4 ((cy)HC=C), 150.2 (C6_{py}), 151.7 (i-C_{ph}), 164.5 (C2_{py}), not observed (o-C_{ph}). ²⁹Si{¹H} NMR (80 MHz, C₆D₆, 296 K): δ 2.84, 8.17 (Si(CH₃)₂'Bu). ¹⁵N NMR (60 MHz, C₆D₆, 296 K): δ 173.7 (N-Si(CH₃)₂'Bu), 189.1 (N-C(Me)C(Cy)), 191.4 (NPh₂), 294.2 (N-Si(CH₃)₂'Bu), 282.1 (L-N_{py}). IR (Nujol, NaCl): ν 1653 w, 1595 m, 1463 s, 1377 s, 1261 s, 1197 m, 1170 w, 1093 m, 1039 m 1012 sh, 894 w, 865 w, 801 s, 755 w, 722 m, 698 cm⁻¹. Anal. Calcd for C₄₂H₆₅N₅Si₂Zr: C, 64.07; H, 8.32; N, 8.89. Found: C, 64.45; H, 8.20; N, 8.85.

Preparation of [Hf(κ⁴N,N,N,N-N₂^{TBS}N_{py}NC(Me)=CHCy-(NPh₂)] (**7b**). A solution of [Hf(N₂^{TBS}N_{py})(κ²-N,C-(CH₂C(=CH-Cy))N(NPh₂))(py)] (**5b**; 600 mg, 0.63 mmol) in toluene (60 mL) was heated with stirring overnight to 80 °C. The reaction mixture was filtered, the volatiles were removed under reduced pressure, and the residue was dissolved in methylcyclohexane and then placed into a -30 °C freezer. After 24 h, the yellow solid that formed was collected by filtration and then dried in vacuo to yield 190 mg (34%) of **7b**. ¹H NMR (C₆D₆, 600.13 MHz, 296 K): δ -0.13 (s, 3 H, Si(1)-CH₃), -0.09 (s, 3 H, Si(1)-CH₃), 0.33 (s, 3 H, Si(2)-CH₃), 0.92 (s, 9 H, Si(2)-C(CH₃)₃), 0.95 (s, 9 H, Si(1)-C(CH₃)₃), 1.01 (s, 3 H, C-CH₃), 1.20–1.28 (m, 3 H, cy-CH₂), 1.30–1.58 (m, 2 H, cy-CH₂), 1.62–1.69 (m, 1 H, cy-CH₂), 1.72–1.81 (m, 2 H, cy-CH₂), 1.86–1.95 (m, 2 H, cy-CH₂), 2.12 (s, 3 H, C=C-CH₃), 2.22–2.28 (m, 1 H, cy-CH_{ipso}), 2.95–3.01 (m, 2 H, Si(2)-CH₂), 3.41 (d, ²J(HH) = 12.5 Hz, 2 H, CH₂H_b-N(2)), 3.49 (d, ²J(HH) = 12.5 Hz, 2 H, CH₂H_b-N(2)), 3.57 (d, ²J(HH) = 12.3 Hz, 2 H, CH₂H_b-N(1)), 4.04 (d, ²J(HH) = 12.3 Hz,

2 H, $\text{CH}_a\text{H}_b\text{-N}(1)$), 4.51 (d, $^3J(\text{H}_c\text{H}) = 8.5$ Hz, 1 H, $\text{C}=\text{C}(\text{Cy})\text{H}$), 6.32 (t, $^3J(\text{H}_5\text{py}\text{H}_6\text{py}\text{H}_4\text{py}) = 6.5$ Hz, 1 H, H_5py), 6.80 (d, $^3J(\text{H}_3\text{py}\text{H}_4\text{py}) = 8.0$ Hz, 1 H, H_3py), 6.87 (t, $^3J(\text{o-H}_{\text{Ph}}\text{p-H}_{\text{Ph}}) = 6.8$ Hz, 2 H, p- H_{Ph}), 6.92 (t, $^3J(\text{H}_5\text{py}\text{H}_3\text{py}\text{H}_4\text{py}) = 7.8$ Hz, 1 H, H_4py), 7.14–7.28 (m, 8 H, m- H_{Ph} , o- H_{Ph}), 9.51–9.52 (m, 1 H, H_6py). $^{13}\text{C}\{\text{H}\}$ NMR (C_6D_6 , 150.92 MHz, 296 K): δ –5.6 ($\text{Si}(1)\text{-CH}_3$), –3.8, –2.2 ($\text{Si}(2)\text{-CH}_3$), 20.1 ($\text{Si}(2)\text{-C}(\text{CH}_3)_3$), 20.3 ($\text{C}=\text{C-CH}_3$), 20.5 ($\text{Si}(1)\text{-C}(\text{CH}_3)_3$), 23.6 (C-CH_3), 26.9 (cy- CH_2), 27.0 ($\text{Si-C-(CH}_3)_3$), 27.2 (cy- CH_2), 28.3 ($\text{Si-C-(CH}_3)_3$), 35.5 (d, $J = 5.4$ Hz, cy- CH_2), 36.2 ($\text{Si}(2)\text{-CH}_2\text{-N}$), 37.8 (cy- $\text{C}_{\text{ipso}}\text{H}$), 52.0 (C-CH_3), 61.1 ($\text{N}(1)\text{-CH}_2$), 63.3 ($\text{N}(2)\text{-CH}_2$), 109.8 ($\text{C}=\text{C}(\text{Cy})\text{H}$), 119.9 (C_3py), 120.8 (p- C_{Ph}), 122.2 (o-/m- C_{Ph}), 122.3 (C_5py), 139.0 (o-/m- C_{Ph}), 139.6 (C_4py), 147.5 ($\text{C}=\text{C-CH}_3$), 150.3 (C_6py), 151.7 (ipso- C_{Ph}), 164.8 (C_2py). ^{15}N NMR (C_6D_6 , 60.84 MHz, 296 K): δ 166.2 ($\text{N}(1)\text{-TBS}$), 175.6 ($\text{N}(2)\text{-Si}$), 181.2 (Hf-N(4)), 192.7 (Hf-N(5)Ph_2), 281.8 ($\text{N}(3)\text{py}$). $^{29}\text{Si}\{\text{H}\}$ NMR (C_6D_6 , 79.45 MHz, 296 K): δ 4.52 ($\text{Si}(1)(\text{CH}_3)_2(\text{'Bu})$), 6.74 ($\text{Si}(2)(\text{CH}_3)_2(\text{'Bu})$). IR (Nujol, NaCl) ν 2925 vs, 2854 vs, 1646 w, 1463 s, 1377 m, 1260 w, 1018 w, 902 w, 828 w, 800 w, 722 w cm^{-1} . Anal. Calcd for $\text{C}_{42}\text{H}_{64}\text{N}_2\text{Si}_2\text{Hf}$: C, 57.67; H, 7.49; N, 8.01. Found: C, 58.35; H, 8.04; N, 7.34. Despite repeated recrystallizations we were unable to obtain more accurate data for C and N.

Generation and NMR Spectroscopic Identification of [Zr-(N₂^{TBS}N_{py})(κ²N,C-(Ph)NC₆H₄(Me)=C(Ph)NH)] (8) and Regioisomer 8' as Well as [Zr(κ⁴-N,N,N,N-TBSN_{py}NC(Me)=CHPh)(NPh₂)] (9). A C_6D_6 solution of [Zr(N₂^{TBS}N_{py})(κ²N,C-N(NPh₂)CH₂C=CH(Ph))(py)] (4a) was heated overnight to 60 °C. The reaction mixture contained three major components, namely diazirconacycles 8 and 8' and a third compound which was identified as [Zr(κ⁴-N,N,N,N-TBSN_{py}NC(Me)=CHPh))(NPh₂)] (9) by ¹H NMR spectroscopy. ¹H NMR (600 MHz, C_6D_6 , 296 K): δ –0.40, 0.04, 0.29 (s, 3 H, Si(CH₃)₂), 0.88, 0.93 (s, 9 H, Si-C(CH₃)₃), 1.05 (s, 3 H, CH₃), 1.98 (s, 3 H, C=C-CH₃), 2.89 (d, $^2J_{\text{HH}} = 14.4$ Hz, 1 H, Zr-CHH), 3.01 (d, $^2J_{\text{HH}} = 14.4$ Hz, 1 H, CHH), 3.28 (d, $^2J_{\text{HH}} = 12.2$ Hz, 1 H, CHH), 3.36 (d, $^2J_{\text{HH}} = 12.2$ Hz, 1 H, CHH), 3.81 (d, $^2J_{\text{HH}} = 12.2$ Hz, 1 H, CHH), 4.01 (d, $^2J_{\text{HH}} = 12.2$ Hz, 1 H, CHH), 4.84 (d, $^3J_{\text{HH}} = 6.8$ Hz, 1 H, C=CH), 6.28 (t, $^3J(\text{H}_5\text{py}\text{H}_4\text{py}/\text{H}_6\text{py}) = 6.8$ Hz, 1 H, H_5py), 6.60–7.66 (m, 17 H, H_{Ar}), 8.96 (d, $^3J(\text{H}_6\text{py}\text{H}_5\text{py}) = 5.8$ Hz, 2 H, H_6py).

X-ray Crystal Structure Determinations. Crystal data and details of the structure determinations are given in Table 2. Full shells of intensity data were collected at low temperature ($T = 100$ K) with a Bruker AXS Smart 1000 CCD diffractometer (Mo K α radiation, graphite monochromator, $\lambda = 0.710\,73$ Å). Data were corrected for air and detector absorption and Lorentz and polarization effects;¹⁸ absorption by the crystal was treated with a semiempirical multiscan method.^{19,20} The structures were solved by the heavy-atom method combined with structure expansion by direct methods applied to difference structure factors (complexes 4b and 2a)²¹ or by the charge flip procedure (complexes 4a and 2b)²² and refined by full-matrix least-squares methods based on F^2 against all unique reflections. All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were placed at calculated positions and refined with a riding model. Appropriate geometry and adp restraints were applied to the disordered toluene molecule in the structure of 2b.²³

ASSOCIATED CONTENT

Supporting Information

CIF files giving crystallographic for 2a,b and 4a,b. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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