# Zirconium and hafnium (1-pyridinio)imido complexes: functionalized terminal hydrazinediido analogues<sup>†</sup>‡

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Reaction of the diamidozirconium complex [ $Zr(N_2^{TBS}N_{py})(NMe_2)_2$ ] (1) ( $N_2^{TBS}N_{py} = CH_3C(C_3H_4N)(CH_2NSiMe_2tBu)_2$ ) or the diamidohafnium complex [ $Hf(N_2^{TBS}N_{py})(NMe_2)_2$ ] (2) with one molar equiv. of 1-aminopyridinium triflate in the presence of one equiv. of pyridine gave the corresponding (1-pyridinio)imido complexes [ $Zr(N_2^{TBS}N_{py})(=N-NC_5H_5)(OTf)(py)$ ] (3) and [ $Hf(N_2^{TBS}N_{py})(=N-NC_5H_5)(OTf)(py)$ ] (4). These were converted to the acetylide complexes [ $Zr(N_2^{TBS}N_{py})(=N-NC_5H_5)(CCPh)(py)$ ] (6) by reaction with lithium phenylacetylide and substitution of the triflato ligand. Upon reaction of 3 and 4 with one molar equivalent of R-NC (R = tBu, Cy, 2,6-xyl), N–N bond cleavage in the (1-pyridinio)imido unit took place and the respective carbodiimido complexes [ $M(N_2^{TBS}N_{py})(N=C=NR)(OTf)(py)$ ] (7–12) were formed instantaneously. A similar type of reaction with CO gave the isocyanato complex [ $Zr(N_2^{TBS}N_{py})(NCO)(OTf)(py)$ ] (13). Finally, the abstraction of the pyridine ligand in compounds 3 and 4 with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> led to the formation of the triflato-bridged dinuclear complexes [ $Zr(N_2^{TBS}N_{py})(=N-NC_5H_5)(OTf)]_2$  (14) and [ $Hf(N_2^{TBS}N_{py})(=N-NC_5H_5)(OTf)]_2$  (15).

# Introduction

Transition metal hydrazides have been studied as key intermediates in the reductive activation of dinitrogen<sup>1,2</sup> as well as transition metal catalysed hydrohydrazinations of carbon-carbon multiple bonds.<sup>3</sup> Whereas the latter has found direct application in the synthesis of substituted indoles<sup>4</sup> and has been extended to three component reactions such as the iminohydrazination of alkynes,<sup>5</sup> other efforts have been directed at the transformation of the metalbonded NNH<sub>2</sub> fragment to more complex organic, in particular N-heterocyclic structures.

The latter has been pioneered in Leigh's and Hidai's groups who studied the conversion of a metal bonded hydrazide to an N-heterocycle and the subsequent (reductive) scission of the N–N bond, giving the organic product and the (frequently unidentified) reduction products of the metal complex.<sup>6,7</sup> This aspect, in particular, has been investigated in some detail for (1-pyridinio)imido complexes of tungsten as well as titanium.<sup>8</sup> The conversion of hydrazides, which have been obtained by the reductive activation of N<sub>2</sub>, to more complex organics provides one of the principal challenges of dinitrogen activation beyond Haber-Bosch equivalent chemistry.

We have recently reported the synthesis and structural characterization of zirconium hydrazides<sup>9</sup> using a tridentate diamidopyridyl ligand  $[N_2^R N_{py}]^{2-} ([N_2^R N_{py}]^{2-} = [CH_3C(C_5H_4N)(CH_2NR)_2]^{2-})$ as a supporting ligand.<sup>10</sup> A first study of its reactivity revealed exciting new patterns of reactivity based on N–N bond cleavage and N–E (E = main group element) bond formation, in which the group 4 metal hydrazide reacts as a synthon for a Zr–N "metallanitrene" fragment.<sup>9,11</sup> Given this potential combination of N–N scission and N–E coupling, we decided to synthesize (1pyridinio)imido zirconium and hafnium complexes to gain further insight into these processes.<sup>12</sup> (1-Pyridinio)imide derivatives are of special interest in this context, since a hydrazide activation pathway involving bent species with N<sub>β</sub>–metal coordination are most likely to be disfavoured for aromatics. In this work we report the synthesis and full characterization of such complexes along with some aspects of their reactivity. Furthermore, this type of chemistry is extended to the heavier group 4 element hafnium for the first time.

# **Results and discussion**

Synthesis and structural characterization of the (1-pyridinio)imido complexes  $[Zr(N_2^{TBS}N_{py})(=N-NC_5H_5)(OTf)(py)]$  (3) and  $[Hf(N_2^{TBS}N_{py})(=N-NC_5H_3)(OTf)(py)]$  (4) and their conversion to the corresponding phenylacetylide complexes  $[Zr(N_2^{TBS}N_{py})(=N-NC_5H_5)(CCPh)(py)]$  (5) and  $[Hf(N_2^{TBS}N_{py})(=N-NC_5H_5)(CCPh)-(py)]$  (6).

Reacting the diamidozirconium complex  $[Zr(N_2^{TBS}N_{py})-(NMe_2)_2]$  (1) or the diamidohafnium complex  $[Hf(N_2^{TBS}N_{py})-(NMe_2)_2]$  (2) with one molar equiv. of 1-aminopyridinium triflate in the presence of one equiv. of pyridine gave the corresponding (1-pyridinio)imido complexes  $[Zr(N_2^{TBS}N_{py})(=N-NC_5H_5)(OTf)(py)]$  (3) and  $[Hf(N_2^{TBS}N_{py})(=N-NC_5H_5)(OTf)(py)]$  (4) in good yield (Scheme 1).

The analytical data as well as the <sup>1</sup>H, <sup>13</sup>C and <sup>29</sup>Si NMR spectra are consistent with the molecular structures of **3** and **4** as displayed in Scheme 1. Both complexes undergo rapid pyridine

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Scheme 1 Synthesis of the zirconium and hafnium pyridinioimido complexes 3 and 4 and the substitution of the triflato ligands by phenyl acetylide.

dissociation and association on the NMR time scale which renders them effectively  $C_s$ -symmetric. Complex **3** and **4** also displayed characteristic <sup>15</sup>N-NMR spectroscopic features which are discussed in detail for the zirconium complex. The assignment of the signals in the {<sup>1</sup>H}<sup>15</sup>N-NMR spectrum of **3** (recorded at 335 K) was partially achieved by <sup>15</sup>N-HMBC in which the resonance of the *ortho* protons of the pyridinioimido unit correlate with the <sup>15</sup>N signal at 276.9 ppm, which is therefore assigned as that of the N<sub>β</sub> atom. In an analogous way, the resonances at 156.5 ppm and 314.4 ppm were identified as those of the silylamido groups and the pyridyl group of the ancillary tripod ligand. The signal of the N<sub>α</sub> nucleus of the pyridinioimido group was not observed in the <sup>15</sup>N-HMBC experiment but could be detected in a directly recorded <sup>15</sup>N NMR spectrum at 317.1 ppm (all <sup>15</sup>N chemical shifts relative to <sup>15</sup>NH<sub>3</sub> as reference).

In order to establish the structural details of both complexes, single crystal X-ray structure analyses were carried out. Their very similar molecular structures are depicted in Fig. 1a and b and a comparison of the principal bond lengths and angles is provided in Table 1. The overall structural arrangement in 3 and 4 is best described as distorted octahedral with the (1pyridinio)imido ligand in trans disposition to the pyridyl unit of the facially coordinating polydentate ligand [M-N(3) 2.405(3) Å (M = Zr); 2.408(5), 2.420(4) Å (M = Hf)]. The two amido functions, the pyridine and the triflato ligand lie in the plane orthogonal to the (1-pyridinio)imido ligand. In both structures the latter bends away from the bulky tBuMe<sub>2</sub>Si substituents of the amides  $[N(3)-M-N(4) \ 166.6(1)^{\circ} \ (M = Zr); \ 166.3(2), \ 167.0(2)^{\circ}$ (M = Hf)] and the Zr=N-N chain in the "hydrazido" Zr=N- $NC_5H_5$  fragment also deviates slightly from linearity [M–N(4)–  $N(5) 171.4(3)^{\circ} (M = Zr); 172.5(5), 171.2(4)^{\circ} (M = Hf)].$  Its Zr=N bond is longer [Zr(1)–N(4) 1.945(3) Å] whilst the adjacent N– N bond is significantly shorter [N(4)-N(5) 1.321(4) Å] than in Bergman's hydrazido complex [Cp<sub>2</sub>Zr(N<sub>2</sub>Ph<sub>2</sub>)(dmap)] [1.873(7)



Fig. 1 Molecular structures of complexes 3 (a) and 4 (b, only one of the two independent molecules is shown). Selected bond lengths and angles are listed in Table 1.

and 1.364(10), respectively],<sup>13</sup> however, the latter is similar to the N–N distances previously reported by Hidai and coworkers for titanium compounds with the pyridinioimido ligand (1.361–1.369 Å)<sup>8</sup> and indicates the conjugation of the Zr=N and pyridine  $\pi$ -systems.

Reaction of complexes **3** and **4** with lithium phenylacetylide led to a substitution of the triflato ligand (Scheme 1) while leaving the pyridinioimido unit intact. Both reaction products  $[Zr(N_2^{TBS}N_{py})(=N-NC_5H_5)(CCPh)(py)]$  (**5**) and  $[Hf(N_2^{TBS}N_{py})(=N-NC_5H_5)(CCPh)(py)]$  (**6**) were isolated as yellow powders. The moderate isolated yields are due to the extreme sensitivity of both compounds towards oxygen and moisture as well as their high solubility in both aliphatic and aromatic hydrocarbon solvents. Whilst the general <sup>1</sup>H, <sup>13</sup>C and <sup>29</sup>Si NMR

Table 1	Selected bond lengths and angles of the compounds 3 and 4 (data
for the se	cond independent molecule of 4 in the unit cell in brackets)

	3 (M = Zr)	$4\left(M=Hf\right)$
M(1)–N(1)	2.102(3)	2.067(5) [2.086(4)]
M(1) - N(2)	2.088(3)	2.074(5) [2.072(5)]
M(1) - N(3)	2.405(3)	2.373(5) [2.377(5)]
M(1) - N(4)	1.945(3)	1.933(5) [1.940(5)]
M(1) - N(6)	2.456(3)	2.408(5) [2.420(4)]
N(4) - N(5)	1.321(4)	1.331(7) [1.318(6)]
M(1)–O(1)	2.286(2)	2.283(4) [2.241(4)]
N(1)–M(1)–N(2)	93.85(10)	93.3(2) [94.8(2)]
N(1)-M(1)-N(3)	82.28(10)	84.3(2) [83.4(2)]
N(1)-M(1)-N(4)	106.37(12)	105.7(2) [105.0(2)]
N(1)-M(1)-N(6)	85.11(10)	162.3(2) [162.3(2)]
N(1)-M(1)-O(1)	156.03(10)	93.9(2) [93.0(2)]
N(2)-M(1)-N(3)	83.27(10)	82.0(2) [82.9(2)]
N(2)-M(1)-N(4)	105.85(12)	106.2(2) [106.0(2)]
N(2)-M(1)-N(6)	161.56(10)	84.5(2) [86.0(2)]
N(2)-M(1)-O(1)	93.74(10)	156.4(2) [156.3(2)]
N(3)-M(1)-N(4)	166.64(11)	166.3(2) [167.0(2)]
N(3)-M(1)-N(6)	78.34(9)	78.0(2) [79.2(2)]
N(3)-M(1)-O(1)	76.09(9)	76.4(2) [75.8(2])
N(4)-M(1)-N(6)	92.05(11)	91.7(2) [91.72(2)]
N(4)-M(1)-O(1)	93.32(11)	93.5(2) [93.5(2)]
N(6) - M(1) - O(1)	80.57(9)	81.9(2) [80.10(1)]
M(1)-N(4)-N(5)	171.4(3)	172.5(5) [171.2(4)]

spectroscopic patterns of **5** and **6** are similar to those of the starting materials, albeit slightly shifted, both compounds display the characteristic <sup>13</sup>C NMR signals of the phenyl acetelide at  $\delta = 77.8$  and 110.9 for **5** [ $\delta = 82.6$  and 112.7 for **6**]. These are comparable to those reported for [Cp\*Zr(N(<sup>i</sup>Pr)CMeN(<sup>i</sup>Pr))(C<sub>2</sub>H<sub>4</sub>Ph)(C=CPh)] which were found at 72.7 ppm and 108.8.<sup>14</sup>

A potential coupling reaction of the acetylide and the imido unit was not observed even upon heating. Compound **5** remained stable in toluene solution upon prolongued heating at  $110 \,^{\circ}$ C.

The molecular structure of **5** (Fig. 2) may be best described as distorted octahedral with the pyridinioimido ligand occupying the coordination site *trans* to the pyridyl unit of the tripod ligand [N(3)–Zr–N(4) 167.5(1)°]. The two amido groups of the latter [Zr–N(1) 2.095(3) Å, Zr–N(2) 2.154(3) Å], the pyridine and the formally anionic phenylacetylide unit are almost perfectly arranged in a plane orthogonal to the pyridinioimide. The acetylide in the equatorial position adopts the expected almost linear coordination [Zr–C(32)–C(33) 178.9(3)°], the C(32)–C(33) bond length of 1.220(5) Å corresponds to a C=C triple bond and the Zr–C(32) distance of 2.359(4) Å is slightly longer than the average Zr–C<sub>sp</sub> bond [2.237(13) Å].<sup>15</sup> For comparison, in the related complex Li[Cp<sub>2</sub>Zr(C=CPh)(η<sup>2</sup>-1,2-PhC<sub>2</sub>C=CPh)] the Zr–C bond length was found to be 2.314(2) Å and the C=C contiguous distance 1.223(2) Å.<sup>16</sup>

# N–N bond cleavage and N–C bond formation in the reactions of $[Zr(N_2^{TBS}N_{py})(=N-NC_5H_5)(OTf)(py)]$ (3) and $[Hf(N_2^{TBS}N_{py})(=N-NC_5H_{5y})(OTf)(py)]$ (4) with isonitriles and CO

Upon reaction of **3** and **4** with one molar equivalent of R–NC (R = *t*Bu, Cy, 2,6-xyl), N–N bond cleavage in the (1-pyridinio)imido unit took place and the respective carbodiimido complexes  $[M(N_2^{TBS}N_{py}](N=C=NR)(OTf)(py)]$  (7–12) were formed instantaneously (Scheme 2). The IR spectra of the reaction



Fig. 2 Molecular structure of complex 5. Selected bond lengths [Å] and angles [°]: Zr-N(1) 2.095(3), Zr-N(2) 2.154(3), Zr-N(3) 2.406(3), Zr-N(4)1.954(3), Zr-N(6) 2.486(3), Zr-C(32) 2.359(4), N(4)-N(5) 1.335(4), C(32)-C(33) 1.220(5), C(33)-C(34) 1.431(5); N(1)-Zr-N(2) 92.51(11), N(1)-Zr-N(3) 83.0(1), N(1)-Zr-N(4) 106.5(1), N(1)-Zr-N(6) 161.8(1), N(1)-Zr-C(32) 100.0(1), N(2)-Zr-N(3) 80.4(1), N(2)-Zr-N(4) 106.9(1), N(2)-Zr-N(6) 83.7(1), N(2)-Zr-C(32) 155.3(1), N(3)-Zr-N(4) 167.5(1), N(3)-Zr-N(6) 78.8(1), N(3)-Zr-C(32) 80.1(1), N(4)-Zr-N(6) 91.7(1), N(4)-Zr-C(32) 90.0(1), N(6)-Zr-C(32) 77.7(1), Zr-N(4)-N(5) 163.0(2), Zr-C(32)-C(33) 178.9(3), C(32)-C(33) 173.4(4).



Scheme 2 N–N bond cleavage and C–N coupling in the reaction of 3 and 4 with isonitriles to give the carbodiimido complexes 7–12.

products display a characteristic band at around  $\tilde{v} \approx 2100 \text{ cm}^{-1}$ , which is assigned to a NCN stretching vibration.

The analytical data as well as the <sup>1</sup>H, <sup>13</sup>C and <sup>29</sup>Si NMR spectra are consistent with the molecular structures displayed in Scheme 2. As for **3** and **4**, rapid pyridine exchange (or, possibly, exchange involving the triflato ligand) renders these complexes  $C_{\rm s}$ -symmetric on the NMR time scale. In the <sup>15</sup>N-NMR spectra of **7–12** the carbodiimido ligand displayed characteristic resonances: Whereas the signals of the  $\gamma$ -nitrogen were observed between

 $\delta=76.1$  and 64.0 the  $N_{\alpha}$  nuclei of these groups resonate between 193.1 ppm and 197.8 ppm.

The details of the molecular structure of complex 7 have been established by X-ray diffraction and are depicted in Fig. 3 along with the principal bond lengths and angles. The arrangement of the ligands in 7 is similar to that in the starting material, the (1-pyridinio)imido group having been replaced by the *tert*-butylcarbodiimido unit. The latter has a typical diazacumulene structure [C(22)–N(4) 1.201(3) Å, C(22)–N(5) 1.227(3) Å, N(4)–C(22)–N(5) 172.7(2)°] which has resulted from a formal nitrene–isocyanide coupling, similar to that observed in the thermal degradation of palladium azides.<sup>17</sup> We recently reported the related carbodiimido–zirconium compounds [Zr(N<sub>2</sub><sup>TBS</sup>N<sub>py</sub>)(N=C=NR)(NPh<sub>2</sub>)],<sup>9a</sup> while there is no precedent in hafnium chemistry. However, several titanium complexes have been reported which were synthesized by reaction of a Ti precursor with metallated preformed carbodiimide.<sup>18</sup>



Fig. 3 Molecular structure of complex 7. Selected bond lengths [Å] and angles [°]: Zr(1)-N(1) 2.048(2), Zr(1)-N(2) 2.060(2), Zr(1)-N(3) 2.353(2), Zr(1)-N(4) 2.081(2), Zr(1)-N(6) 2.457(2), Zr(1)-O(1) 2.261(1), C(22)-N(4) 1.201(3), C(22)-N(5) 1.227(3); N(1)-Zr(1)-N(2) 92.85(7), N(1)-Zr(1)-N(3) 86.72(6), N(1)-Zr(1)-N(4) 102.19(7), N(1)-Zr(1)-N(6) 84.85(6), N(1)-Zr(1)-O(1) 163.02(6), N(2)-Zr(1)-N(3) 79.87(6), N(2)-Zr(1)-N(4) 111.10(7), N(2)-Zr(1)-N(6) 157.60(6), N(2)-Zr(1)-O(1) 98.80(6), N(3)-Zr(1)-N(4) 165.17(6), N(3)-Zr(1)-N(6) 77.76(6), N(3)-Zr(1)-O(1) 83.25(6), N(4)-Zr(1)-N(6) 91.12(6), N(4)-Zr(1)-O(1) 85.14(6), N(6)-Zr(1)-O(1) 79.66(5), Zr(1)-N(4)-C(22) 174.6(2), N(4)-C(22)-N(5) 172.7(2), C(22)-N(5)-C(23) 126.2(2).

The formation of an isocyanato complex by reaction of  $[Cp_2ZrNNPh_2]$  with CO has been described previously by Bergman *et al.*<sup>13</sup> Bubbling purified and dried (P<sub>4</sub>O<sub>10</sub> column) CO through a solution of **3** for 10 minutes gave the complex  $[Zr(N_2^{TBS}N_{py}](NCO)(OTf)(py)]$  (**13**) in 67% yield (Scheme 3).

The generation of an isocyanato ligand was first indicated by the IR spectrum of **13** which displayed an intense absorption band  $\tilde{v} = 2206 \text{ cm}^{-1}$  which is consistent with an NCO unit and similar to the vibrational band reported for the same unit in [{Cp<sub>2</sub>Zr(NCO)}<sub>2</sub>O] ( $\tilde{v} = 2210 \text{ cm}^{-1}$ ).<sup>19</sup> The signal patterns in the <sup>1</sup>H and <sup>13</sup>C NMR spectra of **13** are very similar to those of **7–12**, however, we were unable to detect the <sup>13</sup>C signal of the quarternary C atom in the



Scheme 3 Cleavage of the hydrazide and N–CO coupling in the synthesis of the isocyanato complex 13.

NCO unit. Its formation was unambiguously established by a single crystal X-ray structure analysis of **13**. Its molecular structure is displayed in Fig. 4 along with selected bond lengths and angles.



Similar to the carbodiimide group in 7–12, the isocyanato ligand in 13 is *trans* disposed with respect to the pyridyl donor of the tripodal diamido donor ligand  $[N(3)-Zr-N(4) 163.89(6)^{\circ}]$ . The NCO unit is slightly bent  $[Zr-N(4)-C(22) 167.5(2)^{\circ}]$  which we attribute to electronic rather than steric factors in view of the almost linear coordination of the sterically more bulky carbodiimide 7  $[Zr-N(4)-C(22) 174.6(2)^{\circ}]$ . We note that in the previously published  $[Cp_2Zr(NCO)_2]$  the Zr-N-C angles were found to be  $172.6(3)^{\circ}$  and  $177.5(3)^{\circ}$  and are thus closer to the expected linearity than in 13.<sup>19</sup> However, the Zr-N distances [2.119(3) Å and 2.101(3) Å] and N–C bond lengths [1.140(5) Å and



Scheme 4 Abstraction of the equatorial pyridine ligand in 3 and 4 with  $B(C_6F_5)_3$  and dimerization to the dinuclear  $\mu$ -triflato complexes 14 and 15.

Si(2)

N(1)

N(2)

1.156(5) Å] in  $[Cp_2Zr(NCO)_2]$  are close to those of 13 (2.121(2)) and 1.177(3) Å, respectively). All other structural features of 13 are very similar to those established for the analogous carbodiimide 7.

#### Synthesis and structural characterization of the triflato-bridged dimeric complexes [Zr(N2<sup>TBS</sup>Npy)(=N-NC5H5)(OTf)]2 (14) and $[Hf(N_2^{TBS}N_{pv})(=N-NC_5H_5)(OTf)]_2$ (15)

Upon reaction of compounds 3 and 4 with  $B(C_6F_5)_3$  in  $C_6D_6$ (Scheme 4) only one signal at -3.4 ppm is observed in the <sup>11</sup>B NMR spectra, which is assigned to the borane-pyridine adduct. No further transformation involving the borane occurs. Apart from the proton resonances of the borane-pyridine adduct, the virtually identical NMR spectra of both product solutions display the signal patterns of a new  $C_s$ -symmetric species, barely shifted signals of the pyridinioimido unit and the absence of free pyridine.

Within several hours crystalline solids, light yellow 14 and yellow 15 (Scheme 4), precipitated from the  $C_6D_6$  solutions which proved to be insoluble in aromatic solvents but were readily dissolved in THF. Single crystals of the zirconium complex 14, which were suitable for X-ray diffraction, were used to establish its detailed structure. The molecular structure of 14 is depicted in Fig. 5 along with the principal bond lengths and angles.

Complex 14 adopts a dimeric structure in the solid state in which the zirconium atoms possess distorted octahedral coordination geometries similar to that of the starting material 3. Both molecular halves are related by a centre of symmetry which coincides with the crystallographic inversion centre. The pyridinioimido ligand at each Zr fragment is trans disposed with respect to the pyridyl group of the tridentate ligand  $[N(3)-Zr-N(4) 165.5(2)^{\circ}]$ . The two triflato ligands are bridging the metal centres, with Zr-O distances of 2.352(3) and 2.379(4) Å being slightly greater than the corresponding distance in complex 3 [2.286(2) Å]. As in complex 3 the nearly linear pyridinioimido unit is slightly tilted away from the sterically demanding tert-butyl groups of the SiMe<sub>2</sub>tBu substituents at the amido groups  $[Zr-N(4)-N(5) 170.8(4)^{\circ}]$ .

Whereas the dinuclear structure of complex 14 in the solid state was thus unambiguously established, the question concerning its structure in solution remained open. In order to gain additional insight <sup>1</sup>H-DOSY-NMR experiments of solutions of 14 in THF were carried out which indicated a monomeric structure in this

0(2A) 0(1A) N(4 Si(1 Fig. 5 Molecular structure of complex 14. Selected bond lengths [Å] and angles  $[\circ]$ : Zr-N(1) 2.073(4), Zr-N(2) 2.079(4), Zr-N(3)

2.429(4), Zr-N(4) 1.928(4), Zr-O(1) 2.352(3), ZrA-O(2) 2.379(4), N(4)-N(5) 1.347(6); N(1)-Zr(1)-N(2) 92.47(16), N(1)-Zr(1)-N(3) 85.83(15), N(1)-Zr-N(4) 106.22(17), N(1)-Zr-N(3) 85.83(15), N(2)-Zr-N(3) 80.89(15), N(2)-Zr-N(4) 106.09(19), N(3)-Zr-N(4) 165.50(18), N(1)-Zr(1)-O(1) 158.33(14), N(2)-Zr-O(1) 93.36(14), N(3)-Zr(1)-O(1) 74.54(14), N(4)-Zr-O(1) 92.15(16), N(1)-Zr-O(2A) 91.44(15), N(2)-Zr-O(2A) 161.76(14), N(3)-Zr-O(2A) 81.64(14), N(4)-Zr-O(2A) 89.86(19), O(1)-Zr-O(2A) 76.92(13), Zr(1)-N(4)-N(5) 170.8(4). Operator for generating equivalent atoms: -x + 1, -y, -z.

F(3

£

 $\cap(1)$ 

S(1

F(2)

solvent. Compared with the mononuclear starting material 3 (D = $1.6 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ ) complex 14 was found to possess an almost identical diffusion constant of  $D = 1.8 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ . In contrast to aromatic solvents, in which 14 and 15 are insoluble, the donor solvent THF appears to be capable of stabilizing the mononuclear species. The coordinated THF seems to undergo rapid exchange processes as is indicated by the <sup>1</sup>H and <sup>13</sup>C NMR resonance pattern which are consistent with an effective molecular  $C_{s}$ -symmetry. This interpretation is also consistent with the observation of only four signals for the five nitrogen atoms in the <sup>15</sup>N-NMR spectrum of the monomeric species. The signal assigned to the  $\alpha$ -nitrogen atom of the pyridinioimido ligand is observed at 315.9 ppm while  $N_{\beta}$  resonates at  $\delta = 276.6$ . The signals of the silvlamido groups are found at a characteristic 155.5 ppm and the resonance of the pyridyl unit appears at  $\delta = 280.9$ .

In this work, we have provided a general synthetic method for the preparation of group 4 metal pyridinioimido complexes and have extended previous efforts involving titanium compounds in this field to their heavier metal congeners.<sup>8</sup> As recently found for N<sub>β</sub>disubstituted hydrazinediides,<sup>9</sup> the systems reported here undergo N-N bond cleavage and N-element bond formation reactions. A first assessment of their reactivity has shown them to be somewhat less reactive that the diphenylhydrazinediido complexes which may prove to be beneficial in the quest for selective transformations involving the N-N bond. We attribute this trend to the partial conjugation of the N-N bond with the aromatic heterocycle,<sup>12</sup> a notion which is consistent with the shorter N-N bond found for the pyridinioimides as compared to more "conventional" hydrazides(2-). Current work in our lab focuses on the possibility of cleaving the pyridinioimido N-N bond reductively, as probed by Hidai<sup>8</sup> for Ti and the attempt to identify the metal containing fragments.

#### **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 glove box. Solvents were dried over sodium (toluene), potassium (hexanes) or sodiumpotassium alloy (pentane, diethyl ether), distilled, and degassed prior to use. Deuterated solvents were dried over potassium ( $C_6 D_6$ , THF- $d_8$ ), vacuum distilled and stored in Teflon valve ampoules 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 200, 400 and 600 NMR spectrometers and were referenced internally, using the residual protio solvent (<sup>1</sup>H) or solvent (<sup>13</sup>C) resonances or externally to SiMe<sub>4</sub> and <sup>15</sup>NH<sub>3</sub>. Elemental analyses were recorded by the analytical service of the Heidelberg Chemistry Department. The diamido-pyridine protioligand  $H_2N_2^{TBS}N_{py}$  and  $[Zr(N_2^{TBS}N_{py})(NMe_2)_2]$  (1) were prepared according to published procedures.9,10 All other reagents were obtained from commercial sources and used as received unless explicitly stated.

#### (A) Preparation of the complexes

**[Hf(N<sub>2</sub><sup>TBS</sup>N<sub>py</sub>)(NMe<sub>2</sub>)<sub>2</sub>] (2).** Hf(NMe<sub>2</sub>)<sub>4</sub> (0.97 g, 2.7 mmol) and H<sub>2</sub>N<sub>2</sub><sup>TBS</sup>N<sub>py</sub> (1.08 g, 2.7 mmol) were dissolved in toluene (20 ml) and placed under partial vacuum. After stirring the reaction mixture at 95 °C for 18 h, the solution was filtered and the volatiles were removed under reduced pressure to yield [Hf(N<sub>2</sub><sup>TBS</sup>N<sub>py</sub>)(NMe<sub>2</sub>)<sub>2</sub>] as a yellow solid. Yield 1.78 g (2.6 mmol, 98%). (Found: C, 45.61; H, 8.11; N, 10.64. Calc. for C<sub>23</sub>H<sub>48</sub>N<sub>5</sub>Si<sub>2</sub>Hf: C, 44.99; H, 7.98; N, 10.53%); υ<sub>max</sub>(Nujol)/cm<sup>-1</sup> 2764 m, 1600 w, 1461 s, 1381 w, 1248 m, 1151 m, 965 w, 900 m, 873 s, 767 m, 663 w; <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>, 296 K): δ = 0.25, 0.29 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>), 0.78 (s, 18H, Si–C(CH<sub>3</sub>)<sub>3</sub>), 1.02 (s, 3H, CH<sub>3</sub>), 3.16, 3.23 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 3.55 (d, <sup>2</sup>J<sub>HH</sub> = 12.4 Hz, 2H, CHH), 3.81 (d, <sup>2</sup>J<sub>HH</sub> = 12.4 Hz, 2H, CHH), 6.56 (ddd, <sup>3</sup>J<sub>H5pyH4py</sub> = 7.5 Hz, <sup>3</sup>J<sub>H5pyH6py</sub> = 5.3 Hz, <sup>4</sup>J<sub>H5pyH3py</sub> = 1.1 Hz, 1H, H5<sub>py</sub>), 6.84 (d, <sup>3</sup>J<sub>H3pyH4py</sub> = 8.0 Hz, 1H, H3<sub>py</sub>), 7.03 (m, 1H, H4<sub>py</sub>), 8.29 (dd,

<sup>3</sup>*J*<sub>H6pyH5py</sub> = 5.3 Hz, <sup>4</sup>*J*<sub>H6pyH4py</sub> = 1.1 Hz, 1H, *H*6<sub>py</sub>); <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 296 K):  $\delta$  = -4.1, -3.8 (Si(CH<sub>3</sub>)<sub>2</sub>), 20.2 (Si-*C*(CH<sub>3</sub>)<sub>3</sub>), 24.5 (CH<sub>3</sub>), 27.9 (Si-C(CH<sub>3</sub>)<sub>3</sub>), 42.1, 45.0 (N(CH<sub>3</sub>)<sub>2</sub>), 47.8 (*C*-CH<sub>3</sub>), 63.0 (*C*H<sub>2</sub>), 120.3 (*C*3<sub>py</sub>), 121.7 (*C*5<sub>py</sub>), 138.3 (*C*4<sub>py</sub>), 147.1 (*C*6<sub>py</sub>), 163.2 (*C*2<sub>py</sub>); <sup>29</sup>Si {<sup>1</sup>H} NMR (80 MHz, C<sub>6</sub>D<sub>6</sub>, 296 K):  $\delta$  = 3.4 (*Si*(CH<sub>3</sub>)<sub>2</sub>'Bu); <sup>15</sup>N NMR (60 MHz, C<sub>6</sub>D<sub>6</sub>, 296 K):  $\delta$  = 133.9, 138.6 (*N*Me<sub>2</sub>), 144.8 (*N*-Si(CH<sub>3</sub>)<sub>2</sub>'Bu), 292.7 (L-*N*<sub>py</sub>).

 $[Zr(N_2^{TBS}N_{nv})(NNC_5H_5)(OTf)(py)]$  (3). A Schlenk tube was charged with  $[Zr(N_2^{TBS}N_{py})(NMe_2)_2](1)$  (1.76 g, 3.1 mmol), 180 µl pyridine (3.1 mmol) and 40 ml of toluene. Aminopyridiniumtriflate (0.53 g, 3.1 mmol) was added slowly in small portions. The reaction mixture was placed under partial vacuum and stirred for 18 h at 40 °C. After filtration, the volatiles were removed under reduced pressure and the crude product was washed with pentane  $(3 \times 20 \text{ ml})$  and dried *in vacuo* to yield 1.71 g (2.1 mmol, 68%) of an orange powder. Single crystals for X-ray diffraction were grown from a saturated toluene solution at 10 °C. (Found: C, 52.00; H, 6.62; N, 9.57. Calc. for C<sub>32</sub>H<sub>51</sub>F<sub>3</sub>N<sub>6</sub>SO<sub>3</sub>Si<sub>2</sub>Zr (+C<sub>7</sub>H<sub>8</sub>): C, 52.26; H, 6.63; N, 9.38%); v<sub>max</sub>(Nujol)/cm<sup>-1</sup> 1601 w, 1455 m, 1318 m, 1237 m, 1169 w, 895 w, 849 m; <sup>1</sup>H NMR (600 MHz, d<sub>8</sub>-thf, 335 K):  $\delta = -0.12, 0.12$  (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>), 0.89 (s, 18H, Si-C(CH<sub>3</sub>)<sub>3</sub>), 1.47 (s, 3H, CH<sub>3</sub>), 3.37 (d,  ${}^{2}J_{HH} = 12.0$  Hz, 2H, CHH), 3.72 (d,  ${}^{2}J_{HH} =$ 12.0 Hz, 2H, CHH), 7.12 (t,  ${}^{3}J_{pHmH} = 7.6$  Hz, 1H, p-H<sub>B</sub>), 7.23  $(pt, {}^{3}J_{mHo/pH} = 6.2 \text{ Hz}, 4 \text{ H}, \text{m-}H_{A/B}), 7.32 \text{ (dd, } {}^{3}J_{H5pvH4pv} = 6.6 \text{ Hz},$  ${}^{3}J_{\text{H5pyH6py}} = 5.0$  Hz, 1H,  $H5_{\text{py}}$ ), 7.59 (d,  ${}^{3}J_{\text{H3pyH4py}} = 8.1$  Hz, 1 H,  $H3_{py}$ ), 7.65 (t,  ${}^{3}J_{pHmH} = 7.6$  Hz, 1H, p- $H_{A}$ ), 7.95 (m, 1H,  $H4_{py}$ ), 8.39 (d,  ${}^{3}J_{oHmH}$  = 6.7 Hz, 2H, o-*H*<sub>B</sub>), 8.54 (d,  ${}^{3}J_{oHmH}$  = 4.3 Hz, 2H, o- $H_A$ ), 8.96 (d,  ${}^{3}J_{H_{6pyH5py}} = 5.0$  Hz, 1H,  $H_{6py}$ );  ${}^{13}C$  { ${}^{1}H$ } NMR (100 MHz,  $d_8$ -thf, 335 K):  $\delta = -4.0, -2.5$  (Si(CH<sub>3</sub>)<sub>2</sub>), 20.9 (Si-C(CH<sub>3</sub>)<sub>3</sub>), 24.7 (C-CH<sub>3</sub>), 29.1 (Si-C(CH<sub>3</sub>)<sub>3</sub>), 51.9 (C-CH<sub>3</sub>), 63.2 (CH<sub>2</sub>), 121.1 (C3<sub>ру</sub>), 122.1 (C5<sub>ру</sub>), 124.4 (m-C<sub>A/B</sub>), 124.7 (p-C<sub>B</sub>), 126.7 (m- $C_{A/B}$ ), 136.8 (*p*- $C_A$ ), 140.8 ( $C4_{py}$ , o- $C_B$ ), 148.6 ( $C6_{py}$ ), 151.3 (o- $C_A$ ), 166.2 ( $C2_{py}$ ), n.o. ( $CF_3$ ); <sup>29</sup>Si {<sup>1</sup>H} NMR (80 MHz,  $d_8$ -thf, 296 K):  $\delta = 3.1 (Si(CH_3)_2 Bu)$ ; <sup>19</sup>F {<sup>1</sup>H} NMR (376 MHz,  $d_8$ -thf, 296 K):  $\delta = -78.3 (CF_3)$ ; <sup>15</sup>N-NMR ( $d_8$ -thf, 60 MHz, 335 K):  $\delta = 156.5 (N-Si(CH_3)_2 Bu), 276.9 (Zr-NN_{py}), 281.6 (L-N_{py}), 314.4$  $(Zr-N_{py})$ , 317.1  $(Zr-NN_{py})$ .

Preparation of  $[Hf(N_2^{TBS}N_{pv})(NNC_5H_5)(OTf)(py)]$  (4). A Schlenk tube was charged with  $[Hf(N_2^{TBS}N_{pv})(NMe_2)_2]$  (2) (1.24 g, 1.9 mmol), 146 µl pyridine (1.9 mmol) and 20 ml of toluene. Aminopyridiniumtriflate (356 mg, 1.9 mmol) was added slowly in small portions. The reaction mixture was placed under partial vacuum and stirred for 40 h at 50 °C. After filtration the volatiles were removed under reduced pressure and the crude product was washed with pentane  $(3 \times 10 \text{ ml})$  and dried in vacuo to yield 1.10 g (1.3 mmol, 66%) of an orange powder. Single crystals for X-ray diffraction were grown from a saturated toluene solution at 10 °C. (Found: C, 42.69; H, 5.72; N, 9.32. Calc. for C<sub>32</sub>H<sub>51</sub>N<sub>6</sub>SF<sub>3</sub>Si<sub>2</sub>Hf: C, 43.11; H, 5.77; N, 9.43%); v<sub>max</sub>(Nujol)/cm<sup>-1</sup> 1602 m, 1464 s, 1377 m, 1339 m, 1170 w, 1032 m, 903 w, 857 m, 755 w, 633 s.; <sup>1</sup>H NMR (600 MHz,  $d_8$ -thf, 335 K):  $\delta = -0.15, 0.06 (s, 6H, Si(CH_3)_2),$ 0.89 (s, 18H, Si–C(CH<sub>3</sub>)<sub>3</sub>), 1.44 (s, 3H, CH<sub>3</sub>), 3.48 (d,  ${}^{2}J_{HH} =$ 12.0 Hz, 2H, CHH), 3.85 (d,  ${}^{2}J_{HH} = 12.0$  Hz, 2H, CHH), 7.03 (t,  ${}^{3}J_{\text{pHmH}} = 7.7$  Hz, 1H, p-H<sub>B</sub>), 7.19 (t,  ${}^{3}J_{\text{mHo/pH}} = 7.1$  Hz, 2H, m- $H_{\rm B}$ ), 7.26 (t,  ${}^{3}J_{\rm mHo/pH} = 6.0$  Hz, 2H, m- $H_{\rm A}$ ), 7.31 (t,  ${}^{3}J_{\rm H5pyH4py/H6py} =$ 6.2 Hz, 1H,  $H5_{py}$ ), 7.62 (d,  ${}^{3}J_{H3pyH4py} = 6.0$  Hz, 1H,  $H3_{py}$ ), 7.70 (t,  ${}^{3}J_{\text{pHmH}} = 7.9 \text{ Hz}, 1\text{H}, \text{ p-}H_{\text{A}}), 7.96 \text{ (t, }{}^{3}J_{\text{H4pyH5py/H6py}} = 7.9 \text{ Hz}, 1\text{H},$  $H4_{pv}$ ), 8.31 (d,  ${}^{3}J_{oHmH} = 6.5$  Hz, 2H, o- $H_{B}$ ), 8.57 (bs, 2H, o- $H_{A}$ ), 8.88 (bs, 1H,  $H6_{py}$ ); <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, d<sub>s</sub>-thf, 335 K): δ = -3.89, -2.5 (Si(CH<sub>3</sub>)<sub>2</sub>), 21.2 (Si–C(CH<sub>3</sub>)<sub>3</sub>), 25.8 (C-CH<sub>3</sub>), 29.3 (Si–C(CH<sub>3</sub>)<sub>3</sub>), 51.7 (C-CH<sub>3</sub>), 63.1 (CH<sub>2</sub>), 120.0 (q, |<sup>1</sup>J<sub>CF</sub>| = 319 Hz, CF<sub>3</sub>), 121.3 (C3<sub>py</sub>), 122.5 (C5<sub>py</sub>), 123.2 (p-C<sub>B</sub>), 124.7 (m-C<sub>A</sub>), 126.6 (m-C<sub>B</sub>), 137.6 (*p*-C<sub>A</sub>), 141.1 (C4<sub>py</sub>), 141.8 (o-C<sub>B</sub>), 149.9 (C6<sub>py</sub>), 151.7 (o-C<sub>A</sub>), 166.8 (C2<sub>py</sub>); <sup>29</sup>Si {<sup>1</sup>H} NMR (80 MHz, d<sub>s</sub>-thf, 296 K): δ = 3.2 (*Si*(CH<sub>3</sub>)<sub>2</sub>'Bu); <sup>19</sup>F {<sup>1</sup>H} NMR (376 MHz, d<sub>s</sub>-thf, 296 K): δ = -78.3 (CF<sub>3</sub>); <sup>15</sup>N-NMR (d<sub>s</sub>-thf, 60 MHz, 335 K): δ = 141.1 (*N*-Si(CH<sub>3</sub>)<sub>2</sub>'Bu), 281.6 (Hf-NN<sub>py</sub>), 282.2 (L-N<sub>py</sub>), 332.7 (Hf-*N*N<sub>py</sub>), n.o. (Hf-N<sub>py</sub>).

 $[Zr(N_2^{TBS}N_{py})(NNC_5H_5)(CCPh)(py)]$  (5). To a stirred solution of [Zr(N<sub>2</sub><sup>TBS</sup>N<sub>py</sub>)(NNC<sub>5</sub>H<sub>5</sub>)(OTf)(py)] (3) (1.0 g, 1.24 mmol) in toluene (50 ml) LiCCPh (135 mg, 1.24 mmol) was added in small portions over 5 min. The mixture was stirred for 18 h. The precipitated LiOTf was removed by filtration and the volatiles were removed under reduced pressure. The brown solid was extracted with pentane (40 ml) and filtered away from insoluble impurities. The solvent was removed from the extract under reduced pressure and the yellow solid was finally washed with cold pentane (-78 °C,  $2 \times 10$  ml). Yield 378 mg (0.5 mmol, 40%). Single crystals for X-ray diffraction were grown from a saturated toluene solution at -40 °C.; (Found: C, 61.83; H, 7.39; N, 10.87. Calc. for C<sub>39</sub>H<sub>56</sub>N<sub>6</sub>Si<sub>2</sub>Zr: C, 61.94; H, 7.46; N, 11.11%); v<sub>max</sub>(Nujol)/cm<sup>-1</sup> 1597 m, 1450 s, 1315 s, 1248 w, 1170 w, 1053 m, 1011 m, 891 m, 848 s, 757 w; <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 296 K):  $\delta = 0.16, 0.40$ (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>), 1.12 (s, 18H, Si-C(CH<sub>3</sub>)<sub>3</sub>), 1.26 (s, 3H, CH<sub>3</sub>),  $3.58 (d, {}^{2}J_{HH} = 12.3 Hz, 2H, CHH), 4.03 (d, {}^{2}J_{HH} = 12.3 Hz, 2H,$ CHH), 6.08 (t,  ${}^{3}J_{pHmH} = 7.5$  Hz, 1H, p-H<sub>B</sub>), 6.27 (pt,  ${}^{3}J_{mHo/pH} =$ 7.1 Hz, 2H, m- $H_B$ ), 6.53 (dd,  ${}^{3}J_{H4pyH3/5py} = 6.4$  Hz, 1H,  $H4_{py}$ ), 6.58  $(m, 1H, m-H_A), 6.89 (t, {}^{3}J_{pHmH} = 7.2 Hz, 1H, p-H_A), 6.97-7.14 (sh,$ 5H, m/p- $H_{Ph}$ ,  $H3_{py}$ ,  $H5_{py}$ ), 7.67 (d,  ${}^{3}J_{oHmH} = 7.3$  Hz, 2H, o- $H_{Ph}$ ), 8.58 (d,  ${}^{3}J_{oHmH} = 6.3$  Hz, 2H, o- $H_{B}$ ), 8.69 (d,  ${}^{3}J_{oHmH} = 4.3$  Hz, 2 H, o- $H_A$ ), 10.01 (d,  ${}^{3}J_{H5pvH6pv} = 4.4$  Hz, 1H,  $H6_{pv}$ );  ${}^{13}C$  { ${}^{1}H$ } NMR (100 MHz,  $C_6D_6$ , 296 K):  $\delta = -4.2, -3.2$  (Si(*C*H<sub>3</sub>)<sub>2</sub>), 20.8 (Si-C(CH<sub>3</sub>)<sub>2</sub>), 28.4 (Si-C(CH<sub>3</sub>)<sub>2</sub>), 50.3 (C-CH<sub>3</sub>), 63.2 (CH<sub>2</sub>), 77.8, 110.9 ( $C \equiv C$ ), 119.9 (p- $C_B$ ), 120.1, 125.3, 128.4 ( $C3_{pv}$ ,  $C5_{pv}$ , m/p- $C_{\rm Ph}$ ), 123.4 (p- $C_{\rm A}$ ), 125.3 (m- $C_{\rm B}$ ), 128.4 (m- $C_{\rm A}$ ), 131.5 (o- $C_{\rm Ph}$ ),  $138.5 (o-C_B), 138.9 (C4_{py}), 151.0 (C6_{py}), 151.3 (o-C_A), 164.2 (C2_{py});$ <sup>29</sup>Si {<sup>1</sup>H} NMR (80 MHz, C<sub>6</sub>D<sub>6</sub>, 296 K):  $\delta = 2.1$  (*Si*(CH<sub>3</sub>)<sub>2</sub><sup>*i*</sup>Bu).

 $[Hf(N_2^{TBS}N_{py})(NNC_5H_5)(CCPh)(py)]$  (6). To a stirred solution of [Hf(N2<sup>TBS</sup>N<sub>py</sub>)(NNC5H5)(OTf)(py)] (4) (0.5 g, 0.56 mmol) in toluene (20 ml) LiCCPh (61 mg, 0.56 mmol) was added in small portions over 5 min. The mixture was stirred for 18 h. The precipitated LiOTf was removed by filtration and the volatiles were removed under reduced pressure. Yield 300 mg (0.36 mmol, 64%). (Found: C, 53.95; H, 6.79; N, 9.56. Calc. for C<sub>39</sub>H<sub>56</sub>N<sub>6</sub>Si<sub>2</sub>Hf: C, 55.53; H, 6.69; N, 9.96%); v<sub>max</sub>(Nujol)/cm<sup>-1</sup> 1599 s, 1459 s, 1378 m, 1335 s, 1248 m 1201 w, 1134 w, 1090 m, 1052 s, 1008 s, 898 s, 856 s, 827 s, 767 m, 694 w, 637 sh; <sup>1</sup>H NMR (600 MHz,  $C_6D_6$ , 296 K):  $\delta = 0.14$ , 0.40 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>), 1.09 (s, 18 H, Si- $C(CH_3)_3$ , 1.19 (s, 3H, CH<sub>3</sub>), 3.70 (d,  ${}^2J_{HH} = 12.1$  Hz, 2H, CHH), 4.10 (d,  ${}^{2}J_{HH} = 12.0$  Hz, 2H, CHH), 6.06 (t,  ${}^{3}J_{pHmH} = 7.5$  Hz, 1H,  $p-H_B$ , 6.29 (t,  ${}^{3}J_{mHo/pH} = 7.1$  Hz, 2H, m- $H_B$ ), 6.55 (m, 2H, m- $H_A$ ), 6.84-6.89 (sh, p- $H_A$ ,  $H5_{py}$ ), 6.99–7.03 (sh, 2H, p- $H_{Ph}$ ,  $H3_{py}$ ), 7.07  $(dt, {}^{3}J_{H4pyH3py/H5py} = 7.7 \text{ Hz}, {}^{4}J_{H4py/H6py} = 1.8 \text{ Hz}, 1\text{H}, H4_{py}), 7.11 (t, t)$  ${}^{3}J_{\text{mHo/pH}} = 7.5 \text{ Hz}, 2\text{H}, \text{m-}H_{\text{Ph}}), 7.68 \text{ (d, }{}^{3}J_{\text{oHmH}} = 7.5 \text{ Hz}, 2\text{H}, \text{ o-}$  $H_{\rm Ph}$ ), 8.45 (d,  ${}^{3}J_{\rm oHmH} = 6.3$  Hz, 2H, o- $H_{\rm B}$ ), 8.74 (d,  ${}^{3}J_{\rm oHmH} = 3.5$  Hz, 2H, o- $H_A$ ), 10.20 (bs, 1H,  $H6_{pv}$ ); <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>,

296 K):  $\delta = -4.2$ , -3.5 (Si(CH<sub>3</sub>)<sub>2</sub>), 20.8 (Si–C(CH<sub>3</sub>)<sub>2</sub>), 24.9 (CH<sub>3</sub>), 28.3 (Si–C(CH<sub>3</sub>)<sub>2</sub>), 49.7 (C-CH<sub>3</sub>), 63.0 (CH<sub>2</sub>), 82.6, 112.7 ( $C \equiv C$ ), 118.9 (p- $C_{\rm B}$ ), 119.0 ( $C3_{\rm py}$ ), 121.3 ( $C5_{\rm py}$ ), 121.5 (m- $C_{\rm A}$ ), 125.3 (m- $C_{\rm B}$ ), 126.0 (p- $C_{\rm ph}$ ), 128.5 (m- $C_{\rm ph}$ ), 131.5 (o- $C_{\rm ph}$ ), 136.9 (p- $C_{\rm A}$ ), 138.5 (C4<sub>py</sub>), 139.5 (o- $C_{\rm B}$ ), 150.8 (C6<sub>py</sub>), 151.8 (o- $C_{\rm A}$ ), 158.7 (i- $C_{\rm ph}$ ), 164.0 ( $C2_{\rm py}$ ); <sup>29</sup>Si {<sup>1</sup>H} NMR (80 MHz, C<sub>6</sub>D<sub>6</sub>, 296 K):  $\delta =$ 2.7 (Si(CH<sub>3</sub>)<sub>2</sub>'Bu); <sup>15</sup>N-NMR (60 MHz, C<sub>6</sub>D<sub>6</sub>, 296 K):  $\delta =$  146.6 (N-Si(CH<sub>3</sub>)<sub>2</sub>'Bu), 284.6 (Hf-NN<sub>py</sub>), 286.4 (L-N<sub>py</sub>), 295.3 (Hf-N<sub>py</sub>), 353.5 (Hf-NN<sub>py</sub>).

 $[Zr(N_2^{TBS}N_{nv})(OTf)(NCNtBu)(py)]$  (7). To a stirred solution of [Zr(N<sub>2</sub><sup>TBS</sup>N<sub>pv</sub>)(NNC<sub>5</sub>H<sub>5</sub>)(OTf)(py)] (3) (350 mg, 0.44 mmol) in toluene (20 ml) tBuNC (46.7 µl, 0.44 mmol) was added dropwise. The red reaction mixture was stirred overnight before removing the solvent in vacuo to yield (7) as a red solid. Quantitative Yield. Crystals suitable for X-Ray diffraction were grown from a saturated toluene solution at 10 °C. (Found: C, 47.76; H, 6.93; N, 10.46. Calc. for C<sub>32</sub>H<sub>55</sub>F<sub>3</sub>N<sub>6</sub>O<sub>3</sub>SSi<sub>2</sub>Zr: C, 47.55; H, 6.86; N, 10.40%); v<sub>max</sub>(Nujol)/cm<sup>-1</sup> 2149 sh, 2094 s, 1604 w, 1464 m, 1375 w, 1330 m, 1238 m, 1203 s, 1091 w, 1013 m, 903 w, 825 m, 776 m, 631 m; <sup>1</sup>H NMR (600 MHz,  $d_8$ -thf, 335 K):  $\delta = -0.01, 0.26$  (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>), 0.91 (s, 18H, Si–C(CH<sub>3</sub>)<sub>3</sub>), 1.30 (s, 9H, NC(CH<sub>3</sub>)<sub>3</sub>), 1.55 (s, 3H, CH<sub>3</sub>), 3.35 (d,  ${}^{2}J_{HH} = 12.4$  Hz, 2H, CHH), 3.88 (d,  ${}^{2}J_{HH} =$ 12.3 Hz, 2H, CHH), 7.25 (m, 2H, m-H<sub>py</sub>), 7.43 (m, 1H, H5<sub>py</sub>), 7.68 (t,  ${}^{3}J_{pHmH} = 7.6$  Hz, 1H, p- $H_{py}$ ), 7.71 (d,  ${}^{3}J_{H3pyH4py} = 8.1$  Hz, 1H,  $H3_{py}$ ), 8.08 (ddd,  ${}^{3}J_{H4pyH3/5py} = 8.0$  Hz,  ${}^{4}J_{H4pyH6py} = 1.7$  Hz, 1H,  $H4_{py}$ ), 8.52 (bs, 2H, o- $H_{py}$ ), 8.85 (d,  ${}^{3}J_{H6pyH5py} = 4.7$  Hz, 1H,  $H6_{pv}$ ); <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, d<sub>8</sub>-thf, 335 K):  $\delta = -5.3, -3.2$ (Si(CH<sub>3</sub>)<sub>2</sub>), 20.0 (Si-C(CH<sub>3</sub>)<sub>3</sub>), 23.3 (C-CH<sub>3</sub>), 27.7 (Si-C(CH<sub>3</sub>)<sub>3</sub>), 32.0 (NC(CH<sub>3</sub>)<sub>3</sub>), 50.7 (C-CH<sub>3</sub>), 53.9 (NC(CH<sub>3</sub>)<sub>3</sub>), 62.2 (CH<sub>2</sub>N), 120.7 (p-C<sub>py</sub>), 122.3 (C5<sub>py</sub>), 123.6 (m-C<sub>py</sub>), 136.0 (C3<sub>py</sub>), 141.1  $(C4_{py})$ , 148.1  $(C6_{py})$ , 150.3  $(o-C_{py})$ , 163.3  $(C2_{py})$ , n.o.  $(CF_3)$ ; <sup>29</sup>Si {<sup>1</sup>H} NMR (80 MHz,  $d_8$ -thf, 296 K):  $\delta = 4.7 (Si(CH_3)_2 Bu)$ ; <sup>19</sup>F {<sup>1</sup>H} NMR (376 MHz,  $d_8$ -thf, 296 K):  $\delta = -77.7 (CF_3)$ ; <sup>15</sup>N-NMR  $(d_8$ -thf, 60 MHz, 335 K):  $\delta = 76.1$  ('BuN), 166.9 (N-Si(CH<sub>3</sub>)<sub>2</sub>'Bu), 193.1 (Zr-NCN), 275.6 (L-N<sub>py</sub>), n.o. (Zr-N<sub>py</sub>).

 $[Hf(N_2^{TBS}N_{pv})(OTf)(NCNtBu)(py)]$  (8). To a stirred solution of [Hf(N<sub>2</sub><sup>TBS</sup>N<sub>pv</sub>)(NNC<sub>5</sub>H<sub>5</sub>)(OTf)(py)] (4) (400 mg, 0.45 mmol) in toluene (20 ml) tBuNC (51.1 µl, 0.45 mmol) was added dropwise. The red reaction mixture was stirred overnight and the volatiles were removed under reduced pressure. The residue was washed with pentane  $(2 \times 5 \text{ ml})$  and dried in vacuo to yield 250 mg (0.28 mmol, 62%) of (8) as a yellow solid. (Found: C, 42.42; H, 6.03; N, 9.10. Calc. for C<sub>32</sub>H<sub>55</sub>F<sub>3</sub>N<sub>6</sub>O<sub>3</sub>SSi<sub>2</sub>Hf: C, 42.92; H, 6.19; N, 9.38%); v<sub>max</sub>(Nujol)/cm<sup>-1</sup> 2157 sh, 2103 s, 1606 w, 1463 s, 1377 w, 1328 w, 1212 m, 1020 w, 840 m, 732 m; <sup>1</sup>H NMR (600 MHz,  $d_8$ -thf, 335 K):  $\delta = -0.04$ , 0.16 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>), 0.92 (s, 18H, Si-C(CH<sub>3</sub>)<sub>3</sub>), 1.30 (s, 9H, NC(CH<sub>3</sub>)<sub>3</sub>), 1.50 (s, 3H, CH<sub>3</sub>), 3.50 (d,  ${}^{2}J_{\text{HH}} = 12.3 \text{ Hz}, 2\text{H}, \text{CH}H), 4.03 (d, {}^{2}J_{\text{HH}} = 12.2 \text{ Hz}, 2\text{H}, \text{C}H\text{H}),$ 7.29 (bs, 2H, m-H<sub>py</sub>), 7.43 (m, 1H, H5<sub>py</sub>), 7.70-7.74 (sh, 2H, H3<sub>py</sub>,  $p-H_{pv}$ ), 8.10 (t,  ${}^{3}J_{H4pvH3/5pv} = 8.0$  Hz, 1H,  $H4_{pv}$ ), 8.55 (bs, 2H, o- $H_{pv}$ ), 8.81 (bs, 1H,  $H6_{py}$ ); <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, d<sub>8</sub>-thf, 335 K):  $\delta =$ -3.6, -2.1 (Si(CH<sub>3</sub>)<sub>2</sub>), 21.4 (Si-C(CH<sub>3</sub>)<sub>3</sub>), 25.4 (C-CH<sub>3</sub>), 29.0 (Si-C(CH<sub>3</sub>)<sub>3</sub>), 33.1 (NC(CH<sub>3</sub>)<sub>3</sub>), 51.7 (C-CH<sub>3</sub>), 54.8 (NC(CH<sub>3</sub>)<sub>3</sub>), 62.6 (CH<sub>2</sub>N), 122.2 (C3<sub>py</sub>), 123.6 (C5<sub>py</sub>), 124.9 (m-C<sub>py</sub>), 137.8 (p-C<sub>py</sub>), 142.6 (*C4*<sub>py</sub>), 149.3 (o-*C*<sub>py</sub>), 151.7 (*C*6<sub>py</sub>), 165.3 (*C2*<sub>py</sub>), n.o. (*C*F<sub>3</sub>); <sup>29</sup>Si {<sup>1</sup>H} NMR (80 MHz, d<sub>8</sub>-thf, 296 K):  $\delta = 4.8 (Si(CH_3)_2 Bu);$ <sup>19</sup>F {<sup>1</sup>H} NMR (376 MHz,  $d_8$ -thf, 296 K):  $\delta = -77.5$  (CF<sub>3</sub>).

1329 m, 1235 w, 1207 m, 1181 w, 1019 m, 902 w, 830 m, 770 w,

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 $[Zr(N_2^{TBS}N_{PV})(OTf)(NCNCy)(py)]$  (9). To a stirred solution of [Zr(N2<sup>TBS</sup>N<sub>DV</sub>)(NNC5H5)(OTf)(py)] (3) (300 mg, 0.37 mmol) in toluene (20 ml) CyNC (46.7 µl, 0.37 mmol) was added dropwise. The red solution was stirred overnight before removing the solvent in vacuo to yield (9) as a red solid. Quantitative Yield (Found: C, 48.57; H, 6.81; N, 10.03. Calc. for C<sub>34</sub>H<sub>57</sub>F<sub>3</sub>N<sub>6</sub>O<sub>3</sub>SSi<sub>2</sub>Zr: C, 48.95; H, 6.89; N, 10.07%); v<sub>max</sub>(Nujol)/cm<sup>-1</sup> 2113 s, 1604 m, 1463 s, 1376 m, 1326 m, 1257 w, 1206 m, 1065 w, 900 m, 828 s, 778 m, 632 m; <sup>1</sup>H NMR (600 MHz, d<sub>8</sub>-thf, 335 K):  $\delta = -0.03, 0.26$  (bs, 6H, Si(CH<sub>3</sub>)<sub>2</sub>), 0.91 (s, 18H, Si–C(CH<sub>3</sub>)<sub>3</sub>), 1.29 (m, 4H, m/p-H<sub>Cy</sub>), 1.43  $(m, 2H, o-H_{Cy}), 1.51 (m, 2H, m-H_{Cy}), 1.55 (s, 3H, CH_3), 1.89 (m,$ 2H, o- $H_{Cy}$ ), 3.29 (m, 1H,  $H_{Cy}$ ), 3.35 (d,  ${}^{2}J_{HH}$  = 12.5 Hz, 2H, CHH), 3.88 (d,  ${}^{2}J_{\text{HH}} = 12.3$  Hz, 2H, CHH), 7.27 (m, 2H, m- $H_{\text{py}}$ ), 7.44 (bs, 1H,  $H5_{py}$ ), 7.69 (bs, 1H, p- $H_{py}$ ), 7.72 (d,  ${}^{3}J_{H3pyH4py} = 8.2$  Hz, 1H,  $H3_{py}$ ), 8.08 (ddd,  ${}^{3}J_{H4pyH3py/5py} = 7.9$  Hz,  ${}^{4}J_{H4pyH6py} = 1.6$  Hz, 1H,  $H4_{py}$ ), 8.53 (bs, 2H, o- $H_{py}$ ), 8.86 (bs, 1H,  $H6_{py}$ ); <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz,  $d_8$ -thf, 335 K):  $\delta = -5.2, -3.3$  (Si(*C*H<sub>3</sub>)<sub>2</sub>), 20.0  $(Si-C(CH_3)_3)$ , 24.5 (C-CH<sub>3</sub>), 24.7 (p-C<sub>Cy</sub>), 26.0 (m-C<sub>Cy</sub>), 27.9 (Si- $C(CH_3)_3$ , 36.0 (o- $C_{C_V}$ ), 50.7 (C- $CH_3$ ), 54.5 ( $C_{C_V}$ ), 62.0 ( $CH_2N$ ), 120.7 (p- $C_{pv}$ ), 122.0 ( $C5_{pv}$ ), 123.4 (m- $C_{pv}$ ), 136.0 ( $C3_{pv}$ ), 141.1  $(C4_{py})$ , 148.0  $(C6_{py})$ , 150.1  $(o-C_{py})$ , 163.2  $(C2_{py})$ , n.o.  $(CF_3)$ ;); <sup>29</sup>Si {<sup>1</sup>H} NMR (80 MHz,  $d_8$ -thf, 296 K):  $\delta = 4.6 (Si(CH_3)_2 Bu)$ ; <sup>19</sup>F {<sup>1</sup>H} NMR (376 MHz, d<sub>8</sub>-thf, 296 K):  $\delta = -77.6 (CF_3)$ ; <sup>15</sup>N-NMR  $(d_8$ -thf, 60 MHz, 335 K):  $\delta = 64.0 (CyN)$ , 164.2 (N-Si(CH<sub>3</sub>)<sub>2</sub><sup>t</sup>Bu), 192.9 (Zr-NCN), 275.6 (L- $N_{py}$ ), n.o. (Zr- $N_{py}$ ).

 $[Hf(N_2^{TBS}N_{py})(OTf)(NCNCy)(py)]$  (10). To a stirred solution of [Hf(N<sub>2</sub><sup>TBS</sup>N<sub>py</sub>)(NNC<sub>5</sub>H<sub>5</sub>)(OTf)(py)] (4) (200 mg, 0.22 mmol) in toluene (10 ml) CyNC (27.9 µl, 0.22 mmol) was added dropwise. The red reaction mixture was stirred overnight and the volatiles were removed under reduced pressure. The residue was washed with pentane  $(2 \times 2 \text{ ml})$  and dried *in vacuo*, to yield 150 mg (0.17 mmol, 74%) of (10) as an orange solid. (Found: C, 44.20; H, 5.94; N, 9.15. Calc. for C<sub>34</sub>H<sub>57</sub>F<sub>3</sub>N<sub>6</sub>O<sub>3</sub>SSi<sub>2</sub>Hf: C, 44.31; H, 6.23; N, 9.12%); v<sub>max</sub>(Nujol)/cm<sup>-1</sup> 2123 s, 1606 m, 1463 s, 1260 m, 1203 s, 1023 sh, 907 w, 841 m, 633 m; <sup>1</sup>H NMR (600 MHz, d<sub>8</sub>-thf, 335 K):  $\delta = -0.03, 0.26$  (bs, 6H, Si(CH<sub>3</sub>)<sub>2</sub>), 0.91 (s, 18H, Si–C(CH<sub>3</sub>)<sub>3</sub>), 1.29 (m, 4H, m/p- $H_{Cv}$ ), 1.43 (m, 2H, o- $H_{Cv}$ ), 1.51 (m, 2H, m- $H_{Cv}$ ), 1.55 (s, 3H, CH<sub>3</sub>), 1.89 (m, 2H, o-H<sub>Cy</sub>), 3.29 (m, 1H, H<sub>Cy</sub>), 3.35 (d,  ${}^{2}J_{\rm HH} = 12.5$  Hz, 2H, CHH), 3.88 (d,  ${}^{2}J_{\rm HH} = 12.3$  Hz, 2H, CHH), 7.27 (m, 2H, m-H<sub>py</sub>), 7.44 (bs, 1H, H5<sub>py</sub>), 7.69 (bs, 1H, p-H<sub>py</sub>), 7.72 (d,  ${}^{3}J_{H3pvH4pv} = 8.2$  Hz, 1H,  $H3_{pv}$ ), 8.08 (ddd,  ${}^{3}J_{H4pvH3pv/5pv} =$ 7.9 Hz,  ${}^{4}J_{H4pvH6pv} = 1.6$  Hz, 1H,  $H4_{pv}$ ), 8.53 (bs, 2H, o- $H_{pv}$ ), 8.86 (bs, 1H,  $H6_{py}$ ); <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, d<sub>8</sub>-thf, 335 K):  $\delta =$ -5.2, -3.3 (Si(CH<sub>3</sub>)<sub>2</sub>), 20.0 (Si-C(CH<sub>3</sub>)<sub>3</sub>), 24.5 (C-CH<sub>3</sub>), 24.7 (p- $C_{C_{V}}$ , 26.0 (m- $C_{C_{V}}$ ), 27.9 (Si–C( $CH_{3}$ )<sub>3</sub>), 36.0 (o- $C_{C_{V}}$ ), 50.7 (C-CH<sub>3</sub>), 54.5 (C<sub>cy</sub>), 62.0 (CH<sub>2</sub>N), 120.7 (p-C<sub>py</sub>), 122.0 (C5<sub>py</sub>), 123.4 (m- $C_{\text{pv}}$ ), 136.0 ( $C3_{\text{pv}}$ ), 141.1 ( $C4_{\text{pv}}$ ), 148.0 ( $C6_{\text{pv}}$ ), 150.1 (o- $C_{\text{pv}}$ ), 163.2  $(C2_{py})$ , n.o.  $(CF_3)$ ; <sup>29</sup>Si {<sup>1</sup>H} NMR (80 MHz, d<sub>8</sub>-thf, 296 K):  $\delta =$ 4.6 (*Si*(CH<sub>3</sub>)<sub>2</sub><sup>*i*</sup>Bu); <sup>19</sup>F {<sup>1</sup>H} NMR (376 MHz, d<sub>8</sub>-thf, 296 K):  $\delta =$  $-77.6 (CF_3).$ 

 $[Zr(N_2^{TBS}N_{py})(OTf)(NCNXyl)(py)]$  (11). To a stirred solution of  $[Zr(N_2^{TBS}N_{py})(NNC_5H_5)(OTf)(py)]$  (3) (500 mg, 0.54 mmol) in toluene (30 ml) a solution of 2,6-XylNC (71.4 mg, 0.54 mmol) in toluene (10 ml) was added dropwise. The red reaction mixture was stirred overnight before removing the solvent *in vacuo* to yield (11) as a red solid. Quantitative Yield. (Found: C, 49.63; H, 6.36; N, 9.66. Calc. for C<sub>36</sub>H<sub>55</sub>F<sub>3</sub>N<sub>6</sub>O<sub>3</sub>SSi<sub>2</sub>Zr: C, 50.49; H, 6.47; N, 9.81%); v<sub>max</sub>(Nujol)/cm<sup>-1</sup> 2195 sh, 2130 s, 2107 s, 1604 w, 1591 w, 1462 m, 633 m; <sup>1</sup>H NMR (600 MHz,  $d_8$ -thf, 335 K):  $\delta = -0.01$ , 0.30 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>), 0.91 (s, 18H, Si-C(CH<sub>3</sub>)<sub>3</sub>), 1.56 (s, 3H, CH<sub>3</sub>), 2.33 (s, 6H,  $(CH_3)_2C_6H_3$ ), 3.36 (d,  ${}^2J_{HH} = 12.8$  Hz, 2H, CHH), 3.92 (d,  ${}^{2}J_{HH} = 12.8$  Hz, 2H, CHH), 6.70 (t,  ${}^{3}J_{pHmH} = 7.4$  Hz, 1H, p- $H_{Xyl}$ ), 6.86 (d,  ${}^{3}J_{mHpH} = 7.4$  Hz, 2H, m- $H_{Xyl}$ ), 7.23 (dd,  ${}^{3}J_{mHoH} =$ 5.8 Hz,  ${}^{3}J_{\rm mHpH} = 7.6$  Hz, 2H, m- $H_{\rm py}$ ), 7.44 (dd,  ${}^{3}J_{\rm H5pyH6py} = 4.9$  Hz,  ${}^{3}J_{\text{H5pyH4py}} = 7.9 \text{ Hz}, 1\text{H}, H5_{\text{py}}), 7.66 (t, {}^{3}J_{\text{pHmH}} = 7.6 \text{ Hz}, 1\text{H}, \text{p-}H_{\text{pv}}),$ 7.72 (d,  ${}^{3}J_{H3pyH4py} = 7.9$  Hz, 1H,  $H3_{py}$ ), 8.09 (ddd,  ${}^{3}J_{H4pyH3py/5py} =$ 7.9 Hz,  ${}^{4}J_{H4pyH6py} = 1.7$  Hz, 1H,  $H4_{py}$ ), 8.51 (bs, 2H, o- $H_{py}$ ), 8.88 (d,  ${}^{3}J_{H6pvH5pv} = 4.9$  Hz, 1H,  $H6_{pv}$ );  ${}^{13}C$  { ${}^{1}H$ } NMR (100 MHz, d<sub>8</sub>-thf, 335 K):  $\delta = -5.4, -3.4$  (Si(CH<sub>3</sub>)<sub>2</sub>), 18.4 (CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 19.9 ((Si-C(CH<sub>3</sub>)<sub>3</sub>), 25.9 (C-CH<sub>3</sub>), 27.6 (Si-C(CH<sub>3</sub>)<sub>3</sub>), 50.8 (C-CH<sub>3</sub>), 61.9  $(CH_2N)$ , 120.9 $(C3_{py})$ , 121.9  $(p-C_{Xyl})$ , 122.2  $(C5_{py})$ , 123.4  $(m-C_{py})$ , 127.3 (m- $C_{Xvl}$ ), 131.9 (o- $C_{Xvl}$ ), 136.0 (p- $C_{pv}$ ), 137.7 ( $C_{Xvl}$ ), 141.3  $(C4_{py})$ , 148.0  $(C6_{py})$ , 150.1  $(o-C_{py})$ , 163.0  $(C2_{py})$ , n.o.  $(CF_3)$ ; <sup>29</sup>Si {<sup>1</sup>H} NMR (80 MHz, d<sub>8</sub>-thf, 296 K):  $\delta = 5.7 (Si(CH_3)_2 Bu)$ ; <sup>19</sup>F {<sup>1</sup>H} NMR (376 MHz,  $d_8$ -thf, 296 K):  $\delta = -77.8 (CF_3)$ ; <sup>15</sup>N-NMR  $(d_8$ -thf, 60 MHz, 335 K):  $\delta = 64.0$  ('BuN), 160.9 (N-Si(CH<sub>3</sub>)<sub>2</sub>'Bu), 197.8 (Zr-NCN), 274.9 (L-N<sub>py</sub>), n.o. (Zr-N<sub>py</sub>).

 $[Hf(N_2^{TBS}N_{py})(OTf)(NCNXyl)(py)]$  (12). To a stirred solution of [Hf(N2<sup>TBS</sup>N<sub>pv</sub>)(NNC5H5)(OTf)(py)] (4) (300 mg, 0.34 mmol) in toluene (10 ml) a solution of 2,6-XylNC (44.1 mg, 0.34 mmol) in toluene (5 ml) was added dropwise. The red reaction mixture was stirred overnight and the volatiles were removed under reduced pressure. The residue was washed with pentane  $(2 \times 5 \text{ ml})$  and dried in vacuo, to yield 193 mg (0.20 mmol, 60%) of (12) as a yellow solid. (Found: C, 45.52; H, 5.81; N, 8.67. Calc. for C<sub>36</sub>H<sub>55</sub>F<sub>3</sub>N<sub>6</sub>O<sub>3</sub>SSi<sub>2</sub>Hf: C, 45.82; H, 5.88; N, 8.91%); v<sub>max</sub>(Nujol)/cm<sup>-1</sup> 2200 sh, 2138 s, 1605 w, 1462 s, 1377 m, 1331 m, 1208 m, 1019 s, 909 w, 814 s, 799 w; <sup>1</sup>H NMR (600 MHz,  $d_8$ -thf, 335 K):  $\delta = 0.00, 0.20$  (s, 6 H, Si(CH<sub>3</sub>)<sub>2</sub>), 0.96 (s, 18H, Si–C(CH<sub>3</sub>)<sub>3</sub>), 1.55 (s, 3H, CH<sub>3</sub>), 2.37 (s, 6H,  $(CH_3)_2C_6H_3$ ), 3.57 (d,  ${}^2J_{HH} = 12.2$  Hz, 2H, CHH), 4.12 (d,  ${}^{2}J_{\text{HH}} = 12.2 \text{ Hz}, 2\text{H}, CH\text{H}), 6.73 (t, {}^{3}J_{\text{pHmH}} = 7.5 \text{ Hz}, 1 \text{ H}, \text{ p-}H_{\text{Xyl}}),$ 6.90 (d,  ${}^{3}J_{\text{mHpH}} = 7.4$  Hz, 2H, m- $H_{Xyl}$ ), 7.35 (bs, 2H, m- $H_{py}$ ), 7.45  $(t, {}^{3}J_{H5pyH4py/H6py} = 4.9 \text{ Hz}, {}^{3}J_{H5py} = 5.8 \text{ Hz}, 1\text{H}, H5_{py}), 7.75-7.82 \text{ (sh,}$ 2H, p- $H_{py}$ ,  $H3_{py}$ ), 8.13 (t,  ${}^{3}J_{H4pyH3py/5py} = 7.7$  Hz, 1H,  $H4_{py}$ ), 8.59 (bs, 2H, o- $H_{py}$ ), 8.88 (bs, 1H,  $H6_{py}$ ); <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, d<sub>8</sub>-thf, 335 K):  $\delta = -4.2, -2.5$  (Si(CH<sub>3</sub>)<sub>2</sub>), 19.5 (CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 21.1 (Si-C(CH<sub>3</sub>)<sub>3</sub>), 25.1 (C-CH<sub>3</sub>), 28.7 (Si-C(CH<sub>3</sub>)<sub>3</sub>), 51.4 (C-CH<sub>3</sub>), 62.4  $(CH_2N)$ , 120.9 (q,  $|{}^{1}J_{CF}| = 319$  Hz,  $CF_3$ ), 122.1( $C3_{py}$ ), 122.8 (p- $C_{Xvl}$ , 123.4 ( $C_{5vv}$ ), 124.8 (m- $C_{vv}$ ), 128.3 (m- $C_{Xvl}$ ), 132.9 (o- $C_{Xvl}$ ), 138.3 (p- $C_{py}$ ), 138.5 ( $C_{Xyl}$ ), 142.5 ( $C4_{py}$ ), 148.9 ( $C6_{py}$ ), 151.6 (o- $C_{py}$ ), 164.8 ( $C2_{py}$ ); <sup>29</sup>Si {<sup>1</sup>H} NMR (80 MHz, d<sub>8</sub>-thf, 296 K):  $\delta =$ 5.9 (*Si*(CH<sub>3</sub>)<sub>2</sub><sup>*i*</sup>Bu); <sup>19</sup>F {<sup>1</sup>H} NMR (376 MHz, d<sub>8</sub>-thf, 296 K):  $\delta =$  $-74.2 (CF_3).$ 

[Zr(N<sub>2</sub><sup>TBS</sup>N<sub>py</sub>)(OTf)(NCO)(py)] (13). [Zr(N<sub>2</sub><sup>TBS</sup>N<sub>py</sub>)(NNC<sub>5</sub>H<sub>5</sub>)-(OTf)(py)] (3) (500 mg, 0.54 mmol) was dissolved in toluene (30 ml) and dry CO was bubbled through the solution for 10 min. The saturated solution was stirred overnight before removing the volatiles under reduced pressure. The resulting red solid was washed with pentane (2 × 20 ml) and dried *in vacuo* to yield 13 as an orange solid. Yield 269 mg (0.36 mmol, 67%). Single crystals suitable for X-ray diffraction were grown from a saturated toluene solution at 10 °C. (Found: C, 43.54; H, 6.23; N, 9.34. Calc. for C<sub>28</sub>H<sub>46</sub>F<sub>3</sub>N<sub>5</sub>O<sub>4</sub>SSi<sub>2</sub>Zr: C, 44.65; H, 6.16; N, 9.30%);  $v_{max}$ (Nujol)/cm<sup>-1</sup> 2206 s, 1605 w, 1463 s, 1331 m, 1236 m, 1203 s, 1089 w, 1018 m, 903 w, 828 m, 776 w, 634 m; <sup>1</sup>H NMR (600 MHz,

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Table 2Details of the crystal structure determinations of the complexes 3, 4, 5, 7, 13 and 14

FormulaFormulaC.g.H., N.O.SSI; Zr.C.H. TrichinicC.y.H., N.O.SSI; Zr.C.H. TrichinicC.y.H., N.O.SSI; Zr.C.H. TrichinicC.y.H., N.O.SSI; Zr.C.H. TrichinicC.y.H., N.O.SSI; Zr.C.H. TrichinicC.y.H., N.O.SSI; Zr.C.H. TrichinicC.y.H., N.O.SSI; Zr.C.H. PMonoclinicC. PTrichinicTrichinicTrichinicTrichinicTrichinicTrichinicPPTrichinicPPTrichinicPPTrichinicPP <t< th=""><th></th><th>3</th><th>4</th><th>5</th><th>7</th><th>13</th><th>14</th></t<>		3	4	5	7	13	14
$d_{1}$ $(0.51(3))$ $(0.531(3))$ $(0.531(3))$ $(0.531(3))$ $(0.531(3))$ $(0.531(3))$ $(0.531(3))$ $(0.531(3))$ $(0.531(3))$ $(0.531(3))$ $(0.531(3))$ $(0.531(3))$ $(0.531(3))$ $(0.531(3))$ $(0.531(3))$ $(0.531(3))$ $(0.531(3))$ $(0.538(1))$ $(0.538(1))$ $(0.538(1))$ $(0.538(1))$ $(0.538(1))$ $(0.538(1))$ $(0.538(1))$ $(0.538(1))$ $(0.538(1))$ $(0.538(1))$ $(0.533(1))$	Formula Crystal system Space group	$\begin{array}{c} C_{32}H_{51}F_3N_6O_3SSi_2Zr\cdot C_7H_8\\ Triclinic\\ p\bar{1}\end{array}$	C <sub>32</sub> H <sub>51</sub> F <sub>3</sub> HfN <sub>6</sub> O <sub>3</sub> SSi <sub>2</sub> ·C <sub>7</sub> H <sub>8</sub> Triclinic Pī	C <sub>39</sub> H <sub>56</sub> N <sub>6</sub> Si <sub>2</sub> Zr·C <sub>7</sub> H <sub>8</sub> Triclinic <i>P</i> I	C <sub>32</sub> H <sub>55</sub> F <sub>3</sub> N <sub>6</sub> O <sub>3</sub> SSi <sub>2</sub> Zr Monoclinic P2, /n	$C_{28}H_{46}F_5N_5O_4SSi_2Zr\cdot1.5 C_7H_8$ Triclinic $p\bar{1}$	$\begin{array}{l} C_{54}H_{92}F_6N_{10}O_6S_2Si_4Zr_2\\ Triclinic\\ p\overline{1}\end{array}$
$ \begin{array}{ccccccc} b/\dot{A} & 13.9752(15) & 13.308(6) & 14.2917(11) & 19.0633(9) & 13.3201(9) \\ a/c & B/c & 8.247(01) & 31.0427(19) & 15.795(11) & 20.8233(10) & 85.88(11) \\ b/c & B/c & 8.268(17) & 8.3470(11) & 19.0633(9) & 13.530(11) & 92.1600(11) \\ b/c & T/c & 75.184(2) & 82.7560(13) & 10.4640(13) & 10.2123(11) & 10.4440(1) \\ 7/c & 75.184(2) & 75.5280(1) & 74.071(2) & 10.2123(11) & 10.34330(1) \\ 7/c & 75.184(2) & 75.5280(1) & 74.071(2) & 10.2123(11) & 10.3430(1) \\ 7/c & 75.184(2) & 75.5280(1) & 74.071(2) & 10.2123(11) & 10.3430(1) \\ 7/c & 75.184(2) & 75.5280(1) & 74.071(2) & 10.2123(11) & 10.4440(1) \\ 7/c & 75.184(2) & 75.5280(1) & 74.071(2) & 10.2123(11) & 10.34330(1) \\ 7/c & 75.184(2) & 75.5280(1) & 74.071(2) & 10.2440(1) & 10.2123(1) & 10.4400(1) \\ 7/c & 7.5184(2) & 74.95 & 52.84338(2) & 10.2440(1) & 2.268.343) & 4072.7(3) & 2.29302(2) \\ 7/d & 0.396 & 93.65 & 848.43 & 808.28 & 891.36 \\ 7/d & 0.396 & 0.396 & 0.3496 & 0.333 & 0.432 & 0.402 \\ 7/d & 0.396 & 0.3496 & 0.3496 & 0.5464 & 0.6932 & 0.7464 & 0.6932 \\ 0.7464 & 0.6332 & 0.7464 & 0.6332 & 0.7464 & 0.6945 & 0.564 & 0.6946 & 0.6946 & 0.0033 & 0.097 \\ 0.7464 & 0.6332 & 0.7464 & 0.6332 & 0.7464 & 0.6332 & 0.7464 & 0.6945 & 0.0049 & 0.0187 \\ 0.7464 & 0.6332 & 0.7464 & 0.6332 & 0.7464 & 0.6332 & 0.7464 & 0.6946 & 0.6946 & 0.0033 & 0.097 \\ 0.7464 & 0.6332 & 0.7464 & 0.6332 & 0.7464 & 0.6332 & 0.7464 & 0.633 & 0.0258 & 0.0496 & 0.0393 & 0.097 \\ 0.0407 & 0.0497 & 0.0497 & 0.0496 & 0.0496 & 0.0335 & 0.072 & 0.0496 & 0.0393 & 0.097 \\ 0.0420 & 0.1187 & 0.0744 & 0.1507 & 0.0456 & 0.0490 & 0.1187 & 0.0417 & 0.0668 & 0.0333 & 0.072 & 0.0496 & 0.0538 & 0.0333 & 0.073 & 0.0496 & 0.0540 & 0.1063 & 0.05348 & 0.0333 & 0.073 & 0.0456 & 0.05640 & 0.05640 & 0.0538 & 0.0333 & 0.073 & 0.0456 & 0.05640 & 0.05348 & 0.0333 & 0.073 & 0.0456 & 0.05640 & 0.05640 & 0.05348 & 0.0333 & 0.073 & 0.0456 & 0.05640 & 0.05640 & 0.0538 & 0.0333 & 0.073 & 0.0456 & 0.05640 & 0.0538 & 0.0333 & 0.073 & 0.0456 & 0.0564 & 0.0558 & 0.0333 & 0.073 & 0.0456 & 0.05640 & 0.0564 & 0.0558 & 0.0333 & 0.073 & 0.0456$	a/Å	10.8684(11)	10.8631(7)	11.0651(8)	10.4937(5)	9.9979(6)	10.451(3)
$c/Å$ $15.6286(17)$ $31.0427(19)$ $15.7951(11)$ $20.8233(10)$ $18.5380(1)$ $g/\circ$ $83.6470(1)$ $71.6280(1)$ $71.6280(1)$ $71.6280(1)$ $10.2123(1)$ $10.3433(1)$ $g/\circ$ $83.6470(1)$ $82.640(1)$ $10.2123(1)$ $10.2480(1)$ $10.440(1)$ $\gamma/\circ$ $75.184(2)$ $82.568(1)$ $2268.3(3)$ $4072.7(3)$ $2230.2(2)$ $U/Å$ $2261.6(4)$ $4459.4(5)$ $2268.3(3)$ $4072.7(3)$ $2230.2(2)$ $U/Å$ $286.38$ $983.65$ $888.43$ $808.28$ $891.36$ $M_1$ $200$ $2008$ $933.65$ $888.43$ $808.28$ $891.36$ $M_2$ $1.316$ $1.316$ $1.465$ $1.242$ $1.318$ $1.327$ $M_2$ $1.316$ $1.346$ $0.6332$ $0.7464, 0.6932$ $0.7464, 0.6932$ $Max$ , min transmission $0.7460, 0.6318$ $0.4949, 0.4157$ $0.736, 0.6332$ $0.7464, 0.6932$ $0.7464, 0.6932$ $Max$ , min transmission $0.7460, 0.6318$ $0.7162.0$ $0.7464, 0.6932$ $0.7464, 0.6932$ $0.7464, 0.6932$ $Max$ , min transmission $0.7460, 0.6318$ $0.7162.0$ $0.7464, 0.6932$ $0.7464, 0.6932$ $0.7464, 0.6932$ $Max$ , min transmission $0.7460, 0.6318$ $0.7162.0, 0.750$ $1.910.250$ $0.7464, 0.6932$ $0.7464, 0.6932$ $Max$ , min transmission $0.7464, 0.6332$ $0.7164, 0.6932$ $0.7464, 0.6932$ $0.7464, 0.6932$ $Max$ , min transmission $0.7464, 0.632, 0.712$ $10.162.0$ $0.7464, 0.6932$ $0.7464, 0.6$	$b/ m{\AA}$	13.9752(15)	13.8086(9)	14.2917(11)	19.0633(9)	13.3201(9)	10.513(3)
$\alpha''$ 82.742(2)         83.6470(1)         71.3620(1)         92.160(1)         92.160(1) <td>c/Å</td> <td>15.6286(17)</td> <td>31.0427(19)</td> <td>15.7951(11)</td> <td>20.8233(10)</td> <td>18.5380(11)</td> <td>16.952(5)</td>	c/Å	15.6286(17)	31.0427(19)	15.7951(11)	20.8233(10)	18.5380(11)	16.952(5)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	α/° 6.0	82.742(2)	83.6470(1)	71.3620(10)		92.1600(1)	101.762(6)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	p/ 7/°	81.840(2) 75.184(2)	82.1500(1) 75.6280(1)	80.0460(10) 74.071(2)	(1)671.701	110.4440(1) 110.4440(1)	90.208(0) 109.007(5)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$U/Å^3$	2261.6(4)	4459.4(5)	2268.3(3)	4072.7(3)	2230.2(2)	1719.0(8)
$M_{\rm c}$ 896.38         983.65         848.43         808.28         891.36 $d_c/Mgm^3$ 1.316         1.465         1.242         1.318         1.327 $F_{000}$ 0.00         1.666         93.4         93.56         848.43         808.28         891.36 $F_{000}$ 1.316         1.465         1.465         1.242         1.318         1.327 $P_{000}$ 0.300         0.333         0.332         0.3422         0.442, 0.6932         0.7464, 0.6932         0.7464, 0.6945 $Max, min, transmission         0.7460, 0.6318         0.4949, 0.4157         0.7464, 0.6832         0.7464, 0.6932         0$	Ζ	2	4	2	4	2	1
$d_c/Mg m^3$ 1.3161.4651.2421.3181.327 $F_{wo}$ 94020089001.2421.3181.327 $F_{wo}$ 94020080.3330.402934 $Max$ , min. transmission0.7460, 0.63180.4949, 0.41570.7464, 0.68320.402 $Max$ , min. transmission0.7460, 0.63180.4949, 0.41570.7464, 0.68320.7464, 0.69320.402 $Max$ , min. transmission0.7460, 0.63180.7404, 0.6320.7464, 0.69320.7464, 0.69320.7464, 0.6945 $Max$ , min. transmission0.7460, 0.63180.7404, 0.41570.7464, 0.68320.7464, 0.69320.7464, 0.6945 $Max$ , min. transmission19 to $26.7$ 0.7404, 0.41570.7464, 0.68320.7464, 0.69320.7464, 0.6945 $Max$ , min. transmission0.7460, 0.63180.7404, 0.41570.7464, 0.68320.7464, 0.69320.7464, 0.6945 $Max$ , min. transmission1.9 to $26.7$ 0.71021.9 to $25.0$ 1.9 to $26.7$ 0.7464, 0.69320.7464, 0.6932 $Max$ , min. transmission1.9 to $26.7$ 0.71021.9 to $25.0$ 1.9 to $26.7$ 0.7464, 0.69320.7464, 0.69320.7464, 0.6932 $Max$ , master1.13, 1.17, 0-191.18, 1.11, 8331.16, 0-362.10, 10, 25.02.10, 10, 25.02.10, 10, 25.02.10, 20, 25.92.10, 20, 25.9 $Max$ , mine examed9610, 0.06791.18830.03227996, 0.077212, 423, 0.066510, 2423, 0.066510, 2423, 0.0665 $Mark^{F^3}$ Nameters refined901750.0427, 0.0949 <td><math>M_{ m r}</math></td> <td>896.38</td> <td>983.65</td> <td>848.43</td> <td>808.28</td> <td>891.36</td> <td>1450.30</td>	$M_{ m r}$	896.38	983.65	848.43	808.28	891.36	1450.30
$F_{000}$ $F_{000}$ $1696$ $934$ $940$ $2008$ $900$ $1696$ $934$ $\mu(Mo-Kc)/mm^{-1}$ $0.3396$ $0.333$ $0.432$ $0.402$ $0.402$ $Max, min. transmission0.7464, 0.63180.4949, 0.41570.7464, 0.63320.7464, 0.69320.402Max, min. transmission0.7466, 0.63180.7464, 0.63320.7464, 0.69320.7464, 0.69320.402Max, min. transmission0.7466, 0.63180.7464, 0.63320.7464, 0.69320.7464, 0.69320.402RencessRencess1.9 to 25.01.9 to 25.01.9 to 25.01.9 to 25.02.1 to 30.52.1 to 30.0Reflections measured4.31290.716-16, 0-361.9 to 25.01.9 to 25.02.0 to 30.52.1 to 30.0Neflections measured9610, 0.067915.883, 0.03227996, 0.077212.423, 0.066513011, 0.0499Observed [I \ge 2\sigma(I)]701710.183987252.84710.278Neflections measured9610, 0.067915.688, 0.03227996, 0.077212.423, 0.066513011, 0.0499Observed [I \ge 2\sigma(I)]70170.0524, 0.13730.0427, 0.09490.0490, 0.11870.0417, 0.09660.0393, 0.0972Rindices [F > 4\sigma(F^2)]0.0764, 0.15070.0490, 0.10630.0548, 0.10530.0548, 0.10530.0640, 0.10630.0548, 0.1053Reflections measuredR(F)0.0764, 0.15070.0490, 0.11870.0490, 0.1063$	$d_{ m c}/{ m Mg}~{ m m}^{-3}$	1.316	1.465	1.242	1.318	1.327	1.401
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	$F_{000}$	940	2008	900	1696	934	756
Max., min. transmission $0.7460, 0.6318$ $0.4949, 0.4157$ $0.7464, 0.6832$ $0.7464, 0.6932$ $0.7464, 0.722$ $0.7464, 0.720$ $0.7464, 0.729$ $0.7464, 0.729$ $0.7464, 0.6932$ $0.7464, 0.6932$ $0.7464, 0.729$ $0.7464, 0.729$ $0.7464, 0.729$ $0.7464, 0.729$ $0.7464, 0.729$ $0.7464, 0.729$ $0.7464, 0.729$ $0.7464, 0.1633$ $0.0640, 0.1063$ $0.0548, 0.1052$ $0.0640, 0.1063$ <td><math>\mu(Mo-K\alpha)/mm^{-1}</math></td> <td>0.396</td> <td>2.494</td> <td>0.333</td> <td>0.432</td> <td>0.402</td> <td>0.502</td>	$\mu(Mo-K\alpha)/mm^{-1}$	0.396	2.494	0.333	0.432	0.402	0.502
factorsfactors $1.9 \text{ to } 26.7$ $0.7 \text{ to } 25.0$ $1.9 \text{ to } 25.0$ $2.0 \text{ to } 30.5$ $2.1 \text{ to } 30.5$ $\theta \text{ ranges}'^{\circ}$ $1.9 \text{ to } 26.7$ $0.7 \text{ to } 25.0$ $1.9 \text{ to } 25.0$ $2.0 \text{ to } 30.5$ $2.1 \text{ to } 30.5$ $\theta \text{ ranges}'^{\circ}$ $1.9 \text{ to } 27.0$ $1.9 \text{ to } 25.0$ $1.9 \text{ to } 27.0$ $2.0 \text{ to } 30.5$ $2.1 \text{ to } 30.0$ $\theta \text{ ranges}(\text{indep. set}) h, h, h-13-13, -17-17, 0-19-12-12, -16-16, 0-361.9 \text{ to } 27.02.0 \text{ to } 30.52.14-14, 0-27, 0-29-14-13, -18-18Reflections measured4.3 \text{ 129}1.118830.332237559375592.0665513011, 0.04990 \text{ bistive}(R_{10})70177017118830.33227996, 0.077212.423, 0.066513011, 0.04990 \text{ bistive}(R_{10})7017701712.4493561399720.066513011, 0.04990 \text{ bistive}(R_{10})70170.0524, 0.13730.0427, 0.09490.0490, 0.11870.0417, 0.09660.0393, 0.0972N(F^2)N(F)0.0764, 0.15070.0456, 0.09580.0756, 0.12860.0640, 0.10630.0548, 0.1052N(F^2)1.1871.3351.0351.0351.0351.075N(F^2)1.1871.3651.0351.0751.075$	Max., min. transmission	0.7460, 0.6318	0.4949, 0.4157	0.7464, 0.6832	0.7464, 0.6932	0.7464, 0.6945	0.7463, 0.6316
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	factors						
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	$\theta$ range/°	1.9 to 26.7	0.7 to 25.0	1.9 to 25.0	2.0 to 30.5	2.1 to 30.0	2.1 to 25.0
Reflections measured         43 129         111 1833         37 559         98 728         52 847           Unique, $R_{iii}$ 9610, 0.0679         15 688, 0.0322         7996, 0.0772         12 423, 0.0665         13 011, 0.0499           Observed $[I \ge 2\sigma(I)]$ 7017         14 493         5613         5013         10 278           Observed $[I \ge 2\sigma(I)]$ 7017         14 493         5613         5065         13 011, 0.0499           Parameters refined         508         0.0427, 0.0949         0.0490, 0.1187         0.0417, 0.0966         0.0393, 0.0972           R indices $[F > 4\sigma(F)] R(F)$ 0.0524, 0.1373         0.0427, 0.0949         0.0490, 0.1187         0.0417, 0.0966         0.0393, 0.0972           w $R(F^2)$ R indices (all data) $R(F)$ ,         0.0756, 0.1286         0.0640, 0.1063         0.0548, 0.1052           w $R(F^2)$ 1.187         1.35         1.035         1.075         0.0540, 0.1053         0.0548, 0.1052	Index ranges (indep. set) $h,k,l$	-13-13, -17-17, 0-19	-12 - 12, -16 - 16, 0 - 36	-12-13, -15-17, 0-18	-14-14, 0-27, 0-29	-14-13, -18-18, 0-26	-12-12, -12-12, 0-20
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Reflections measured	43 129	111 883	37 559	98728	52 847	26268
Observed $[I \ge 2\sigma(I)]$ 7017     14493     5613     8972     10278       Parameters refined     508     1015     508     447     509       R indices $[F > 4\sigma(F)]$ 0.0524, 0.1373     0.0427, 0.0949     0.0490, 0.1187     0.0417, 0.0966     0.0393, 0.0972 $wR(F^2)$ N     0.0756, 0.1286     0.0640, 0.1063     0.0548, 0.1052 $wR(F^2)$ 1.187     1.335     1.035     1.0355     0.0548, 0.1053	Unique, $R_{\rm int}$	9610, 0.0679	15688,0.0322	7996, 0.0772	12423,0.0665	13011,0.0499	6069, 0.0961
Parameters refined         508         447         509 $R$ indices $[F > 4\sigma(F)]$ 0.0524, 0.1373         0.0427, 0.0949         0.0490, 0.1187         0.0417, 0.0966         0.0393, 0.0972 $wR(F^2)$ 0.0456, 0.0187         0.0417, 0.0966         0.0393, 0.0972         0.0427, 0.0972         0.0490, 0.1187         0.0417, 0.0966         0.0393, 0.0972 $wR(F^2)$ K indices (all data) $R(F)$ ,         0.0764, 0.1507         0.0456, 0.0958         0.0756, 0.1286         0.0640, 0.1063         0.0548, 0.1052 $wR(F^2)$ 1.187         1.335         1.035         1.085         1.073	Observed $[I \ge 2\sigma(I)]$	7017	14493	5613	8972	10 278	4074
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	Parameters refined	508	1015	508	447	509	390
$R$ index (all data) $R(F)$ , 0.0764, 0.1507 0.0456, 0.0958 0.0756, 0.1286 0.0640, 0.1063 0.0548, 0.1052 w( $R^{2}$ ) w $R(F^{2})$ 1.187 1.335 1.035 1.035 1.085 1.073	R indices $[F > 4\sigma(F)] R(F)$ , w $R(F^2)$	0.0524, 0.1373	0.0427, 0.0949	0.0490, 0.1187	0.0417, 0.0966	0.0393, 0.0972	0.0601, 0.1378
WA( <i>F</i> <sup>-</sup> ) CGoF on <i>F</i> <sup>2</sup> 1.187 1.335 1.035 1.085 1.073	R indices (all data) $R(F)$ ,	0.0764, 0.1507	0.0456, 0.0958	0.0756, 0.1286	0.0640, 0.1063	0.0548, 0.1052	0.0961, 0.1521
	$\operatorname{GoF} \operatorname{on} F^2$	1.187	1.335	1.035	1.085	1.073	0.980
Largest residual peaks/e Å <sup>-3</sup> 1.157, -1.001 4.441, -2.388 1.053, -0.610 0.923, -0.864 1.565, -0.541	Largest residual peaks/e Å <sup>-3</sup>	1.157, -1.001	4.441, -2.388	1.053, -0.610	0.923, -0.864	1.565, -0.541	0.806, -0.979

d<sub>8</sub>-thf, 335 K): δ = -0.00, 0.31 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>), 0.91 (s, 18H, Si–C(CH<sub>3</sub>)<sub>3</sub>), 1.58 (s, 3H, CH<sub>3</sub>), 3.36 (d, <sup>2</sup>J<sub>HH</sub> = 12.5 Hz, 2H, CHH), 3.94 (d, <sup>2</sup>J<sub>HH</sub> = 12.5 Hz, 2H, CHH), 7.23 (bs, 2H, m-H<sub>py</sub>), 7.44 (bs, 1H, H5<sub>py</sub>), 7.65 (bs, 1H, p-H<sub>py</sub>), 7.77 (d, <sup>3</sup>J<sub>H3pyH4py</sub> = 8.1 Hz, 1H, H3<sub>py</sub>), 8.14 (m, 1H, H4<sub>py</sub>), 8.53 (bs, 2H, o-H<sub>py</sub>), 8.93 (d, <sup>3</sup>J<sub>H6pyH5py</sub> = 5.0 Hz, 1H, H6<sub>py</sub>); <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, d<sub>8</sub>-thf, 335 K): δ = -5.5, -3.4 (Si(CH<sub>3</sub>)<sub>2</sub>), 20.1 (Si–C(CH<sub>3</sub>)<sub>3</sub>), 24.0 (C-CH<sub>3</sub>), 27.9 (Si–C(CH<sub>3</sub>)<sub>3</sub>), 50.7 (C-CH<sub>3</sub>), 61.8 (CH<sub>2</sub>N), 121.0 (p-C<sub>py</sub>), 122.4 (C5<sub>py</sub>), 123.3 (m-C<sub>py</sub>), 136.0 (C3<sub>py</sub>), 141.6 (C4<sub>py</sub>), 148.4 (C6<sub>py</sub>), 149.9 (o-C<sub>py</sub>), 162.6 (C2<sub>py</sub>), n.o. (CF<sub>3</sub>); <sup>29</sup>Si {<sup>1</sup>H} NMR (376 MHz, d<sub>8</sub>-thf, 296 K): δ = -77.6 (CF<sub>3</sub>).

 $[Zr(N_2^{TBS}N_{DV})(NNC_5H_5)(OTf)]_2$  (14). To a solution of  $[Zr(N_2^{TBS}N_{pv})(NNC_5H_5)(OTf)(py)]$  (3) (200 mg, 0.25 mmol) in toluene (6 ml) a solution of  $B(C_6F_5)_3$  (128 mg, 0.25 mmol) in 2 ml of toluene was added dropwise. The red solution was concentrated and stored at room temperature for two days. Light yellow crystals precipitated directly from the reaction mixture and were washed with toluene and dried in vacuo. Yield: 100 mg (0.07 mmol, 56%). (Found: C, 44.58; H, 6.44; N, 9.62. Calc. for  $C_{54}H_{92}F_6N_{10}O_6S_2Si_4Zr_2$ : C, 44.72; H, 6.39; N, 9.66%); v<sub>max</sub>(Nujol)/cm<sup>-1</sup> 1602 m, 1458 s, 1376 m, 1239 m, 1188 w, 1172 w, 1164 w, 1087 w, 1035 m, 913 w, 826 w, 764 m, 731 w, 675 w, 627 m; <sup>1</sup>H-NMR ( $d_8$ -thf, 400 MHz, 296 K)  $\delta = -0.12, 0.13$  (s, 6H,  $Si(CH_3)_2$ , 0.88 (s, 18H, Si-C(CH\_3)\_3), 1.45 (s, 3H, CH\_3), 3.33 (d,  ${}^{2}J_{\text{HH}} = 12.3 \text{ Hz}, 2\text{H}, \text{CH}H), 3.69 (d, {}^{2}J_{\text{HH}} = 12.3 \text{ Hz}, 2\text{H}, \text{C}H\text{H}),$ 7.14 (t,  ${}^{3}J_{pHmH} = 7.7$  Hz, 1H, p-H), 7.26 (t,  ${}^{3}J_{mHo/pH} = 7.4$  Hz, 2H, m-*H*), 7.32 (t,  ${}^{3}J_{H5pyH4/6py} = 6.0$  Hz, 1H,  $H5_{py}$ ), 7.60 (d,  ${}^{3}J_{H3pyH4py} =$ 8.3 Hz, 1H,  $H3_{py}$ ), 7.98 (dt,  ${}^{3}J_{H4pyH3/5py} = 7.9$  Hz,  ${}^{3}J_{H4pyH6py} = 1.9$  Hz, 1H, H4<sub>pv</sub>), 8.38 (d,  ${}^{3}J_{oHmH}$  = 6.2 Hz, 2H, o-H), 9.01 (d,  ${}^{3}J_{H6pyH5py}$  = 5.9 Hz, 1H,  $H6_{py}$ ); {<sup>1</sup>H}<sup>13</sup>C-NMR (d<sub>8</sub>-THF, 600 MHz, 296 K):  $\delta =$ -5.2, -3.7 (Si(CH<sub>3</sub>)<sub>2</sub>), 19.8 (Si-C(CH<sub>3</sub>)<sub>3</sub>), 24.9 (C-CH<sub>3</sub>), 28.0 (Si-C(CH<sub>3</sub>)<sub>3</sub>), 50.5 (C-CH<sub>3</sub>), 61.8 (CH<sub>2</sub>), 120.0 (C3<sub>py</sub>), 121.0 (C5<sub>py</sub>), 123.7 (p-*C*), 125.7 (m-*C*<sub>в</sub>), 139.5 (*C*4<sub>ру</sub>), 139.8 (o-*C*), 148.4 (*C*6<sub>ру</sub>), 164.7 (C2<sub>py</sub>), n.o. (CF<sub>3</sub>); {<sup>1</sup>H}<sup>29</sup>Si-NMR (d<sub>8</sub>-thf, 80 MHz, 296 K):  $\delta = 2.8 (Si(CH_3)_2 Bu); {}^{15}N-NMR (d_8-thf, 60 MHz, 296 K): \delta =$ 155.5 (N-Si(CH<sub>3</sub>)<sub>2</sub>'Bu), 276.6 (Zr–NN<sub>pv</sub>), 280.9 (N<sub>pv</sub>), 315.9 (Z-r- $NN_{pv}$ ); <sup>19</sup>F-NMR (d<sub>8</sub>-thf, 380 MHz, 296K):  $\delta = -78.3$  (CF<sub>3</sub>).

 $[Hf(N_2^{TBS}N_{pv})(NNC_5H_5)(OTf)]_2$  (15). To a solution of  $[Hf(N_2^{TBS}N_{py})(NNC_5H_5)(OTf)(py)]$  (4) (300 mg, 0.34 mmol) in toluene (10 ml) a solution of  $B(C_6F_5)_3$  (172 mg, 0.34 mmol) in 4 ml of toluene was added dropwise. The red solution was concentrated and stored at room temperature for two days. The vellow crystals, which precipitated, were washed with toluene and dried in vacuo. Yield: 150 mg (0.09 mmol, 54%). (Found: C, 39.84; H, 5.76; N, 8.62. Calc. for C<sub>54</sub>H<sub>92</sub>F<sub>6</sub>N<sub>10</sub>O<sub>6</sub>S<sub>2</sub>Si<sub>4</sub>Hf<sub>2</sub>: C, 39.92; H, 5.71; N, 8.62%); v<sub>max</sub>(Nujol)/cm<sup>-1</sup> 1605 m, 1459 s, 1377 w, 1315 s, 1129 m, 1090 w, 903 s, 856 s, 764 m, 771 m, 670 w, 635 m; <sup>1</sup>H-NMR ( $d_8$ -thf, 600 MHz, 296 K)  $\delta = -0.12, 0.12$  (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>), 0.89 (s, 18H, Si–C(CH<sub>3</sub>)<sub>3</sub>), 1.42 (s, 3H, CH<sub>3</sub>), 3.43 (d,  ${}^{2}J_{HH} =$ 11.9 Hz, 2H, CHH), 3.82 (d,  ${}^{2}J_{HH} = 11.9$  Hz, 2H, CHH), 7.07 (t,  ${}^{3}J_{pHmH} = 7.5$  Hz, 1H, p-H), 7.22 (t,  ${}^{3}J_{mHo/pH} = 7.4$  Hz, 2H, m-*H*), 7.41 (t,  ${}^{3}J_{H5pyH4/6py} = 7.1$  Hz, 1H,  $H5_{py}$ ), 7.63 (d,  ${}^{3}J_{H3pyH4py} =$ 8.1 Hz, 1H,  $H3_{py}$ ), 8.00 (dt,  ${}^{3}J_{H4pyH3/5py} = 7.8$  Hz,  ${}^{3}J_{H4pyH6py} = 1.4$  Hz, 1H,  $H4_{py}$ ), 8.29 (d,  ${}^{3}J_{oHmH}$  = 6.3 Hz, 2H, o-H), 9.05 (d,  ${}^{3}J_{H6pyH5py}$  = 4.9 Hz, 1H,  $H6_{pv}$ ); {<sup>1</sup>H}<sup>13</sup>C-NMR (d<sub>8</sub>-THF, 600 MHz, 296 K):  $\delta =$ -4.1, -2.7 (Si(CH<sub>3</sub>)<sub>2</sub>), 20.9 (Si-C(CH<sub>3</sub>)<sub>3</sub>), 25.6 (C-CH<sub>3</sub>), 29.0 (Si-С(СН<sub>3</sub>)<sub>3</sub>), 51.3 (С-СН<sub>3</sub>), 65.5 (СН<sub>2</sub>), 121.1 (СЗ<sub>ру</sub>), 122.3 (С5<sub>ру</sub>), 123.2 (p-*C*), 126.5 (m-*C*<sub>B</sub>), 141.0 (*C*4<sub>py</sub>), 141.4 (o-*C*), 149.4 (*C*6<sub>py</sub>), 166.2 (*C*2<sub>py</sub>), n.o. (*C*F<sub>3</sub>); {<sup>1</sup>H}<sup>29</sup>Si-NMR (d<sub>8</sub>-thf, 80 MHz, 296 K):  $\delta = 4.2$  (*Si*(CH<sub>3</sub>)<sub>2</sub>'Bu); <sup>19</sup>F-NMR (d<sub>8</sub>-thf, 380 MHz, 296K):  $\delta = -78.2$  (*CF*<sub>3</sub>); <sup>15</sup>N-NMR (d<sub>8</sub>-thf, 60 MHz, 296 K):  $\delta = 140.2$  (*N*-Si(CH<sub>3</sub>)<sub>2</sub>'Bu), 281.4 (Hf-NN<sub>py</sub>), (L-*N*<sub>py</sub>), 327.9 (Hf-*N*N<sub>py</sub>).

#### (B) Crystal Structure Determinations

Crystal data and details of the structure determinations are listed in Table 2. Intensity data were collected at low temperature (complex 3: 150(2) K, all others: 100(2) K) with a Bruker AXS Smart 1000 CCD diffractometer (Mo-K<sub>a</sub> radiation, graphite monochromator, 1 = 0.71073 Å) and corrected for Lorentz, polarization and absorption effects (semiempirical, SADABS).<sup>20</sup>

The structures were solved by the heavy atom method combined with structure expansion by direct methods applied to difference structure factors<sup>21</sup> (complexes **3**, **4**, **7**, **13**), by conventional direct methods<sup>22,23</sup> (complex **5**) or by direct methods with dual-space recycling ("Shake-and-Bake", complex **14**)<sup>24</sup> and refined by fullmatrix least squares methods based on all unique  $F^{2}$ .<sup>33,25</sup> All nonhydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were placed calculated positions and refined with a riding model. Where required, the solvent of crystallization (toluene) was subjected to planarity and appropriate bond length similarity restraints.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center: CCDC-679492 (3), 687175 (4), 687176 (5), 679493 (7), 679494 (13) and 687177 (14). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b807808d

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# References

- Reviews: (a) B. A. MacKay and M. D. Fryzuk, *Chem. Rev.*, 2004, **104**, 385; (b) M. P. Shaver and M. D. Fryzuk, *Adv. Synth. Catal.*, 2003, **345**, 1061; (c) R. R. Schrock, *Acc. Chem. Res.*, 2005, **38**, 955; (d) Y. Ohki and M. D. Fryzuk, *Angew. Chem., Int. Ed.*, 2007, **46**, 3180; (e) N<sub>2</sub>-activation by group 4 metal complexes. Key references: M. D. Fryzuk, T. S. Haddad and S. J. Rettig, *J. Am. Chem. Soc.*, 1990, **112**, 8185; (f) R. Duchateau, S. Gambarotta, N. Beydoun and C. Bensimon, *J. Am. Chem. Soc.*, 1991, **113**, 8986; (g) M. D. Fryzuk, J. B. Love, S. J. Rettig and V. G. Young, *Science*, 1997, **275**, 1445; (h) H. Basch, D. G. Musaev, K. Morokuma, M. D. Fryzuk, J. B. Love, W. W. Seidel, A. Albinati, T. F. Koetzle, W. T. Klooster, S. A. Mason and J. Eckert, *J. Am. Chem. Soc.*, 1999, **121**, 523; (i) J. A. Pool, E. Lobkovsky and P. J. Chirik, *Nature*, 2004, **427**, 527.
- (a) L. Morello, J. B. Love, B. O. Patrick and M. D. Fryzuk, J. Am. Chem. Soc., 2004, **126**, 9480; (b) W. H. Bernskoetter, A. V. Olmos, J. A. Pool, E. Lobkovsky and P. J. Chirik, J. Am. Chem. Soc., 2006, **128**, 10696; (c) W. H. Bernskoetter, E. Lobkovsky and P. J. Chirik, Angew. Chem., Int. Ed., 2007, **46**, 2858.
- 3 (a) J. S. Johnson and R. G. Bergmann, J. Am. Chem. Soc., 2001, 123, 2923; (b) C. Cao, Y. Shi and A. L. Odom, Org. Lett., 2002, 4, 2853; (c) V. Khedkar, A. Tillack, M. Michalik and M. Beller, Tetrahedron Lett., 2004, 45, 3123; (d) L. Ackermann and R. Born, Tetrahedron Lett., 2004, 45, 9541.
- 4 A. Tillack, H. Jiao, I. Garcia Castro, C. G. Hartung and M. Beller, Chem. Eur. J., 2004, 10, 2410.
- 5 (a) S. Banerjee, Y. Shi, C. Cao and A. L. Odom, J. Organomet. Chem., 2005, 690, 5066; (b) S. Banerjee and A. L. Odom, Organometallics, 2006, 25, 3099.

- 6 C. J. Pickett and G. J. Leigh, J. Chem. Soc., Chem. Commun., 1981, 1033.
- 7 (a) H. Seino, Y. Ishii, T. Sasagawa and M. Hidai, J. Am. Chem. Soc., 1994, **116**, 7433; (b) H. Seino, Y. Ishii, T. Sasagawa and M. Hidai, J. Am. Chem. Soc., 1995, **117**, 12181; (c) H. Seino, Y. Ishii and M. Hidai, Inorg. Chem., 1997, **36**, 161.
- 8 (a) M. Retbøll, Y. Ishii and M. Hidai, Organometallics, 1999, 18, 150; (b) Y. Ishii, S. Tokunaga, H. Seino and M. Hidai, Inorg. Chem., 1996, 35, 5118; (c) H. Ishino, S. Tokunaga, H. Seino, Y. Ishii and M. Hidai, Inorg. Chem., 1999, 38, 2489; (d) In general, hydrazidium complexes appear to play an important role in the metal centred cleavage of N–N bonds. For early work, see: T. E. Glassman, M. G. Vale and R. R. Schrock, J. Am. Chem. Soc., 1992, 114, 8098.
- 9 (a) H. Herrmann, J. Lloret Fillol, H. Wadepohl and L. H. Gade, Angew. Chem., Int. Ed., 2007, 46, 8426; (b) H. Herrmann, H. Wadepohl and L. H. Gade, Dalton Trans., 2008, 2111.
- (a) S. Friedrich, M. Schubart, L. H. Gade, I. J. Scowen, A. J. Edwards and M. McPartlin, *Chem. Ber.*, 1997, **130**, 1751; (b) A. J. Blake, P. E. Collier, L. H. Gade, M. McPartlin, P. Mountford, M. Schubart and I. J. Scowen, *Chem. Commun.*, 1997, 1555; (c) A. J. Blake, P. E. Collier, L. H. Gade, P. Mountford, S. E. Pugh, M. Schubart and D. J. M. Trösch, *Inorg. Chem.*, 2001, **40**, 870; (d) B. D. Ward, A. Maisse-François, P. Mountford and L. H. Gade, *Chem. Commun.*, 2004, 704; (e) reviews: L. H. Gade, *Chem. Commun.*, 2000, 173; (f) L. H. Gade and P. Mountford, *Coord. Chem. Rev.*, 2001, **216/217**, 65.
- 11 For a very recent overview of the field, see: D. J. Mindiola, Angew. Chem., Int. Ed., 2008, 47, 1557.
- 12 H. Herrmann, J. Lloret Fillol, H. Wadepohl and L. H. Gade, Organometallics, 2008, 27, 172.

- 13 P. J. Walsh, M. J. Carney and R. G. Bergman, J. Am. Chem. Soc., 1991, 113, 6343.
- 14 D. Kissounko, A. Epshteyn, J. C. Fettinger and L. R. Sita, Organometallics, 2006, 25, 531.
- 15 R. Kempe, S. Brenner and P. Arndt, Organometallics, 1996, 15, 1071.
- 16 R. Choukroun, J. Zhao, C. Lorber, P. Cassoux and B. Donnadieu, *Chem. Commun.*, 2000, 1511.
- 17 (a) Y.-J. Kim, X. Chang, J.-T. Han, M. S. Lim and S. W. Lee, *Dalton Trans.*, 2004, 3699; (b) Y.-J. Kim, Y.-S. Joo, J.-T. Han, W. S. Han and S. W. Lee, *J. Chem. Soc., Dalton Trans.*, 2002, 3611; (c) Y.-J. Kim, Y.-S. Kwak, Y.-S. Joo and S. W. Lee, *J. Chem. Soc., Dalton Trans.*, 2001, 144; (d) Y.-J. Kim, Y.-S. Kwak and S. W. Lee, *J. Organomet. Chem.*, 2000, 603, 152.
- 18 (a) H. Plenio and H. W. Roesky, Z. Naturforsch., 1989, 44, 94; (b) G. Veneziani, S. Shimada and M. Tanaka, Organometallics, 1998, 17, 2926.
- 19 N. Klouras and N. Tzavellas, Z. Anorg. Allg. Chem., 1997, 623, 1027.
- 20 G. M. Sheldrick, SADABS, Bruker AXS, 2004–2008.
- P. T. Beurskens, in: G. M. Sheldrick, C. Krüger and R. Goddard, (eds.), *Crystallographic Computing 3*, Clarendon Press, Oxford, UK, 1985, p. 216; P. T. Beurskens, G. Beurskens, R. de Gelder, J. M. M. Smits, S. Garcia-Granda, R. O. Gould, *DIRDIF-2007*, Raboud University Nijmegen, The Netherlands, 2007.
- 22 G. M. Sheldrick, SHELXS-97, University of Göttingen, 1997.
- 23 G. M. Sheldrick, Acta Cryst., 2008, A64, 112.
- 24 M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori and R. Spagna, J. Appl. Crystallogr., 2005, 38, 381.
- 25 G. M. Sheldrick, SHELXL-97, University of Göttingen, 1997.