ORGANOMETALLICS

Synthesis, Characterization, and Thermal Rearrangement of Zirconium Tetraazadienyl and Pentaazadienyl Complexes

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Supporting Information

ABSTRACT: Reaction of the zirconium dichloro complex $[Zr(N_2^{TBS}N_{py})Cl_2]$ (1) with 1 molar equiv of ArNHLi (Ar = Mes, DIPP) yielded the zirconium imido complexes $[Zr-(N_2^{TBS}N_{py})(=N^{DIPP})(py)]$ (2; $N_2^{TBS}N_{py} = [(2-C_5H_4N)C-(CH_3){CH_2NSi(CH_3)_2tBu}_2]^{2-}$, DIPP = 2,6-diisopropylphenyl) and $[Zr(N_2^{TBS}N_{py})(=N^{Mes})(py)]$ (3; Mes = mesityl). The imido complexes are converted to the tetraazadienido TBS complexes $[Zr(N_2^{TBS}N_{py})(N^{DIPP}N_2N^{Ph})]$ (4) and $Zr-(N_2^{TBS}N_{py})(N^{Mes}N_2N^{Ph})]$ (5) by addition of phenyl azide, whereas the reaction of 2 or 3 with mesityl azide gave the alternative product 7, in which the azide is coupled with the CH activated ancillary tripod ligand. Reaction of 1 molar equiv of trimethylsilyl azide or 1-adamantyl azide with the previously reported hydrazinediido complex $[Zr(N_2^{TBS}N_{py})(N^{TMS}N_3NPh_2)]$ (10 thermally converted into the diazenido complex 12 via loss of 1 ranalogous side-on-bonded diazenido analogue 13 was observed up temperature. On the basis of ¹⁵N labeling and DFT modeling (I



reported hydrazinediido complex $[Zr(N_2^{TBS}N_{py})(=NNPh_2)(py)]$ (9) at ambient temperature resulted in the formation of the five-membered zirconaacacycles $[Zr(N_2^{TBS}N_{py})(N^{TMS}N_3NPh_2)]$ (10) and $[Zr(N_2^{TBS}N_{py})(N^{Ad}N_3NPh_2)]$ (11). Complex 11 was thermally converted into the diazenido complex 12 via loss of 1 molar equiv of molecular N₂. The direct formation of the analogous side-on-bonded diazenido analogue 13 was observed upon reaction of 9 with 1 equiv of mesityl azide at ambient temperature. On the basis of ¹⁵N labeling and DFT modeling (DFT(B3PW91/6-31 g(d))) a mechanism for the reaction pathway leading to 12 and 13 is proposed.

INTRODUCTION

Tetraazadiene complexes have been studied for many d-block metals in different formal oxidation states.¹ The bonding within the N₄ fragment has been of special interest. It may be regarded as a neutral tetraazadiene donor (a), as part of a delocalized π system including the metal atom (b), or as a dianionic tetraazene-1,4-diido ligand with an isolated N=N double bond (c).



Evidence for all three cases has been reported in the literature on the basis of structural data as well as theoretical studies.² While the N_4 unit coordinated to late transition metals tends to be best represented by resonance structures **a** and **b**, the bonding situation in early-transition-metal complexes is adequately represented by resonance form **c**.

Several preparative routes to tetraazadiene complexes have been described in the literature, including the coupling of diazonium cations at the metal center,³ salt metathesis of dihalides with ${\rm Li}_2{\rm N}_4{\rm R}_2$,⁴ and—most commonly—the cycloaddition of organic azides with imido complexes.⁵ The latter may be either isolated starting materials or species generated in situ by thermal fragmentation of azides at low-valent metal centers and subsequent reaction with excess azide to give the cycloaddition product. Furthermore, ruthenium tetrazene intermediates have been proposed to play a key role in the catalyst deactivation in ruthenium-catalyzed "click"-azide– alkyne cycloadditions.⁶ We also note the insertion of an azide into a nitrogen–silicon bond to form an N₄ species⁷ as well as the formation of an iron hexazene complex by reductive dimerization of two molecules of azide reported by Holland and co-workers.⁸

Bergman and co-workers first reported the synthesis of the zirconium tetraazadienido complex $[Cp_2Zr(N_4^tBu_2)]$ by reaction of $[Cp_2Zr(=N^tBu)(thf)]$ with *tert*-butyl azide.⁹ In the presence of phenyl azide the N-bonded phenyl and *tert*-butyl groups underwent exchange, a process which was suggested to proceed via cycloreversion of the tetraazene-1,4-diide (I). The free imide generated in this process was trapped with norbornene to form a [2 + 2] cycloaddition product (II). With 2-butyne [2 + 2] cycloaddition of the alkyne and the thermally generated imide took place, followed by insertion of the free azide into a Zr–C bond to give a metallabicyclic system (III) (Scheme 1).⁹

Received: April 15, 2012 Published: June 4, 2012 Scheme 1. Azide Exchange in [Cp₂Zr(N₄^tBu₂)] via Cycloreversion and Imide Trapping Reactions⁹



We note that Kawaguchi and co-workers recently reported the synthesis of the zirconium tetraazadienido complex $[(Ar^{R}O)_{2}Zr(N_{4}Ad_{2})]$ ($Ar^{R}O = 2,6$ -diadamantyl-4-methylphenolate).¹⁰ In view of the first results of azide cycloaddition to zirconium hydrazinediido complexes, which generated metalbonded N₅ units,¹¹ we began to study the chemistry of zirconium tetraazadienido complexes synthesized from imido zirconium compounds. The propensity of zirconium hydrazinediido complexes to undergo N–N bond cleavage and subsequent conversions is now well established. Therefore, the comparison of the reactivity of their azide cycloaddition products with that of the metallacyclic species derived from the corresponding imido complex was of particular interest to us and is reported in this work.

RESULTS AND DISCUSSION

Synthesis and Structural Characterization of Zirconium Tetraazadienide Complexes. The zirconium imido complexes $[Zr(N_2^{TBS}N_{py})(=N^{DIPP})(py)]$ (2; $N_2^{TBS}N_{py} = [(2-C_5H_4N)C(CH_3)\{CH_2NSi(CH_3)_2tBu\}_2]^{2-}$, DIPP = 2,6-diisopropylphenyl) and $[Zr(N_2^{TBS}N_{py})(=N^{Mes})(py)]$ (3; Mes = mesityl) were synthesized in a *one-pot* procedure from the dichloro precursor $[Zr(N_2^{TBS}N_{py})Cl_2)]$ (1)¹² by reaction with 1 molar equiv of the corresponding lithium amide and subsequent treatment with LiHMDS (HMDS = hexamethyldisilazide) and pyridine (Scheme 1).

The analytical and spectroscopic properties of both imido complexes 2 and 3 are consistent with the structures depicted in Scheme 2.¹³ In order to establish the details of the zirconium imido complexes, an X-ray diffraction study of 2 was carried out. Its molecular structure is shown in Figure 1 and is very

Scheme 2. Formation of the Imido Complexes 2 and 3 from $[Zr(N_2^{TBS}N_{py})Cl_2)]$ (1) and Their Conversion to the Tetraazadienido Complexes 4 and 5 with Phenyl Azide (DIPP = 2,6-Diisopropylphenyl)





Figure 1. Molecular structure of the imido complex 2 (H atoms have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Zr(1)-N(1) = 2.096(2), Zr(1)-N(5) = 2.371(2), Zr(1)-N(2) = 2.104(2), N(4)-C(22) = 1.374(2), Zr(1)-N(3) = 2.315(2); Zr(1)-N(4)-C(22) = 169.9(1), Zr(1)-N(4) = 1.913(2), N(3)-Zr(1)-N(5) = 169.23(5).

similar to that of the previously characterized zirconium imido complex $[Zr(N_2^{TMS}N_{py})(=N^{DIPP})(py)]$ (2a) (in particular, the Zr=N bond length: Zr1–N4 1.9126(17) Å in 2 compared to 1.916(4) Å in 2a).¹⁴

Whereas both complexes 2 and 3 are unreactive toward trimethylsilyl and 1-adamantyl azides, probably due to steric congestion, they readily form the tetrazenido complexes 4 and 5 by reaction with phenyl azide at ambient temperature (Scheme 1). In the ¹H NMR spectra of both tetrazenido complexes the signals for the protons adjacent to the pyridyl nitrogen in the ancillary ligand exhibit a strong high-field shift (in C₆D₆: δ 7.09 (4), 7.07 (5)) in comparison to the signals in the corresponding imido complexes (δ 9.42 (2), 9.37 (3)), which indicates an orientation of these protons toward the anisotropy cones of aromatic DIPP or mesityl rings of the tetraazadienyl unit. The formation of the N₄ chains was supported by the ¹⁵N NMR spectra of 4 and 5, which are shown in Figure 2.

For a complete assignment of the ¹⁵N NMR spectra, chemical shifts were calculated using the DFT-GIAO computational tool (B3PW91 functional;¹⁵ Stuttgart relativistic, small core ECP basis + f polarized function for the Zr; 6-31G for H and 6-31++G(d) for C atoms; 6-311++G(2d) for N).¹⁶ The computed data are in good agreement with the experimental values for the NMR chemical shifts. (Table 1)

Single-crystal structure analyses were carried out for complexes 4 and 5. In both cases, the general features of the N_4 unit were established; however, the quality of the data for complex 4 did not allow a meaningful discussion of its metric parameters. Therefore, only the molecular structure of 5, which is displayed in Figure 3, will be discussed. The coordination geometry in 5 is best described as distorted trigonal bipyramidal. The ancillary ligand is facially coordinated to the metal center, while the tetraazdienido ligand occupies the remaining axial and equatorial coordination sites. The N6–N7 (double) bond length (N6–N7 = 1.264(2) Å) is reduced compared to that in [Cp₂Zr(N₄^tBu₂)] (N=N = 1.281 Å); on the other hand, the Zr–N4 (2.172(2) Å) and Zr–N5 (2.157(2) Å) distances are greater than in [Cp₂Zr(N₄^tBu₂)] (2.126(6), 2.117(6) Å).



440 420 400 380 360 340 320 300 280 260 240 220 200 180 ppm

Figure 2. 15 N NMR spectra at natural abundance of complexes 4 (top) and 5 (bottom).

Table 1. Experimental and Computed $^{15}\mathrm{N}$ NMR Shifts of Complexes 5 and 7

	5		7	
	exptl	theor	exptl	theor
N1/N2	197.4	219.2	164.0/171.9	190.8/198
N3	272.0	301.3	287.4	320.6
N4	278.0	308.1	176.8	200.2
N5	288.5	320.2	288.6	315.9
N6	371.1	403.1	502.2	547.0
N7	387.0	420.2	284.0	307.0



Figure 3. Molecular structure of the tetraazadienido complex 5. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr-N(1) = 2.036(2), Zr-N(2) = 2.044(2), Zr-N(3) = 2.338(2), Zr-N(4) = 2.172(2), Zr-N(5) = 2.157(2), N(4)-N(7) = 1.394(2), N(5)-N(6) = 1.382(2), N(6)-N(7) = 1.264(2), N(4)-C(22) = 1.439(2), N(5)-C(31) = 1.410(2); N(4)-Zr-N(5) = 68.61(6).

The tetraazadienyl complexes 4 and 5 were found to be unreactive toward unsaturated substrates at ambient temperature, and heating led to nonselective decomposition for both complexes. A different course of reaction was observed in the attempted synthesis of a tetraazadienyl complex by reaction of the imido complex **2** with mesityl azide, as evidenced by the signal patterns and chemical shifts in the ¹H and ¹⁵N NMR spectra of the reaction product. The ¹⁵N NMR spectrum displayed in Figure 4, along with an inverse ¹⁵N–¹H COSY, clearly showed the formation of a N–H bond, while the ¹H and ¹³C DEPT NMR spectra indicated the formation of a third CH₂ moiety.



To establish the molecular structure of 7, a single-crystal Xray structure analysis was carried out. The asymmetric unit contains two crystallographically independent but structurally very similar molecules, the molecular structure of one of which is shown in Figure 5. An amido ligand has been formed (Zr– N4 = 2.118(2) (2.101(2)) Å for the second independent molecule)) and is bonded in a trans disposition to the amido atoms N1 and N2 of the tripodal ligand. The mesityl azide is coupled to a methyl group at a silicon atom of the auxiliary ligand, forming an altogether pentadentate ligand. The Zr–N



Figure 5. Molecular structure of the C–H bond activation product 7 (only one of the two independent molecules is shown; H atoms are omitted for clarity, except for the amido H). Selected bond lengths (Å) and angles (deg) (data for the second molecule are given in brackets): Zr(1)-N(1) = 2.096(2) [2.108(3)], N(5)-N(6) = 1.323(3) [1.325(3)], N(6)-N(7) = 1.292(3) [1.302(4)], Zr(1)-N(2) = 2.072(3) [2.075(2)], N(7)-C(10) = 1.456(4) [1.460(4)], Zr(1)-N(3) = 2.399(2) [2.377(2)], C(10)-N(7)-N(6) = 115.3(2) [115.0(3)], Zr(1)-N(4) = 2.118(2) [2.101(2)], N(5)-N(6)-N(7) = 108.0(2) [108.3(2)], Zr(1)-N(5) = 2.338(3) [2.348(3)], N(3)-Zr(1)-N(7) = 136.65(8) [138.27(9)], Zr(1)-N(7) = 2.286(2) [2.280(3)], N(3)-Zr(1)-N(5) = 168.70(8) [166.72(8)], N(6)-N(7) = 1.292(3) [1.302(4)].

Scheme 3. Formation of the C-H Activation Product 7 from Imido Complex 3 and Mesityl Azide



distances of the azide nitrogen atoms lie between typical bond lengths for monoanionic and neutral N-donor ligands, indicating a high degree of electron delocalization in the N₃ chain. The N–N distances (N6–N7 = 1.292(3) Å; N5–N6 = 1.323(3) Å) are also consistent with the formulation of the N₃ chain as an anionic π -allyl analogue.

A complete assignment of the ¹⁵N NMR spectrum in Figure 4 was again achieved by means of a DFT-GIAO computational study. The calculated chemical shifts are also given in Table 1.

In order to obtain some insight into the reaction pathway leading to complex 7, the imido compound 3 was reacted with mesityl azide, which was ¹⁵N-labeled in the γ position. Monitoring the reaction by ¹H and ¹⁵N NMR spectroscopy revealed that, after addition of the azide, the new compound 6 formed immediately (next to unreacted starting material). Its ¹H NMR signal patterns were similar to those of the tetraazadienyl complexes 4 and 5. The ¹⁵N NMR spectrum exhibited the signals of the ¹⁵N-labeled nuclei at δ 386.5 and 388.3, respectively, which are assigned to the nitrogen atoms in the N6 and N7 positions in the tetraazadienyl chain of 6. No further intermediates were detected in the subsequent conversion of 6 to the isolated complex 7 (which contained the ¹⁵N label in the N position of the triazaallyl unit adjacent to the Si–CH₂ fragment). Unfortunately, the observation of other side products, possibly stereoisomers, made this conversion unsuitable for a detailed kinetic study.

We therefore propose that in this multistep reaction complex **6** is formed initially but subsequently undergoes cycloreversion to form the four-coordinate imido complex **A** (Scheme 3). The latter subsequently reacts in a C–H activation step involving the tBuSiMe₂ sustituent of the diamido donor ligand to give intermediate **B**. Such reactivity has been well established since the early pioneering work by Wolczanski and Cummins and has been observed in several studies since then.¹⁷ Finally, the product complex 7 is formed by insertion of the free mesityl azide into the zirconium–carbon bond. We note that there is

precedent for insertions of organoazides in σ -alkyl bonds of group 4 metal complexes in the literature.^{9,18}

Synthesis and Structural Characterization of Zirconium Pentaazadienyl and Diazenido Complexes. The reactivity observed for imidozirconium complexes may be readily extended to the structurally related hydrazinediides. Reaction of 1 molar equiv of trimethylsilyl azide or 1-adamantyl azide with the previously reported hydrazinediido complex $[Zr(N_2^{TBS}N_{py})(=NNPh_2)(py)]$ (9) ^{12,19} at ambient temperature results in the formation of the five-membered zirconaazacycles $[Zr(N_2^{TBS}N_{py})(N^{TMS}N_3NPh_2)]$ (10) and $[Zr-(N_2^{TBS}N_{py})(N^{Ad}N_3NPh_2)]$ (11). As for the reaction of the imido complexes discussed above, the pentaazadienyl units are formed by formal [2 + 3] cycloaddition of the azide with the $Zr=N_{\alpha}$ double bond of the hydrazinediido unit (Scheme 4).

Scheme 4. Formation of the Pentaazadienides 10 and 11 from Hydrazinediide 9 and Organic Azides



Both zirconium pentaazadienyl complexes were structurally characterized. Their molecular structures are depicted in Figure 6, and selected bond lengths and angles are given in Table 2.

The pentaazadienyl units are bound through the N4 and N7 atoms to the zirconium center, with the Zr–N4 and Zr–N5 distances (10, Zr–N4 = 2.139(2) Å, Zr–N7 = 2.159(2) Å; 11, Zr–N4 = 2.153(2) Å, Zr–N7 = 2.151(2) Å) being in the typical range for Zr–N bonds of monoanionic N donors. This



Figure 6. Molecular structures of complexes 10 (left) and 11 (right). H atoms are omitted for clarity. A comparative listing of the principal bond lengths and angles in provided in Table 2.

Table 2. Selected Bond I	Lengths (Å)) and A	Angles (deg) of
Complexes 10 and 11				

	10	11
Zr-N(1)	2.042(2)	2.047(2)
Zr-N(2)	2.034(2)	2.046(2)
Zr-N(3)	2.326(2)	2.320(2)
Zr-N(4)	2.139(2)	2.153(2)
Zr-N(7)	2.159(2)	2.151(2)
N(4) - N(5)	1.397(3)	1.374(3)
N(5) - N(6)	1.260(3)	1.262(3)
N(6) - N(7)	1.395(3)	1.398(3)
N(7)-N(8)	1.415(3)	1.415(3)
N(4)-N(5)-N(6)	114.4(2)	114.9(2)
N(5)-N(6)-N(7)	114.1(2)	113.9(2)
N(6)-N(7)-N(8)	108.7(2)	108.9(2)
N(4)-Zr- $N(7)$	68.15(7)	67.98(7)

is consistent with the formulation of N4 and N7 as formal monoanionic donor ligands, similar to the situation found for the tetraazadienido complex **5**.

The newly formed N_5 chain was further characterized by ¹⁵N NMR spectroscopy. To allow full assignment of the spectra, the ¹⁵N NMR shifts were calculated using DFT-GIAO methods and showed good agreement with the experimental values. In Figure 7 the ¹⁵N NMR spectra of **10** and **11** are displayed. While the signals for the Ph₂N atoms could only be detected by an ¹H–¹⁵N-HMBC experiment, all other resonances were detected directly. A comparison of the experimental and computed NMR shifts is given in Table 3.

Similar to the case for their tetraazadienyl analogues, the pentaazenido complexes **10** and **11** were found to be unreactive toward unsaturated substrates but turned out to be thermally labile. While **10** only showed nonselective degradation by heating to 70 °C in benzene or thf, **11** was converted selectively into the new compound **12** upon heating to 70 °C in thf for 10 days. Its spectroscopic and analytical data are consistent with the loss of 1 molar equiv of molecular N₂ and the formation of a diazenido complex.^{20,21} The direct formation of the side-onbonded diazenido analogue **13** was observed in the reaction of compound **9** with 1 equiv of mesityl azide at ambient temperature (Scheme 5).

The molecular structure of 13 was established by X-ray diffraction and is shown in Figure 8 along with selected bond



Figure 7. ^{15}N NMR spectra at natural abundance of complexes 10 (top) and 11 (bottom).

Table 3. Experimental and Computed ¹⁵N NMR Shifts of Complexes 10 and 11

	10		11	
	exptl	theor	exptl	theor
N1/N2	189.9	209.6	189.1	208.3
N3	275.3	304.8	276.4	308.5
N4	293.8	325.8	303.8	334.7
N5	378.6	408.5	374.7	408.3
N6	411.4	446.2	380.8	410.6
N7	291.3	317.3	292.4	312.2
N8	121.4	143.6	122.2	143.9

lengths and angles. The N_5 chain of the pentaazenido precursor has fragmented and the NPh₂ unit of the original hydrazido ligand is bound as an amido ligand in an equatorial position, while the coordination site in a position trans to the neutral Scheme 5. Formation of Diazenido Complexes 12 and 13 from Hydrazinediide 9 and Organic Azides





Figure 8. Molecular structure of diazenide **13** (H atoms have been omitted for clarity). Selected bond lengths (Å) and angles (deg): Zr–N(1) = 2.101(3), Zr–N(2) = 2.065(3), Zr–N(3) = 2.377(3), Zr–N(4) = 2.231(4), Zr–N(5) = 2.223(3), Zr–N(6) = 2.170(3), N(4)–N(5) = 1.182(5); Zr–N(5)–N(4) = 75.0(3), Zr–N(4)–N(5) = 74.2(3), N(4)–N(5)–C(22) = 119.8(4).

pyridyl donor group is occupied by a formally monoanionic, side-on-bound diazenido ligand.

The diazenides 12 and 13, generated by N_2 extrusion, were also characterized by ¹⁵N NMR spectroscopy and the resonances were again compared to calculated chemical shifts. The ¹⁵N NMR spectra of 12 and 13 are displayed in Figure 9, and a comparison of the experimental and calculated ¹⁵N NMR shifts is provided in Table 4. Particularly notable is the low-field resonance assigned to N4, which is observed at 804.2 ppm for 12 and at 810.9 ppm for 13.

Monitoring the reaction leading to 12 and 13 by ¹⁵N NMR employing both the ¹⁵N_{α}-labeled hydrazinediido complex 9 as well as ¹⁵N_{γ}-labeled mesityl azide (Scheme 6) revealed that the extruded N₂ exclusively originates from the azide unit, more precisely, the N_{β}==N_{γ} fragment of the latter, whereas the Zrbonded N_{α} atom of the hydrazinediido ligand remains bound to the metal in the molecule.

In contrast to the observed reactivity for tetraazadienido complexes 4 and 5, this reactive behavior is reminiscent of thermal fragmentations of cobalt or chromium tetraazadiene complexes observed by Trogler and co-workers.²² The clean N_2 extrusion reaction obviously is promoted by the substitution of a carbon at the tetraazadienyl chain by the NPh₂ fragment. This illustrates the significant change in reactivity pattern when going from imido to hydrazinediido complexes of the group 4 metals observed previously.¹⁹



800 750 700 650 600 550 500 450 400 350 300 250 200 ppm

Figure 9. 15 N NMR spectra at natural abundance of complexes 12 (top) and 13 (bottom).

Table 4. Experimental and Computed ¹⁵N NMR Shifts of Complexes 12 and 13

	12		13	
	exptl	theor	exptl	theor
N1/N2	164.3	186.6	166.4	186.6
N3	286.9	319.9	284.1	315.7
N4	804.2	836.1	810.9	897.1
N5	540.1	542.6	489.1	532.8
N6	201.0	214.9	186.6	208.3

Scheme 6. Distribution of Different ¹⁵N Labels during the Formation of Complex 5



DFT Modeling of the Reaction Pathway Leading to the Diazenido Complexes 12 and 13. The mechanism of the reaction of 1-adamantyl azide and 1-mesityl azide with $[Zr(N_2^{TBS}N_{py})(=N-NPh_2)(py)]$, including the key transition states, was modeled by DFT methods (B3PW91/6-31g(d)) for the full molecular structures. The first step of the reaction of the hydrazinediide I with the azide (Scheme 7) involves an endergonic pyridine–azide ligand exchange (with 1-adamantyl azide and 1-mesityl azide) to form complexes IIa ($\Delta G = 11.2$ kcal/mol) and IIb ($\Delta G = 18.2$ kcal/mol), respectively. All energy/free enthalpy differences represented in Scheme 7 have been calculated with respect to compound I.

In the first intermediate **IIa**,**b** the organic azide bonds to the zirconium atom with the nitrogen bearing the organic substituent. Intermediates **IIa**,**b** are linked to two types of transition states for each azide. The transition state which is lower in energy/free enthalpy, **TS**_{II-IIIa} ($\Delta G^{\ddagger} = 22.8$ kcal/mol)

Scheme 7. General Scheme of the Reactions of the Hydrazinediido Complex $[Zr(N_2^{TBS}N_{py})(=NNPh_2)(py)]$ with 1-Adamantyl Azide and 1-Mesityl Azide (Computed using DFT(B3PW91/6-31g(d))



and $\mathbf{TS}_{\text{II-IIIb}} (\Delta G^{\ddagger} = 19.8 \text{ kcal/mol})$, leads to the formation of the corresponding five-membered metallacycles $[\text{Zr}(N_2^{\text{TBS}}N_{\text{py}}) - (N^{\text{R}}N_3\text{NPh}_2)]$ (IIIa,b with R = adamantyl (IIIa corresponding to compound 11), mesityl (IIIb)). For both transition states, $\mathbf{TS}_{\text{II-IIIa}}$ and $\mathbf{TS}_{\text{II-IIIb}}$, the activation barriers allow the formation of intermediates IIIa,b at room temperature but only the formation of compound IIIa is clearly exergonic ($\Delta G = -5.1$ kcal/mol) and is, in fact, observed experimentally. The computed ΔG value of -0.2 kcal/mol for the reaction of $[\text{Zr}(N_2^{\text{TBS}}N_{\text{py}})(=\text{NNPh}_2)(\text{py})]$ with 1-mesityl azide, for which an error of around ± 2 kcal/mol is to be assumed, may account for the fact that intermediate IIIb is not observed in solution.

Intermediates IIa,b also connect with the highly stabilized IVa ($\Delta G = -23.9 \text{ kcal/mol}$) and IVb ($\Delta G = -32.2 \text{ kcal/mol}$) intermediates via the transition states $\mathbf{TS}_{\text{II-IVa}}$ and $\mathbf{TS}_{\text{II-IVb}}$, in which the extrusion of the dinitrogen molecule takes place. Intermediates IVa,b are subsequently converted via the cyclic triazenido species Va,b to give the diazenides VIa,b, corresponding to complexes 12 and 13. The energies of transition states $\mathbf{TS}_{\text{II-IVa}}$ ($\Delta G^{\ddagger} = 34.3 \text{ kcal/mol}$) and $\mathbf{TS}_{\text{II-IVb}}$ ($\Delta G^{\ddagger} = 28.9 \text{ kcal/mol}$) are in agreement with the observed reactivity (prolonged heating at 70 °C): the transition state for the 1-mesityl azide ($\mathbf{TS}_{\text{II-IVb}}$) is the system that more rapidly reacts to give the diazenide, as observed experimentally.

In this work we have explored the different thermal reactivities of tetraazadienyl and pentaazadienyl complexes which were generated by formal [2 + 3] cycloaddition of azides to the Zr=N bonds of the imido complexes 2 and 3 and the

hydrazinediido complex 9. For this class of compounds the directly detected ¹⁵N NMR spectra recorded at natural ¹⁵N abundance, combined with DFT modeling of the chemical shifts, provided significant structural information.

While the tetraazadienyl complex undergoes retrocycloaddition and subsequent transformation, the hydrazinediido ligand fragments, liberating N_2 and transferring a nitrogen atom to an electronically unsaturated ligand fragment. Here again, the propensity of the Zr-bonded hydrazide to undergo N–N bond cleavage defines the pattern of reactivity and leads to unusual structural motifs.

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. Solvents were dried over sodium (toluene), potassium (hexanes, thf), or sodium/ potassium alloy (pentane, diethyl ether), distilled, and degassed prior to use. Deuterated solvents were dried over potassium (C6D61 thf- d_8 , toluene- d_8), vacuum-distilled, and stored in Teflon valve ampules under argon. Samples for NMR spectroscopy were prepared under argon in 5 mm Wilmad tubes equipped with J. Young Teflon valves. ¹H, ¹³C, ²⁹Si, and ¹⁵N NMR spectra were recorded on Bruker Avance 400 and 600 NMR spectrometers and were referenced internally, using the residual protio solvent (¹H) or solvent (¹³C) resonances, or externally to SiMe4 and ¹⁵NH3. We obtained goodquality ¹⁵N NMR spectra by direct detection of the heteronuclei without isotope enrichment and with "normal" sample concentrations (20-30 mg in 0.5 mL deuterated solvent in 5 mm NMR tubes) with the aid of a cryogenically cooled direct detection probe (Bruker QNPcryoprobe) on the 600 MHz NMR spectrometer.

Elemental analyses were recorded by the analytical service of the chemistry department of the Universität Heidelberg. The dichloro complex $[Zr(N_2^{TBS}N_{py})Cl_2]$ and the hydrazinediido complex $[Zr(N_2^{TBS}N_{py}(=NNPh_2)(py)]$ (9) were prepared as already reported;¹² phenyl azide, mesityl azide, and ${}^{15}N_{\gamma}$ -mesityl azide were prepared according to published procedures.²³ All other reagents were obtained from commercial sources and used as received unless explicitly stated.

from commercial sources and used as received unless explicitly stated. **Preparation of** $[Zr(N_2^{TBS}N_{py})(=N^{DIPP})(py)]$ (2). To a stirred solution of $[Zr(N_2^{TBS}N_{py})Cl_2]$ (1.00 g, 1.8 mmol) in toluene (40 mL) was added a suspension of lithium 2,6-diisopropylaniline (331 mg, 1.8 mmol) in 5 mL of toluene. The reaction mixture was stirred for 2 days at 60 °C. Then pyridine (150 μ L, 1.8 mmol) and a solution of lithium hexamethyldisilazide (303 mg, 1.8 mmol) in 5 mL of toluene was added and the mixture was stirred for 2 days at 80 °C. The reaction mixture was filtered from lithium chloride, and the volatiles were removed in vacuo. The remaining solid was washed with hexane $(3 \times$ 5 mL) and dried to yield 800 mg (1.50 mmol, 61%) of 2 as a light orange solid. Single crystals for X-ray diffraction were grown from a saturated toluene solution at room temperature. ¹H NMR (600 MHz, C₆D₆, 296 K): δ –0.10, 0.21 (s, 6 H, $\tilde{Si}(CH_3)_2$), 0.79 (s, 18 H, Si– $C(CH_3)_3)$, 1.13 (s, 3 H, CH₃), 1.43 (d, ${}^{3}J_{HH} = 6.7$ Hz, 12 H, $CH(CH_3)_2$, 3.49 (d, ${}^2J_{HH}$ = 12.1 Hz, 2 H, CHH), 3.96 (d, ${}^2J_{HH}$ = 12.1 Hz, 2 H, CHH), 4.65 (sep, ${}^{3}J_{HH} = 6.7$ Hz, 2 H, CH(CH₃)₂), 6.50, (t, ${}^{3}J_{HSH6/H4} = 6.6$ Hz, 1H, H5_{py}), 6.59 (t, ${}^{3}J_{mHpH/oH} = 6.7$ Hz, 2 H, m- H_{py}), 6.81 – 6.90 (m, 2 H, $H3_{py}$, p- H_{py}), 7.00–7.08 (m, 2 H, $H4_{py}$, p- H_{DIPP}), 7.35 (d, ${}^{3}J_{\text{mHpH}} = 7.4$ Hz, 2 H, mH_{DIPP}), 9.01 (d, ${}^{3}J_{\text{oHmH}} = 5.1$ Hz, 2 H, o- H_{py}), 9.42 (d, ${}^{3}J_{H6pyH5py}$ = 5.0 Hz, $H6_{py}$). ${}^{13}C{H}$ NMR (150 MHz, $C_{6}D_{6}$, 296 K): δ -4.3, -2.4 (Si(CH₃)₂), 20.3 (Si-(CH₃)₃), 25.6 (C-CH₃), 26.0 (CH(CH₃)₂), 27.3 (CH(CH₃)₂), 27.8 $(Si-C(CH_3)_3)$, 47.3 $(C-CH_3)$, 64.3 (CH_2) , 116.2 $(p-C_{DIPP})$, 120.5 (C3_{py}), 121.0 (C5_{py}), 123.3 (m-C_{DIPP}), 124.0 (m-C_{py}), 139.0 (C4_{py}), 139.2 (p- C_{py}), 140.0 (o- C_{DIPP}), 151.3 ($C6_{py}$), 152.3 (o- C_{py}), 154.8 (i- C_{DIPP}) 161.0 (C2_{py}). ²⁹Si{¹H} NMR (80 MHz, C₆D₆, 296 K): δ 0.80 $(Si(CH_3)_3)$. ¹⁵N⁻NMR (60 MHz, C₆D₆, 296 K): δ 146.0 (N-Si(CH₃)₂^tBu), 278.9 (N_{py}), 288.8 (L- N_{py}), 323.0 (Zr=N). IR (Nujol, NaCl): ν 1601 m, 1462 s, 1410 m, 1377 m, 1225 m, 1273 s, 1254 sh, 1085 w, 1061 m, 1010 w, 935 w, 890 s, 867 s, 826 w, 772 w, 700 w, 663 w cm⁻¹. Anal. Calcd: C, 61.90; H, 8.61; N, 9.50. Found: C, 61.67; H, 8.69; N, 9.63.

Preparation of $[Zr(N_2^{TBS}N_{py})(=N^{Mes})(py)]$ (3). To a stirred solution of [Zr(N₂^{TBS}N_{py})Cl₂] (1.00 mg, 1.8 mmol) in toluene (40 mL) was added a suspension of lithium 2,4,6-trimethylaniline (255 mg, 1.8 mmol) in 5 mL of toluene. The reaction mixture was stirred for 2 days at 60 °C, and then pyridine (150 μ L, 1.8 mmol) and a solution of lithium hexamethyldisilazide (303 mg, 1.8 mmol) in 5 mL of toluene was added and the mixture was stirred for 2 days at 80 °C. The reaction mixture was filtered from lithium chloride, and the volatiles were removed in vacuo. The remaining solid was washed with hexane $(3 \times 5 \text{ mL})$ and dried to yield 800 mg (1.15 mmol, 64%) of 3 as a bright orange solid. ¹H NMR (600 MHz, C₆D₆, 296 K): δ –0.09, 0.25 $(s, 6 H, Si(CH_3)_2), 0.80 (s, 18 H, Si-C(CH_3)_3), 1.13 (s, 3 H, CH_3),$ 2.45 (s, 3 H, p- CH_3), 2.83 (s, 6 H, o- CH_3), 3.50 (d, $^2J_{HH}$ = 12.5 Hz, 2 H, CHH), 3.99 (d, ${}^{2}J_{HH}$ = 12.5 Hz, 2 H, CHH), 6.43 (t, ${}^{3}J_{H5pyH6py/Hpy4}$ $= 6.0 \text{ Hz}, 1\text{H}, HS_{\text{py}}), 6.50 \text{ (t, } {}^{3}J_{\text{m-Hpy}-Hpy} = 6.0 \text{ Hz}, 2 \text{ H}, \text{m-H}_{\text{py}}), 6.80 - 6.86 \text{ (m, 2 H, H}_{3\text{py}}, \text{p-H}_{\text{py}}), 7.03 \text{ (dt, } {}^{3}J_{\text{H4pyH3py}/\text{Spy}} = 7.9 \text{ Hz}, \\ {}^{4}J_{\text{H4pyH6py}} = 1.7 \text{ Hz}, 1 \text{ H}, H4_{\text{py}}), 7.20 \text{ (s, 2 H, m-H}_{\text{mes}}), 8.98 \text{ (d,} \\ {}^{3}J_{\text{o-Hpym-Hpy}} = 6 \text{ Hz}, 2\text{ H}, \text{o-Hpy}), 9.37 \text{ (d, } {}^{3}J_{\text{H6pyH5py}} = 5.8 \text{ Hz}, H6_{\text{py}}). \\ \end{array}$ ¹³C{¹H} NMR (150 MHz, C₆D₆, 296 K): δ -4.0, -2.3 (Si(CH₃)₂), 20.5 (Si-C(CH₃)₃), 21.2 (p-CH₃), 21.7 (o-CH₃), 25.8 (C-CH₃), 27.8 $(Si-C(CH_3)_3)$, 47.2 $(C-CH_3)$, 64.4 (CH_2) , 120.4, $(C3_{pv})$, 121.0 $(C5_{py})$, 123.0 $(p-C_{mes})$, 124.0 $(m-C_{py})$, 128.6 $(o-C_{mes})$, 128.6 $(m-C_{mes})$, 138.7 $(p-C_{py})$, 138.5 $(C4_{py})$, 151.2 $(C6_{py})$, 152.2 $(o-C_{py})$, 156.4 $(i-C_{mes})$, 161.2 $(C2_{py})$. ²⁹Si{¹H} NMR (80 MHz, C₆D₆, 296 K): δ 0.62 $(Si(CH_3)_3)$. ¹⁵N^F/NMR (60 MHz, C₆D₆, 296 K): δ 144.1 (N- $Si(CH_3)_2^tBu)$, 279.1 (N_{py}), 289.3 (L- N_{py}), 330.5 (Zr=N). IR (Nujol, NaCl): v 1601 m, 1463 s, 1377 s, 1311 m, 1253 w, 1210 w, 1161 w, 1088 w, 1054 m, 1010 w, 889 m, 874 s, 824 m, 801 w, 767 w 722 m $cm^{-1}\!.$ Anal. Calcd for $C_{35}H_{57}N_5Si_2Zr\!:$, 60.46; H, 8.26; N, 10.07. Found: C, 59.98; H, 8.17; N, 9.81.

Preparation of $[Zr(N_2^{TBS}N_{py})(N^{Ph}N_2N^{DIPP})]$ (4). To a stirred solution of $[Zr(N_2^{TBS}N_{py})(=N^{DIPP})(py)]$ (2; 300 mg, 0.41 mmol) in toluene (20 mL) was added a solution of phenyl azide (48 mg, 0.41 mmol) in 5 mL of toluene. The reaction mixture was stirred for 16 h at room temperature and filtered, and the volatiles were removed in vacuo. The crude product was washed with hexane $(3 \times 5 \text{ mL})$ and dried to yield 220 mg (0.30 mmol, 72%) of 4 as a bright yellow solid. ¹H NMR (600 MHz, THF- d_8 , 296 K): δ -0.06, 0.12 (s, 6 H, Si(CH₃)₂), 0.70 (s, 18 H, Si–C(CH₃)₃), 1.07, 1,23 (d, ${}^{3}J_{HH} = 6.7$ Hz, 6 H, CH(CH₃)₂), 1.73 (s, 3 H, CH₃), 3.51 (sep, ${}^{3}J_{HH} = 6.7$ Hz, 2 H, CH(CH₃)₂), 3.63 (d, ${}^{2}J_{HH} = 12.7$ Hz, 2 H, CHH), 4.24 (d, ${}^{2}J_{HH} = 12.7$ Hz, 2 H, CHH), 6.79 (t, ${}^{3}J_{p-HPhm-HPh} = 0.7.6$ Hz, 1H, p-H_{ph}), 7.05–7.10 (m, 2 H, $H6_{py}$, $H5_{py}$), 7.73 (t, ${}^{3}J_{m-HPho-HPh/m-HPh} = 7.6$ Hz, 2 H, $m-H_{Ph}$), 7.28 - 7.34 (m, 3 H, p-H_{DIPP}, m-H_{DIPP}), 7.54 (d, ${}^{3}J_{o-HPhm-HPh} = 7.6$ Hz, 2 H, o-H_{Ph}), 7.90 (d, ${}^{3}J_{H3pyH4py} = 8.1$ Hz, $H3_{py}$), 8.11 (t, ${}^{3}J_{H4pyH5py/H3py} = 8.1$ Hz, 1 H, $H4_{py}$). ${}^{13}C{}^{1}H{}$ NMR (150 MHz, THF- d_{8} , 296 K): δ -4.1, -3.5 (Si(CH₃)₂), 20.2 (Si-C(CH₃)₃), 23.9, 26.7 (CH(CH₃)), 27.5 (C-CH₃), 28.5 (Si-C(CH₃)₃), 48.6 (C-CH₃), 63.1 (CH₂), 119.2 (o- $C_{\rm Ph}$), 120.6 (p- $C_{\rm Ph}$), 123.7 (C3_{py}, C5_{py}), 124.4, 127.3 (m- C_{DIPP} , p- C_{DIPP}), 129.0 (m- C_{Ph}), 143.1 ($C_{4_{\text{py}}}$), 146.9 (i- C_{DIPP}), 147.0 (o- C_{DIPP}), 147.7 ($C6_{\text{py}}$), 152.9 (i- C_{ph}), 162.3 ($C2_{\text{py}}$). ²⁹Si {¹H} NMR (80 MHz, THF- d_8 , 296 K): δ 6.86 (Si(CH₃)₃). ¹⁵N NMR (60 MHz, THF- d_8 , 296 K): δ 198.5 (N-Si(CH₃)₂^tBu), 270.8 (L- N_{py}), 273.9 (N–DIPP), 290.2 (N–Ph), 369.4, 390.5 (N=N). IR (Nujol, NaCl): v 2724 w, 1592 w, 1462 s, 1377 s, 1305 w, 1257 m, 1152 w, 1088 w, 1028 m, 1016 m, 935 w, 850 w, 828 w, 802 m, 772 w, 722 s cm⁻¹. Anal. Calcd for C₃₉H₆₃N₇Si₂Zr: C, 60.26; H, 8.17; N, 12.61. Found: C, 59.97; H, 8.18; N, 12.54.

Preparation of $[Zr(N_2^{TBS}N_{py})(\mathbb{N}^{Ph}N_2\mathbb{N}^{Mes})]$ (5). To a stirred solution of $[Zr(N_2^{TBS}N_{py})(=\mathbb{N}^{Mes})(py)]$ (3; 300 mg, 0.43 mmol) in toluene (20 mL) was added a solution of phenyl azide (52 mg, 0.43 mmol) in 5 mL of toluene. The reaction mixture was stirred for 16 h at room temperature and filtered, and the volatiles were removed in vacuo. The crude product was washed with hexane $(3 \times 5 \text{ mL})$ and dried to yield 240 mg (0.33 mmol, 76%) of 5 as a bright yellow solid. Single crystals for X-ray diffraction were grown from a saturated toluene solution at room temperature. ¹H NMR (600 MHz, THF-d₈, 296 K): $\delta = -0.07$, 0.01 (s, 6 H, Si(CH₃)₂), 0.58 (s, 18 H, Si=C(CH₃)₃), 1.68 (s, 3 H, CH₃), 2.28 (s, 6 H, o-CH₃), 2.34 (s, 3 H, p-CH₃), 3.63 (d, ${}^{2}J_{HH}$ = 12.6 Hz, 2 H, CHH), 4.17 (d, ${}^{2}J_{HH}$ = 12.7 Hz, 2 H, CHH), 6.73 (t, ${}^{3}J_{p-HPhm-HPh}$ = 0.7.5 Hz, 1 H, p-H_{Ph}), 6.94 (d, ${}^{3}J_{H6pyH5py}$ = 5.6 Hz, 1 H, $H6_{py}$), 6.96 (s, 3 H, m- H_{mes}), 7.08 (t, ${}^{3}J_{H5pyH4py/H6py} = 5.9$ Hz, 1 H, $H5_{py}$), 7.15 (t, ${}^{3}J_{m-Hpho-HPh/m-HPh} = 7.6$ Hz, 2 H, m- H_{ph}), 7.42 (d, ${}^{3}J_{o-HPhm-HPh} = 7.6 \text{ Hz}, 2 \text{ H}, o-H_{Ph}), 7.86 \text{ (d, } {}^{3}J_{H3pyH4py} = 8.0 \text{ Hz}, H3_{py}), 8.08 \text{ (t, } {}^{3}J_{H4pyH5py/H3py} = 8.0 \text{ Hz}, 1 \text{ H}, H4_{py}). {}^{13}C{}^{1}H} \text{ NMR (150 MHz, THF-}d_{8}, 296 \text{ K}): \delta -3.7 (Si(CH_{3})_{2}), 20.4 (Si-C(CH_{3})_{3}), 21.2 \text{ K})$ (p-CH₃), 21.2 (o-CH₃), 27.4 (C-CH₃), 28.3 (Si-C(CH₃)₃), 48.3 (C-CH₃), 63.1 (CH₂), 118.6 (o-C_{Ph}), 120.4 (p-C_{Ph}), 123.7 (C3_{py}), 124.0 $(C5_{\rm py})$, 129.0 (m- $C_{\rm Ph}$), 130.1 (m- $C_{\rm mes}$), 135.5 (p- $C_{\rm mes}$), 135.9 (o- $C_{\rm mes}$), 143.0 (C4_{py}), 145.9 (i-C_{mes}), 147.2 (C6_{py}), 153.1 (i-C_{Ph}), 162.2 (C2 ²⁹Si{¹H} NMR (80 MHz, THF- d_8 , 296 K): δ 6.16 (Si(CH₃)₃). ¹⁵N NMR (60 MHz, THF-d₈, 296 K): δ 197.4 (N-Si(CH₃)₂^tBu), 272.0 (L-N_{pv}), 278.0 (N-Mes), 288.5 (N-Ph), 371.1, 387.0 (N=N). IR (Nujol, NaCl): ν 1594 s, 1560 w 1462 s, 1377 s, 1300 w, 1258 s, 171 m, 1133 w, 1084 m, 1037 s, 1017 sh, 992 m, 957 w, 932 m, 905 w, 889 w, 853 s, 825 m, 770 s, 723 m, 693 w, 666 m cm⁻¹. Anal. Calcd for C₃₆H₅₇N₇Si₂Zr: C, 58.81; H, 7.81; N, 13.33. Found: C, 58.82; H, 7.86; N, 13.28.

NMR-Scale Detection of [**Zr**(**N**₂^{TBS}**N**_{py})(**N**^{Mes}**N**₂**N**^{Mes})] (6). To a solution of $[Zr(N_2^{TBS}N_{py})(=N^{Mes})(py)]$ (3) in C_6D_6 (10 mg, 0.014 mmol) was added ¹⁵N₇-mesityl azide (2 mg, 0.014 mmol). The NMR tube was transferred immediately to the spectrometer, and a set of ¹H and ¹⁵N NMR spectra were recorded. ¹H NMR (600 MHz, C_6D_6 , 296 K): δ –0.10, 0.28 (s, 6 H, Si(CH₃)₂), 0.69 (s, 18 H, Si–C(CH₃)₃), 0.92 (s, 3 H, CH₃), 2.28 (s, 3 H, p-CH₃), 2.30 (s, 3 H, p-CH₃), 2.58 (s, 6 H, o-CH₃), 2.79 (s, 6 H, o-CH₃), 3.22 (d, ²J_{HH} = 12.5 Hz, 2 H, CHH), 3.87 (d, ²J_{HH} = 12.7 Hz, 2 H, CHH), 6.21 (t, ³J_{HSpH4py/H6py} = 6.7 Hz, 1 H, H5_{py}), 6.69 (d, ³J_{H3pyH4py} = 7.8 Hz, H3_{py}), 6.92 (s, 2 H, m-H_{mes}), 6.94–6.99 (m, 3 H, H4_{py}, m-H_{mes}), 7.54 (d, ³J_{H6pyH5py} = 5.6 Hz,

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1 H, $H6_{py}$). ¹⁵N NMR (60 MHz, C_6D_{67} 296 K): δ 386.5, 388.3 (N=N).

Preparation of $[Zr(\kappa N, N, N, N, C-N_2^{TBS}N_{py})(HN^{Mes}N_2N^{Mes})]$ (7). To a stirred solution of $[Zr(N_2^{TBS}N_{py})(=N^{Mes})(py)]$ (3; 300 mg, 0.43 mmol) in toluene (15 mL) was added a solution of mesityl azide (70 mg, 0.43 mmol) in 5 mL of toluene. The reaction mixture was stirred for 16 h at 80 °C and filtered, and the volatiles were removed in vacuo. The crude product was washed with hexane $(3 \times 5 \text{ mL})$ and dried in vacuo to yield 200 mg (0.26 mmol, 60%) of 7 as a pale yellow solid. Single crystals for X-ray diffraction were grown from a saturated toluene solution at room temperature. ¹H NMR (600 MHz, THF-d₈, 296 K): δ -0.33, 0.24, -0.04 (s, 3 H, Si(CH₃)₂), 0.85 (s, 3 H, CH₃), 1.00 (s, 9 H, Si-C(CH₃)₃), 2.19 (m, 9 H, o-CH₃, m-CH₃), 2.22-2.42 (s, 3 H, p-CH₃, o-CH₃, o-CH₃), 3.14 (d, ${}^{2}J_{HH} = 11.9$ Hz, 1 H, CHH), 3.43 (d, ${}^{2}J_{HH} = 12.9$ Hz, 1 H, CHH), 3.54–3.60 (m, 2 H, CHH, CHH), 3.91 (d, ${}^{2}J_{HH}$ = 13.5 Hz, 1 H, CHH), 4.17 (d, ${}^{2}J_{HH}$ = 12.9 Hz, 1 H, CHH), 6.52 (s, 1 H, Mes-NH), 6.70-6.84 (m, 4 H, H-Mes), 7.20 $(t, {}^{3}J_{H3pyH4py/H6py} = 6.5 \text{ Hz}, 1 \text{ H}, H5_{py}), 7.68 \text{ (d, }^{3}J_{H3pyH4py} = 8.0 \text{ Hz}, 1 \text{ Hz}$ $H3_{py}$), 7.93 (t, $J_{H4pyH5py/H3py} = 7.7$ Hz, 1 H, $H4_{py}$), 8.53 (d, $^{3}J_{H6pyH5} = 5.4$ Hz, 1 H, $H4_{py}$). $^{13}C{}^{1}H$ NMR (150 MHz, THF- d_{8} , 296 K): δ -5.8, -4.1, -3.3 (Si(CH₃)₂), 19.8, 20.9 (Mes-CH₃), 21.1, 21.2 (Si-C(CH₃)₃), 21.3, 22.8 (Mes-CH₃), 24.6 (o-CH₃), 27.8 (C-CH₃), 28.2, 28.3 $(Si-C(CH_3)_3)$, 47.0 (CH_2-Si) , 51.1 $(C-CH_3)$, 61.6, 63.2 (CH_2) , 122.5 $(C3_{py})$, 123.0 $(C5_{py})$, 126.4 $(Mes-C_q)$, 129.3, 130.4 (Mes-Ch), 135.3 $(Mes-C_q)$, 140.8 $(C4_{py})$, 147.3 $(Mes-C_q)$, 148.7 $(C6_{py})$, 150.6 $(Mes-C_q)$, 163.3 $(C2_{py})$. ²⁹Si{¹H} NMR (80 MHz, THF- d_8 , 296 K): δ 0.84, 6.42 $(Si(CH_3)_3)$. ¹⁵N NMR (60 MHz, THF- d_8 , 296 K): δ 164.0 (N-Si(CH₃)₂^tBu), 171.9 (N-SiCH₂), 176.8 (Mes-NH), 284.0 (H_2C-NN) , 287.4 $(L-N_{py})$, 288.6 (NN-Mes), 502.2 (NNN). IR (Nujol, NaCl): v 3286 w, 1602 m, 1464 s, 1377 s, 1303 m, 1252 s, 1162 w, 1090 w, 1069 w, 1040 w, 1014 w, 955 w, 864 s, 852 s, 825 s, 776 m, 727 m. Anal. Calcd for C39H63N7Si2Zr: C, 60.26; H, 8.17; N, 12.61. Found: C, 60.36; H, 8.44; N, 12.15.

Preparation of [Zr(N₂^{TBS}N_{pv})(N^{TMS}N₃NPh₂)] (10). To a stirred solution of $[\rm Zr(N_2^{TBS}N_{py})(\rm NNPh_2)(py)]$ (9; 800 mg, 0.84 mmol) in toluene (20 mL) was added trimethylsilyl azide (178 μ L, 0.84 mmol) dropwise. The reaction mixture was stirred overnight at room temperature. The volatiles were removed under reduced pressure, and the resulting yellow solid was washed with pentane $(3 \times 5 \text{ mL})$ before drying in vacuo to yield 606 mg (65%) of 10 as a pale yellow solid. Single crystals for X-ray diffraction were grown from a saturated toluene solution at 10 °C. ¹H NMR (600 MHz, C₆D₆, 296 K): δ 0.07, 0.19 (s, 6 H, Si(CH₃)₂), 0.62 (s, 18 H, Si-C(CH₃)₃), 0.66 (s, 9 H, Si(CH₃)₃), 0.96 (s, 3 H, CH₃), 3.39 (d, ${}^{2}J_{HH}$ = 13.0 Hz, 2 H, CHH), 3.84 (d, ${}^{2}J_{HH}$ = 13.0 Hz, 2 H, CHH), 6.47 (m, 1 H, H5_{py}), 6.83–6.92 (m, 3 H, H3, p-H_{ph}), 7.06 (t, ${}^{3}J_{H4pyH3py/5py} = 7.1$ Hz, 1 H, $H4_{py}$), 7.16 (t, ${}^{3}J_{mHo/pH} = 8.0$ Hz, 4 H, m-H_{ph}), 7.56 (d, ${}^{3}J_{oHmH} = 8.0$ Hz, ${}^{4}J_{oHpH} = 1.1$ Hz, 4 H, o-H_{ph}), 9.69 (d, ${}^{3}J_{H6pyH5py} = 5.1$ Hz, $H6_{py}$). ${}^{13}C{}^{1}H$ NMR (150 MHz, $C_{6}D_{6}$, 296 K): δ –3.8, –3.2 (Si(CH₃)₂), 1.5 (Si(CH₃)₃), 19.9 (Si-C(CH₃)₃), 26.1 (C-CH₃), 27.8 (Si-C(CH₃)₃), 46.9 (C-CH₃), 62.6 (CH₂), 121.3 (C3_{py}), 122.8 (o-C_{ph}, p-C_{ph}, C5_{py}), 140.5 (C4_{py}), 147.9 (C6_{py}), 151.0 (N-C_{ph}), 160.5 (C2_{py}). ²⁹Si{¹H} NMR (80 MHz, C₆D₆, 296 K): δ 0.47 (Si(CH₃)₃), 5.01 (Si(CH₃)₂'Bu). ¹⁵N NMR (60 MHz, C₆D₆, 296 K): δ 121.4 (NPh₂), 189.9 (N- $Si(CH_3)_2{}^tBu$), 275.3 (L- N_{py}), 291.3 (ZrN), 293.8 (N- $Si(CH_3)_3$), 378.6 (N=N), 411.4 (N=N). IR (Nujol, NaCl): ν 1603 m, 1490 m, 1463 s, 1377 m, 1244 m 1169 w, 1088 w, 1042 m 917 m, 864 s, 825 m, 800 m, 752 m, 694 m, 666 w cm⁻¹. Anal. Calcd for $C_{36}H_{60}N_8Si_3Zr$: C, 55.41; H, 7.75; N, 14.36. Found: C, 55.42; H, 7.87; N, 13.91.

Preparation of [Zr(N₂^{TBS}N_{py})(N^{Ad}N₃NPh₂)] (11). To a stirred solution of [Zr(N₂^{TBS}N_{py})(NNPh₂)(py)] (9; 800 mg, 0.84 mmol) in toluene (20 mL) was added a solution of 1-adamantyl azide (211 mg, 0.84 mmol) in 5 mL of toluene dropwise. The reaction mixture was stirred at room temperature for 10 h. The volatiles were removed under reduced pressure, and the resulting yellow solid was washed with pentane (3 × 5 mL) before drying in vacuo to yield 710 mg (71%) of 11 as a yellow solid. Single crystals for X-ray diffraction were grown from a saturated toluene solution at 10 °C. ¹H NMR (600 MHz, THF-*d*₈, 296 K): δ –0.22, 0.03 (s, 6 H, Si(CH₃)₂), 0.57 (s, 18 H, Si–C(CH₃)₃), 1.59 (s, 3 H, CH₃), 1.72 (d, ²*J*_{HH} = 12.1 Hz, 3 H,

Ad-CHH), 1.79 (d, ${}^{2}J_{HH}$ = 12.1 Hz, 3 H, Ad-CHH), 2.12 (bs, 3H, Ad-CH), 2.21 (bs, 6H, Ad-CH₂), 3.57 (d, ${}^{2}J_{HH}$ = 13.5 Hz, 2 H, CHH), 4.03 (d, ${}^{2}J_{HH}$ = 13.5 Hz, 2 H, CHH), 6.89 (t, ${}^{3}J_{pHmH}$ = 7.6 Hz 2 H, p-H_{ph}), 7.15 (t, ${}^{3}J_{mHo/pH}$ = 7.6 Hz, 4 H, m-H_{ph}), 7.26 (d, ${}^{3}J_{oHmH}$ = 7.6 Hz, 4 H, o-H_{ph}), 7.47 (t, ${}^{3}J_{HSpyH6/H4py}$ = 7.3 Hz, 1 H, H5_{py}), 7.82 (d, ${}^{3}J_{H3pyH4py}$ = 7.3 Hz, 1 H, H3_{py}), 8.10 (t, ${}^{3}J_{HSpyH6/H4py}$ = 7.3 Hz, 1 H, H4_{py}), 9.66 (d, ${}^{3}J_{H6pyH5py}$ = 7.3 Hz, H6_{py}). ${}^{13}C{}^{1}H{}^{1}$ MMR (150 MHz, THF- d_{8} , 296 K): δ -3.2 (Si(CH₃)₂), 20.4 (Si-C(CH₃)₃), 26.5 (C-CH₃), 28.1 (Si-C(CH₃)₃), 31.3 (Ad-CH), 37.9 (Ad-CH₂), 43.7 (Ad-CH₂), 47.5 (C-CH₃), 59.0 (Ad-CN), 63.4 (CH₂), 122.9 (p-C_{ph}), 123.2 (o-C_{ph}), 123.4 (C3_{py}), 123.8 (C5_{py}), 129.2 (m-C_{ph}), 141.9 (C4_{py}), 148.4 (C6_{py}), 151.5 (N-C_{ph}), 161.2 (C2_{py}). ${}^{29}Si{}^{1}H{}$ MMR (80 MHz, THF- d_{8} , 296 K): δ 122.2 (NPh₂), 189.1 (N-Si(CH₃)₂[†]Bu), 276.4 (L-N_{py}), 292.4 (ZrN), 303.8 (N-C₁₀H₁₅), 374.7 (N=N), 380.8 (N=N). IR (Nujol, NaCl): ν 3109 w, 2361 w, 1606 w, 1588 w, 1462 s, 1377 s, 1304 w, 1259 m, 1174 w, 1105 w, 1089 w, 1031 m, 936 m, 866 s, 827 m, 775 m, 752 w cm⁻¹. Anal. Calcd for C₄₃H₆₆Ns₆Si₂Zr: C, 61.31; H, 7.90; N, 13.30. Found: C, 61.25; H, 7.79; N, 12.87.

C, 61.31; H, 7.90; N, 13.30. Found: C, 61.25; H, 7.79; N, 12.87. Preparation of [Zr(N₂^{TBS}N_{py})(NN^{Ad}NPh₂)] (12). A solution of $[Zr(N_2^{TBS}N_{py})(N^{Ad}N_3NPh_2)]$ (11; 800 mg, 0.95 mmol) in THF (20 mL) was strirred for 10 days at 70 °C. The reaction mixture was filtered, and the volatiles were removed in vacuo. The crude product was recrystallized from cold pentane (-78 °C) to yield 220 mg (0.27 mmol, 28%) of 12 as a red solid. ¹H NMR (600 MHz, THF- d_{8} , 296 K): δ 0.00, 0.13 (s, 6 H, Si(CH₃)₂), 0.66 (s, 18 H, Si-C(CH₃)₃), 1.51 (s, 3 H, CH₃), 1.56-1.63 (m, 6 H, Ad-CH₂), 1.66 (bs, 6 H, Ad- CH_2), 2.06 (bs, 3 H Ad-CH), 3.34 (d, ${}^2J_{HH}$ = 12.1 Hz, 2 H, CHH), 4.02 (d, ${}^{2}J_{HH}$ = 12.1 Hz, 2 H, CHH), 6.70 (t, ${}^{3}J_{pHmH}$ = 7.3 Hz 2 H, p- $H_{\rm Ph}$), 6.77 (d, ${}^{3}J_{\rm oHmH}$ = 7.6 Hz, 4 H, o- $H_{\rm Ph}$), 7.02–7.06 (m, 5H, m- $\begin{array}{l} H_{\rm ph}, H_{\rm 5py}), 7.17 - 7.23 \ (m, 1 \ H, H_{\rm 3py}), 7.89 \ (t, {}^{3}J_{\rm H_{4pyH_{5py/H_{6py}}} = 7.6 \ Hz, \\ H_{\rm ph}, H_{\rm 5py}), 8.87 \ (d, {}^{3}J_{\rm H_{6pyH_{5py}}} = 5.0 \ Hz, 1 \ H, H_{6py}). {}^{13}{\rm C}\{{}^{1}{\rm H}\} \ {\rm NMR} \ (150 \ {\rm MHz}, {\rm THF-}d_{8}, 296 \ {\rm K}): \delta - 3.2, -3.7 \ ({\rm Si}({\rm CH}_{3})_{2}), 20.9 \ ({\rm Si-C}({\rm CH}_{3})_{3}), \end{array}$ 25.2 (C-CH₃), 28.6 (Si-C(CH₃)₃), 31.0 (Ad-CH), 37.4 (Ad-CH₂), 40.2 (Ad-CH₂), 50.1 (C-CH₃), 64.0 (CH₂), 76.9 (Ad-CN), 120.8 $(p-C_{Ph})$, 122.2 $(C5_{py})$, 122.6 $(C3_{py})$, 126.1 $(o-C_{Ph})$, 129.1 $(m-C_{Ph})$, 140.3 $(C4_{py})$, 147.3 $(C6_{py})$, 156.8 $(N-C_{ph})$, 164.1 $(C2_{py})$. ²⁹Si{¹H} NMR (80 MHz, THF- d_{g} , 296 K): δ 2.06 $(Si(CH_3)_2$ 'Bu). ¹⁵N NMR (60 MHz, THF- d_{8} , 296 K): δ 164.3 (N-Si(CH₃)₂^tBu), 201.0 (NPh₂), 286.9 (L– N_{py}), 540.1 (N– $C_{10}H_{15}$), 804.2 (ZrN). IR (Nujol, NaCl): ν 2735 w, 1585 w, 1486 sh, 1464 s, 1377 m, 1302 w, 1246 m, 1193 w 1089 m, 1050 s, 858 s, 828 m, 798 w, 751 w, 699 w cm⁻¹. Anal. Calcd for C43H66N6Si2Zr: C, 63.41; H, 8.17; N, 10.32. Found: C, 63.24; H, 8.03; N, 9.83.

Preparation of [Zr(N₂^{TBS}N_{pv})(NN^{Mes}NPh₂)] (13). To a solution of $[Zr(N_2^{TBS}N_{py})(NNPh_2)(py)]$ (9; 500 mg, 0.67 mmol) in toluene (20 mL) was added mesityl azide (107 μ L, 0.67 mmol). The reaction mixture was stirred for 1 h at room temperature and filtered, and the volatiles were removed under reduced pressure. The crude product was washed with pentane $(3 \times 5 \text{ mL})$ and dried in vacuo to yield 310 mg (0.39 mmol, 58%) of 13 as a pink solid. Single crystals for X-ray diffraction were grown from a saturated toluene solution at 10 °C. ¹H NMR (600 MHz, THF- d_{8} , 296 K): δ –0.39, –0.13 (s, 6 H, Si(CH₃)₂), 0.63 (s, 18 H, Si-C(CH₃)₃), 1.56 (s, 3 H, CH₃), 2.17 (s, 6 H, o-Mes-CH₃), 2.29 (s, 3 H, p-Mes-CH₃), 3.57 (d, ${}^{2}J_{HH} = 12.4$ Hz, 2 H, CHH), 3.71 (d, ${}^{2}J_{HH}$ = 12.4 Hz, 2 H, CHH), 6.71 (t, ${}^{3}J_{pHmH}$ = 7.2 Hz 2 H, p-H_{Ph}), 6.89 (d, ${}^{3}J_{oHmH}$ = 8.0 Hz, 4 H, o-H_{Ph}), 6.91 (s, 2 H, o-H_{Mes}), CH₃), 21.1 (Si-C(CH₃)₃), 21.3 (p-Mes-CH₃), 25.8 (C-CH₃), 28.6 $(Si-C(CH_3)_3)$, 49.4 $(C-CH_3)$, 64.3 (CH_2) , 120.4 $(p-C_{Ph})$, 122.2 $(C3_{py})$, 123.2 $(C5_{py})$, 124.4 $(o-C_{Ph})$, 129.7 $(m-C_{Ph})$, 130.8 $(m-C-C_{Ph})$ Mes), 138.9 (Mes–CCH₃), 141.1 (C4_{py}), 150.3 (C6_{py}), 150.8 (Cq–Mes), 155.1 (N–C_{Ph}), 164.0 (C2_{py}). ²⁹Si{¹H} NMR (80 MHz, THF- d_{8} , 296 K): δ 3.09 (Si(CH₃)₂^tBu). ¹⁵N NMR (60 MHz, THF- d_{8} , 296 K): δ 166.4 (N-Si(CH₃)₂^tBu), 186.6 (NPh₂), 284.1 (L-N_{pv}), 489.1 (N-Mes), 810.9 (ZrN). IR (Nujol, NaCl): v 2728 w, 1602 w, 1583 w, 1464 s, 1377 s, 1260 s, 1260 m, 1184 w, 1163 w, 1087 w, 1031 m, 907

Organometallics

	2	5	7	10	11	13
formula	C41H70N5Si2Zr	C ₃₆ H ₅₇ N ₇ Si ₂ Zr	C42H70N7Si2Zr	C ₅₀ H ₇₆ N ₈ SiZr	C53.50H78N8Si2Zr	C42H62N6Si2Zr
$M_{ m r}$	780.42	735.29	820.45	964.68	980.64	798.38
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	$P2_{1}/c$	$P2_1/n$	$P\overline{1}$	$P2_1/n$	$P2_1/n$	$P2_{1}/c$
a/Å	16.110(9)	11.902(6)	14.881(6)	12.089(1)	12.184(2)	14.713(2)
b/Å	14.099(8)	19.455(9)	15.938(7)	24.999(2)	26.096(4)	10.081(2)
c/Å	19.575(12)	17.797(10)	22.278(11)	16.865(1)	16.732(3)	28.870(4)
$\alpha/{ m deg}$			71.86(1)			
β/\deg	100.81(1)	108.790(8)	75.37(1)	97.037(2)	97.041(3)	98.683(3)
γ/deg			67.36(1)			
$V/Å^3$	4367(4)	3901(4)	4581(4)	5058.4(7)	5280(1)	4233(1)
Ζ	4	4	4	4	4	4
F ₀₀₀	1676	1560	1756	2056	2092	1696
$d_{\rm c}/{\rm Mg}~{\rm m}^{-3}$	1.187	1.252	1.190	1.267	1.234	1.253
μ (Mo $K\alpha$)/mm ⁻¹	0.339	0.377	0.328	0.330	0.296	0.352
max, min transmissn factors	1.0000, 0.8980	0.7464, 0.6887	0.7461, 0.6222	0.7464, 0.6786	0.7458, 0.6850	0.7464, 0.6637
heta range/deg	1.9-30.5	2.1-30.5	1.0-28.3	1.9-25.0	1.9-28.7	2.1-30.0
index ranges (indep set) <i>h,k,l</i>	-23 to +22, 0-20, 0-27	-16 to +16, 0- 27, 0-25	-19 to +19, -19 to +21, 0-29	-14 to +14, 0-29, 0-20	-16 to +16, 0-35, 0-22	-20 to +20, 0-14 0-40
no. of rflns measd	105 978	95 286	95 644	85 154	114 872	79 980
no. of unique rflns (R_{int})	13 321 (0.0721)	11 898 (0.0719)	22 728 (0.0666)	8898 (0.0454)	13 644 (0.0782)	12 354 (0.0537)
no. of obsd rflns $(I \ge 2\sigma(I))$	9832	9072	15 574	7469	9902	8709
no. of params refined	517	429	967	511	645	552
GooF on F^2	1.016	1.029	1.057	1.075	1.053	1.111
$R \text{ indices } (F > 4\sigma(F)):$ $R(F), R_w(F^2)$	0.0386, 0.0748	0.0376, 0.0791	0.0533, 0.1350	0.0346, 0.0868	0.0452, 0.0997	0.0665, 0.1776
R indices (all data): $R(F)$, $R_w(F^2)$	0.0672, 0.0852	0.0604, 0.0894	0.0890, 0.1500	0.0453, 0.0932	0.0791, 0.1203	0.0937, 0.1923
largest residual peaks/e Å ⁻³	0.682, -0.362	0.984, -0.545	2.089, -0.952	1.668, -0.529	1.053, -0.717	2.797, -1.262

w, 799 m, 776 m, 748 w, 722 w, 697 m cm $^{-1}$. Anal. Calcd for $C_{42}H_{62}N_6Si_2Zr;$ C, 63.18; H, 7.83; N, 10.53. Found: C, 62.98; H, 7.81; N, 10.14.

X-ray Crystal Structure Determinations,. Crystal data and details of the structure determinations are given in Table 5. Preliminary accounts of the structures of 10, 11, and 13 have appeared. $^{11}\,$ Full shells of intensity data were collected at low temperature with a Bruker AXS Smart 1000 CCD diffractometer (T = 100 K, Mo K α radiation, graphite monochromator, λ = 0.710 73 Å). Data were corrected for air and detector absorption, Lorentz, and polarization effects;²⁴ absorption by the crystal was treated by numerical means²⁵ or with a semiempirical multiscan method.^{25,26} The structures were solved by the charge flip procedure²⁷ (complexes 2, 5, and 7), by conventional direct methods^{28,29} (complex 11), by direct methods with dual-space recycling^{29,30} (complex 10), or by the heavy-atom method combined with structure expansion by direct methods applied to difference structure factors³¹ (complex 13) and refined by full-matrix least-squares methods based on F^2 against all unique reflections.^{29,32} All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were placed at calculated positions and refined with a riding model.²⁹ When found necessary, disordered groups and/or solvent molecules where subjected to suitable geometry and adp restraints. Due to severe disorder and fractional occupancy, electron density attributed to the solvent of crystallization was removed from the structures (and the corresponding F_0 values) of 7 (hexane) and 10 (toluene) with the BYPASS procedure,³³ as implemented in PLATON (SQUEEZE).³

Computational Studies. The B3PW91 hybrid functional¹⁵ has been employed to model all the systems by DFT using a 6-31g(d) basis set for *C*, N, and H atoms and an SDD + f function effective core potential basis set for Zr.^{16,35} All the calculations have been carried out with the GAUSSIAN09³⁶ program package. Stationary points were verified by frequency analysis.

Theoretical ¹⁵N NMR Shifts. NMR calculations have been carried out with the GIAO-B3PW91 hybrid functional³⁶ with a 6-311++g(2d,2p) basis set for N, 6-31++g(d) basis set³⁷ for C and Si, 6-31g for H, and SDD + f function effective core potential basis set for Zr.³⁶

ASSOCIATED CONTENT

S Supporting Information

Tables giving Cartesian coordinates of all stationary points and CIF files giving crystallographic data for compounds 2, 5, 7, 10, 11, and 13. 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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