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New Group 4 Organometallic and Imido Compounds of Diamide-Diamine and Related Dianionic O_2N_2-Donor Ligands

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New group 4 compounds supported by the tetradentate diamide-diamine ligand N_2NN' are reported (N_2NN' = $(2\text{-}C_5H_4N)CH_2N(CH_2CH_2NSiMe_3)_2$) along with some comparative studies with the new bis(alkoxide)-diamine ligand O_2NN' (O_2NN' = $(2\text{-}C_5H_4N)CH_2N(CH_2CMe_2O)_2$). Reaction of the previously described $ZrCl_2(N_2NN')$ (**1**) with 2 equiv of MeLi or $PhCH_2MgCl$ gave $ZrR_2(N_2NN')$ (R = Me (**2**) or CH_2Ph (**3**)). Reaction of **1** with 1 equiv of RCH_2MgCl gave the monoalkyl analogues $ZrCl(R)(N_2NN')$ (R = CH_2Ph (**6**) or CH_2SiMe_3 (**7**)). Reaction of $Zr(CH_2R)_4$ (R = $SiMe_3$ or CMe_3) with H_2N_2NN' in C_6D_6 gave the corresponding $Zr(CH_2R)_2(N_2NN')$, but these decomposed over several hours. Reaction of **1** with allylmagnesium chloride gave $ZrCl\{(2\text{-}NC_5(6\text{-}C_3H_5)H_4)CH_2N(CH_2CH_2NSiMe_3)_2\}$, in which the pyridyl group has undergone nucleophilic attack. Reaction of **2** with BAr^F_3 ($Ar^F = C_6F_5$) in benzene led to the cyclometalated cation $[Zr\{(2\text{-}NC_5H_4)CH_2N(CH_2CH_2NSiMe_3)(CH_2CH_2NSiMe_2CH_2-)\}]^+$ via $SiMe_3$ group C−H activation, but in the presence of THF the methyl cation $[ZrMe(THF)(N_2NN')]^+$ was formed. Reaction of **6** with BAr^F_3 gave the chloride cation $[ZrCl(N_2NN')]^+$. Reaction of Li_2N_2NN' with $Ti(NR)Cl_2(py)_3$ gave the five-coordinate imides $Ti(NR)(N_2NN')$ (R = ^tBu or Ar (**15**), Ar = $2,6\text{-}C_6H_3{}^iPr_2$). Zirconium imides $Zr(NAr)(N_2NN')$ and $Zr(N^tBu)(py)(N_2NN')$ (**18**) were prepared by sequential reaction of **1** with $LiCH_2SiMe_3$ (2 equiv) and the appropriate amine and pyridine for the latter. Reaction of **1** with $LiNH^tBu$ (2 equiv) gave $Zr(NH^tBu)_2(N_2NN')$. Reaction of **18** with piperidine gave $Zr(NH^tBu)(NC_5H_{10})(N_2NN')$ (**19**) via N−H bond activation. For comparative purposes the group 5 imides $M(N^tBu)Cl(N_2NN')$ (M = Nb (**20**) or Ta (**21**)) were prepared from Li_2N_2NN' and the corresponding $M(N^tBu)Cl_3(py)_2$. Reaction of 2-aminomethylpyridine with an excess of isobutylene oxide afforded H_2O_2NN' (**22**). Reaction of H_2O_2NN' (1 or 2 equiv) with $Ti(NMe_2)_4$ gave $Ti(O_2NN')_2$, which reacted with $TiCl_4(THF)_2$ to form $TiCl_2(O_2NN')$. Reaction of H_2O_2NN' with $Zr(CH_2SiMe_3)_2Cl_2(Et_2O)_2$, $Zr(NMe_2)_4$, or $Zr(CH_2SiMe_3)_4$ gave $ZrX_2(O_2NN')$ (X = Cl, NMe_2, or CH_2SiMe_3 (**27**)). Reaction of **27** with BAr^F_3 in the presence of THF formed $[Zr(CH_2SiMe_3)(THF)(O_2NN')]^+$**,** but in the absence of a Lewis base the μ-alkoxide-bridged dimer $[Zr_2(CH_2SiMe_3)_2(O_2NN')_2]^{2+}$ was formed. The compounds **3**, **6**, **15**, **19**, **21**, **22**, and **27** were crystallographically characterized.

Introduction

The development of polydentate ligand frameworks containing anionic nitrogen or oxygen donors has accompanied many of the advances in early transition metal organometallic and related chemistry over the past ca. 15 years.[1−9] The success of these supporting ligands can be attributed to the hard nature of the N and O donor atoms, the diversity and relative ease of manipulation of ligand topology (macrocylic or podand/open-chain), chirality, and coordination number, as well as the "tunability" of the associated steric factors. Many of the developments in the area have been in the context of Ziegler−Natta olefin polymerization[2,6,7] and the stoichiometric and catalytic activation and transformation of small organic molecules.[1a,b,f,j,l] Diamide ligands, in particular those incorporating one or two additional Lewis base donors (e.g., N, O, or P), have been widely studied in all of these contexts.[1a,b,f,g,h,2,3]

With the aim of developing the chemistry of diamide-donor ligand chemistry, we recently reported the synthesis of the diamide-diamine protio ligands $(2\text{-}C_5H_4N)CH_2N(CH_2CH_2N(H)R)_2$ (R = $SiMe_3$ (H_2N_2NN'), $SiMe_2{}^tBu$, or mesityl) and their corresponding lithiated derivatives.[10a−c] These are precursors to new zirconium

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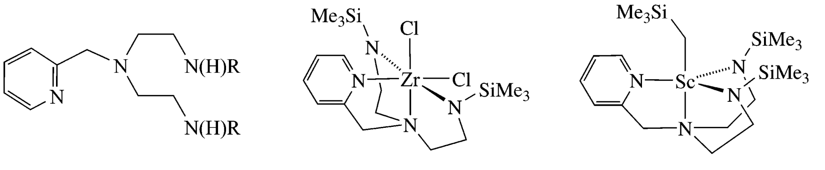
10.1021/om0506365 CCC: $30.25

Chart 1



R = $SiMe_3$ (H_2N_2NN'), $SiMe_2{}^tBu$ or mesityl

1

and hafnium coordination compounds such as $ZrCl_2(N_2NN')$ (**1**, Chart 1),[10b] as well as to a range of organometallic and coordination complexes of the group 3[10d] (e.g., $Sc(CH_2SiMe_3)(N_2NN')$, Chart 1) and lanthanide[10c] metals. However, apart from the simple dichloride and bis(dimethylamide) coordination compounds $MX_2(N_2NN')$ (M = Zr or Hf; X = Cl or NMe_2), no other group 4 chemistry of N_2NN' has been described. Therefore we report here new group 4 organometallic and related compounds containing N_2NN', together with complementary comparative studies with a bis(alkoxide) analogue. In one instance studies have extended to some isoelectronic group 5 imido systems. Part of this work has been communicated.[10a]

Results and Discussion

Neutral and Cationic Group 4 Organometallic Complexes of N_2NN'. The protio ligand H_2N_2NN' (Chart 1) and its lithiated derivative Li_2N_2NN' were prepared according to methods previously described.[10b] Although six-coordinate zirconium and hafnium compounds $MX_2(N_2NN')$ (X = Cl or NMe_2) could be prepared,[10b] the titanium congeners could not, and only complex mixtures of products were obtained. In exploring the group 4 organometallic chemistry of N_2NN' we therefore focused on zirconium, starting either from the protio ligand H_2N_2NN' or the readily prepared dichloride $ZrCl_2(N_2NN')$ (**1**).

Scheme 1 summarizes the reactions of **1** with MeLi and Grignard reagents. Reaction with MeLi (2 equiv) in benzene afforded the dimethyl compound $ZrMe_2(N_2NN')$ (**2**) as a white solid in 88% isolated yield. It was necessary to add the lithiating reagent in two stages, otherwise a mixture of products (containing **2** as a minor component) was obtained. $PhCH_2MgCl$ (2 equiv) could be added in one portion, and after stirring at room temperature for 18 h, $Zr(CH_2Ph)_2(N_2NN')$ (**3**) was obtained as a yellow solid in 62% yield. The NMR data

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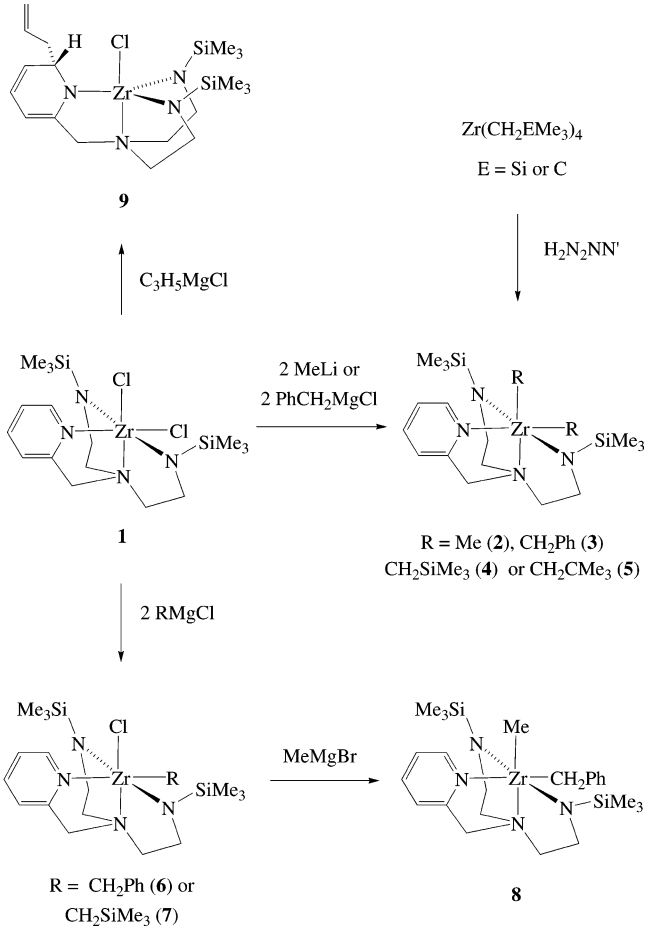
Scheme 1. Synthesis of Zirconium Alkyl, Dialkyl, and Allyl Complexes of N_2NN'



for **2** and **3** are consistent with the C_s symmetrical products illustrated in Scheme 1, and **3** has been structurally characterized (see below). Reaction of $Zr(CH_2SiMe_3)_4$ or $Zr(CH_2CMe_3)_4$ with H_2N_2NN' in C_6D_6 gave quantitative conversion to $Zr(CH_2R)_2(N_2NN')$ (R = $SiMe_3$ (**4**) or CMe_3 (**5**)) and the expected side-products $SiMe_4$ or CMe_4. The same organometallic products could also be obtained on an NMR tube scale from **1** and $LiCH_2R$ (2 equiv). However, regardless of the method of preparation, both complexes were unstable in solution at room temperature, decomposing completely over 6 h to a mixture of products (including free $SiMe_4$ or CMe_4). No attempt was made to isolate either compound on a preparative scale. It is possible that excessive steric crowding promotes alkane elimination and decomposition. It is not known whether the decomposition occurs through attack at one of the $SiMe_3$ C−H bonds (σ-bond metathesis) or via α-C−H abstraction to form transient and reactive alkylidenes.

The monoalkyl derivatives $ZrCl(R)(N_2NN')$ (R = CH_2Ph (**6**) or CH_2SiMe_3 (**7**)) were obtained in 87−97% yield by reaction of **1** with 1 equiv of alkylating agent. Compound **7** appears to be indefinitely stable at room temperature, unlike the bis(trimethylsilylmethyl) analogue **4**. Reaction of $ZrCl(CH_2Ph)(N_2NN')$ (**6**) with MeMgBr in benzene gave the mixed-alkyl product $ZrMe(CH_2Ph)(N_2NN')$ (**8**) in very good yield. An NOE (nuclear Overhauser effect) experiment showed that the methyl ligand lies in the position previously occupied by chloride in **6** (i.e., *cis* to the pyridyl nitrogen, as confirmed by X-ray crystallography for **6**; see below).

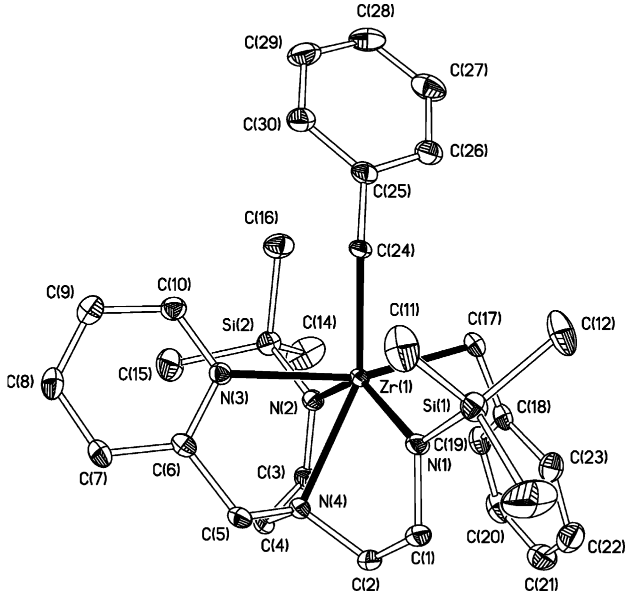


Figure 1. Displacement ellipsoid plot (25% probability) of $Zr(CH_2Ph)_2(N_2NN')$ (**3**). H atoms omitted for clarity.

Surprisingly, reaction of **1** with allyl Grignard gave exclusive attack at the N_2NN' pyridyl group 6 position, forming $ZrCl\{(2\text{-}NC_5(6\text{-}C_3H_5)H_4)CH_2N(CH_2CH_2NSiMe_3)_2\}$ (**9**) as a yellow oil in 74% yield. Addition of a further equivalent of Grignard in an attempt to substitute the chloride ligand did not lead to an isolable product. Metalation of pyridines in the 6-position has been reported previously,[11] but it is not clear why the pyridyl group of **1** should be attacked only in the case of allyl reagent and not with the other alkylating reagents used. We have recently reported the successful use of C_3H_5MgCl in chloride substitution in a complex supported by a related diamide-pyridine ligand.[12] The modified N_4 donor ligand in **9** is now a triamide-amine rather than diamide-diamine.

The molecular structures of $Zr(CH_2Ph)_2(N_2NN')$ (**3**) and $ZrCl(CH_2Ph)(N_2NN')$ (**6**) are shown in Figures 1 and 2, respectively. Selected bond distances and angles are listed in Tables 1 and 2. The overall geometries (distorted octahedral because of the constraining nature of N_2NN') of **3** and **6** are similar to the coordination complexes $ZrX_2(N_2NN')$ (X = Cl (**1**) and NMe_2), which have been structurally characterized previously.[10b] The $Zr-N_{N2NN'}$ distances in **3** are intermediate between those in $ZrCl_2(N_2NN')$ and $Zr(NMe_2)_2(N_2NN')$, with the capping nitrogen (N(4)) showing the smallest variation in Zr−N distance, presumably because it is the most constrained by the ligand framework. The $Zr-N_{N2NN'}$ distances in **6** are all slightly shorter than the corresponding ones in **3**, as would be expected. Surprisingly the Zr−Cl distance in **6** (2.458(2) Å) is shorter than the corresponding bond length in **1** (2.4760(4) Å) despite the presence of the good σ-donor benzyl group in the former.

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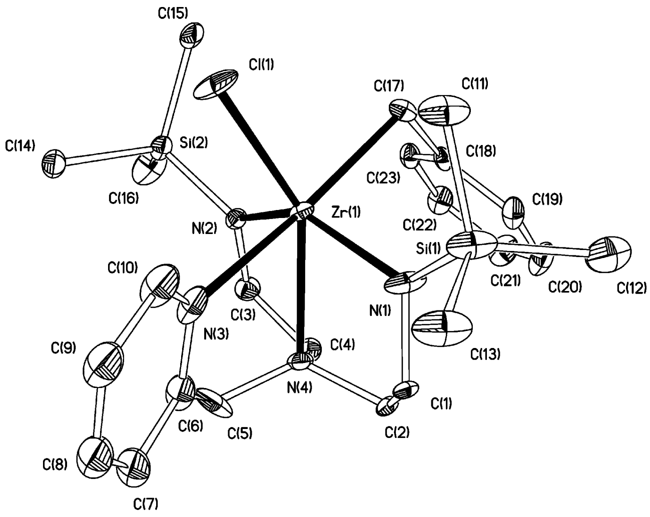


Figure 2. Displacement ellipsoid plot (25% probability) of $ZrCl(CH_2Ph)(N_2NN')$ (**6**). H atoms omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $Zr(CH_2Ph)_2(N_2NN')$ (3)

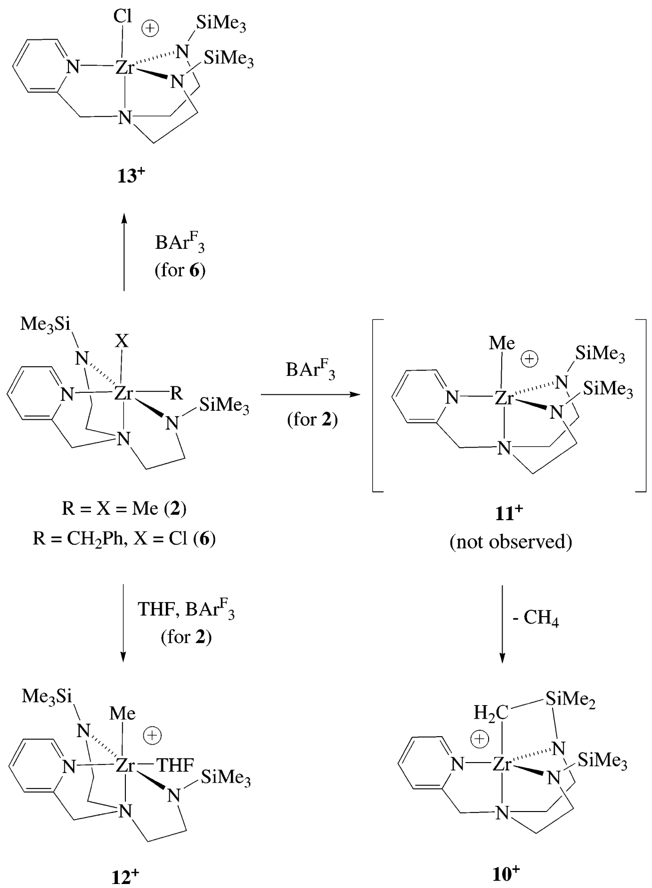
Zr(1)–N(1)	2.111(2)	Zr(1)–N(4)	2.442(2)
Zr(1)–N(2)	2.112(2)	Zr(1)–C(17)	2.342(3)
Zr(1)–N(3)	2.479(2)	Zr(1)–C(24)	2.344(2)
N(1)–Zr(1)–N(2)	137.29(9)	N(3)–Zr(1)–C(17)	163.04(9)
N(1)–Zr(1)–N(3)	99.82(8)	N(4)–Zr(1)–C(17)	126.99(9)
N(2)–Zr(1)–N(3)	87.56(8)	N(1)–Zr(1)–C(24)	99.54(9)
N(1)–Zr(1)–N(4)	71.84(8)	N(2)–Zr(1)–C(24)	123.16(8)
N(2)–Zr(1)–N(4)	72.44(8)	N(3)–Zr(1)–C(24)	80.51(8)
N(3)–Zr(1)–N(4)	67.77(7)	N(4)–Zr(1)–C(24)	144.51(8)
N(1)–Zr(1)–C(17)	93.58(9)	C(17)–Zr(1)–C(24)	87.09(9)
N(2)–Zr(1)–C(17)	89.62(9)	Zr(1)–C(17)–C(18)	104.4(2)
Zr(1)–C(24)–C(25)	130.2(2)		

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $ZrCl(CH_2Ph)(N_2NN')$ (6)

Zr(1)–Cl(1)	2.458(2)	Zr(1)–N(3)	2.465(6)
Zr(1)–N(1)	2.104(5)	Zr(1)–N(4)	2.376(5)
Zr(1)–N(2)	2.096(5)	Zr(1)–C(17)	2.319(6)
Cl(1)–Zr(1)–N(1)	116.5(2)	N(2)–Zr(1)–N(4)	71.7(2)
Cl(1)–Zr(1)–N(2)	102.1(1)	N(3)–Zr(1)–N(4)	69.9(3)
N(1)–Zr(1)–N(2)	140.9(2)	Cl(1)–Zr(1)–C(17)	90.6(2)
Cl(1)–Zr(1)–N(3)	79.0(2)	N(1)–Zr(1)–C(17)	92.1(3)
N(1)–Zr(1)–N(3)	82.8(3)	N(2)–Zr(1)–C(17)	93.5(2)
N(2)–Zr(1)–N(3)	99.5(3)	N(3)–Zr(1)–C(17)	164.7(3)
Cl(1)–Zr(1)–N(4)	146.3(2)	N(4)–Zr(1)–C(17)	122.4(2)
N(1)–Zr(1)–N(4)	72.7(2)	Zr(1)–C(17)–C(18)	104.5(4)

The $Zr-CH_2-C_{ipso}$ angles for the benzyl ligands in **3** are substantially different. The angle subtended at C(17) (*trans* to pyridyl N) is very acute (104.4(2)°) in comparison to that subtended at C(24) (130.2(2)°). The corresponding angle at C(17) in **6** is 104.5(4)°, confirming that this is not simply a consequence of intermolecular packing forces, for example. The additional $Zr\cdots C_{ipso}$ interactions in these two compounds presumably help reduce the electron deficiency at the formally 12 valence electron Zr centers (ignoring any likely $N(2p\pi) \rightarrow Zr(4d\pi)$ donation from the trigonal planar sp^2-hybridized N_{amide} atoms). Such $M\cdots C_{ipso}$ interactions are well-known in early transition metal chemistry.[13] It appears that steric factors favor the formation of the $Zr\cdots C_{ipso}$ interaction approximately *trans* to pyridyl nitrogen as opposed to the analogous position approximately *trans* to the apical nitrogen N(4) since the amide $SiMe_3$ substituents are slightly oriented "up" toward this site.

Scheme 2. Synthesis of Cationic Zirconium Complexes of N_2NN' (anions omitted for clarity)



Group 4 complexes of polydentate amide ligands are important in the polymerization of olefins.[2b,3a,f,h,l,n,y,z] Regrettably, attempts to polymerize ethylene (5 bar pressure, toluene solvent) using $ZrX_2(N_2NN')$ (X = Cl (**1**) or Me (**2**)) with methyl aluminoxane or (for **2**) BAr^F_3 ($Ar^F = C_6F_5$) or $[CPh_3][BAr^F_4]$ yielded no activity. Cationic alkyl cations are accepted as being the active species in group 4 olefin polymerization catalysts,[2b,14] and so we were interested to see if the N_2NN' ligand could be used for the stoichiometric generation of such species, despite the lack of catalytic activity. Scheme 2 shows the reactions of **2** or $ZrCl(CH_2Ph)(N_2NN')$ (**6**) with BAr^F_3. Analogous NMR tube scale experiments were carried out using $[CPh_3][BAr^F_4]$ and yielded the same cations.

Reaction of **2** in benzene with BAr^F_3 gave $[Zr\{(2\text{-}NC_5H_4)CH_2N(CH_2CH_2NSiMe_3)(CH_2CH_2NSiMe_2CH_2-)\}][MeBAr^F_3]$ (**10**-$MeBAr^F_3$) as a white solid in 60% yield. The cation $\mathbf{10}^+$ was unambiguously identified by NMR spectroscopy (see the Experimental Section) as the C–H bond activation product illustrated in Scheme 2 in which one of the $SiMe_3$ groups of N_2NN' has been metalated. This presumably occurs via a σ-bond metathesis reaction with the Zr-Me group of the transient $[ZrMe(N_2NN')]^+$ cation $\mathbf{11}^+$ (Scheme 2), which is isoelectronic with the structurally characterized scandium alkyl $Sc(CH_2SiMe_3)(N_2NN')$ (Chart 1) reported by us previously.[10d] Evidence for the postulated intermediate five-coordinate cation $\mathbf{11}^+$ was obtained by reacting **2** with BAr^F_3 in the presence of an excess of THF, which afforded [ZrMe-

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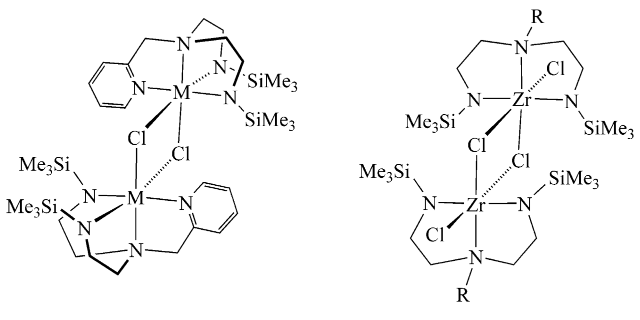
Chart 2



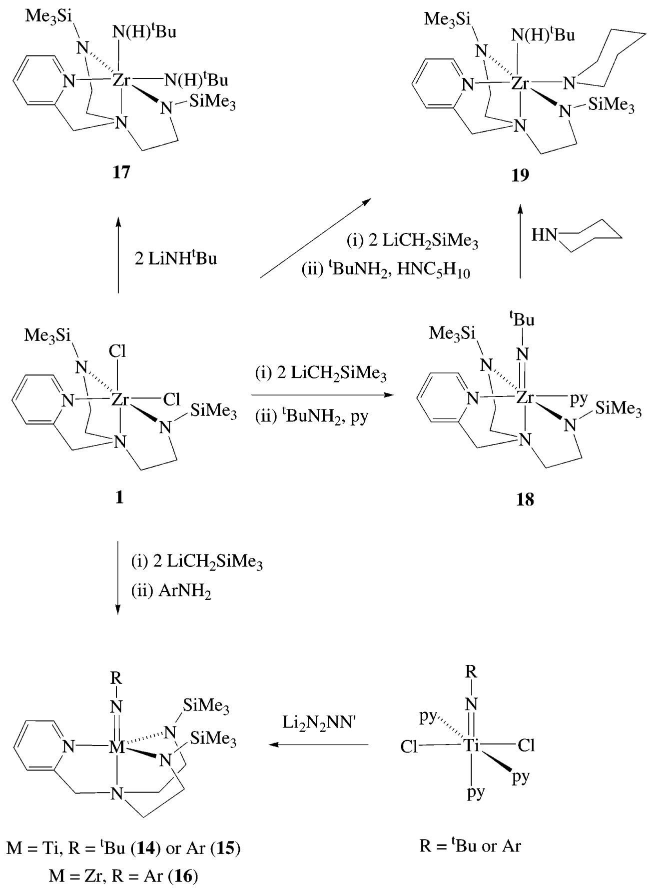
I (M = Y or Sm) **II** (R = $SiMe_3$ or Me)

(THF)(N_2NN')][$MeBAr^F{}_3$] (**12**-$MeBAr^F{}_3$) in quantitative yield (Scheme 2). Cation $\mathbf{12}^+$ is stable for days at room temperature in CD_2Cl_2 solution.

When the reaction between **2** and $BAr^F{}_3$ was followed by NMR (C_6D_6), an additional singlet was observed at ca. 0.8 ppm, which is assigned to CH_4, the expected side-product of σ-bond metathesis. The cyclometalated cation $\mathbf{10}^+$ is also formed in the reaction of $Zr(CH_2Ph)_2(N_2NN')$ with $BAr^F{}_3$ (NMR tube scale reaction) along with 1 equiv of toluene and the anion $[PhCH_2BAr^F{}_3]^-$. This reaction presumably occurs via a transient mono(benzyl) cation $[Zr(CH_2Ph)(N_2NN')]^+$. The $[RBAr^F{}_3]^-$ (R = Me or $PhCH_2$) anions appear to be noncoordinating according to the ^1H and ^{19}F NMR spectra.[3y,15] The intramolecular C−H bond activation leading to $\mathbf{10}^+$ is well precedented in the chemistry of polydentate silylamido ligands, including cationic alkyl zirconium derivatives.[3y,16] Such reactions have previously been identified as catalyst deactivation pathways,[17] although stable zirconium alkyl cations can be formed with silylated polyamide ligands by careful choice of ligand backbone.[3a] The ready formation of the four-membered zirconocyclic ring in $\mathbf{10}^+$ accounts for the lack of catalytic activity of **2**. Exposure of CD_2Cl_2 solutions of $\mathbf{10}^+$ to ethylene (1 atm) gave only a slow consumption (several days) of the cation and the formation a small quantity of white precipitate (presumably polyethylene). Attempted scale-up of this reaction, however, afforded no isolable polymer.

A chloride analogue of $\mathbf{11}^+$ was prepared by the reaction of $ZrCl(CH_2Ph)(N_2NN')$ (**6**) with $BAr^F{}_3$, which gave [$ZrCl(N_2NN')$][$PhCH_2BAr^F{}_3$] (**13**-$PhCH_2BAr^F{}_3$) as a white solid. The ^1H and ^{19}F NMR spectra are consistent with a noncoordinating $[PhCH_2BAr^F{}_3]^-$ anion. It was not possible to obtain diffraction-quality crystals of **13**-$PhCH_2BAr^F{}_3$. We recently[10c,18] found than the isoelectronic yttrium and samarium complexes $M_2(\mu\text{-}Cl)_2(N_2NN')_2$ exist as chloride-bridged dimers in the solid state with the structures illustrated in Chart 2. Likewise, the related diamide-amine compounds $Zr_2Cl_2(\mu\text{-}Cl)_2\{RN(CH_2CH_2SiMe_3)_2\}_2$ (**II**, R = $SiMe_3$[3x] or Me[3a]) form chloride-bridged dimers. The N_2NN'-supported dimers **I** possess no plane of symmetry, and the N_2NN' $SiMe_3$ groups occupy chemically inequivalent sites. The NMR spectrum of **13**-$PhCH_2BAr^F{}_3$ in CD_2Cl_2 at 20 °C indicated C_s symmetry for the N_2NN' cation resonances (e.g., equivalent $SiMe_3$ groups). This is consistent with the monomeric structure illustrated for $\mathbf{13}^+$ in Scheme 2 or a dimeric, dicationic compound with C_s symmetry. Cooling a sample of **13**-$PhCH_2BAr^F{}_3$ in CD_2Cl_2 to −90 °C led to broadening of the ^1H NMR (500 MHz) N_2NN' resonances, while those for the anion remained sharp. Unfortunately a well-defined low-temperature limiting spectrum could not be obtained. It is therefore possible that $\mathbf{13}^+$ may be dimeric in solution, at least at low temperature, but even at −90 °C is rather fluxional. This lability is attributable to repulsive effects of the positively charged Zr centers.

Scheme 3. Synthesis of Group 4 imido and Bis(amide) Complexes of N_2NN'



Imido Complexes of N_2NN'. There is a rich and diverse chemistry associated with early transition metal imido compounds supported by the tridentate diamide-amine ligands $Me_3SiN(CH_2CH_2SiMe_3)_2$ and (2-C_5H_4N)-$C(Me)(CH_2NSiMe_3)_2$[1f,3b,d,12,19] and their analogues.[1a] Scheme 3 summarizes the synthesis of titanium and zirconium terminal imido and related compounds using N_2NN'.

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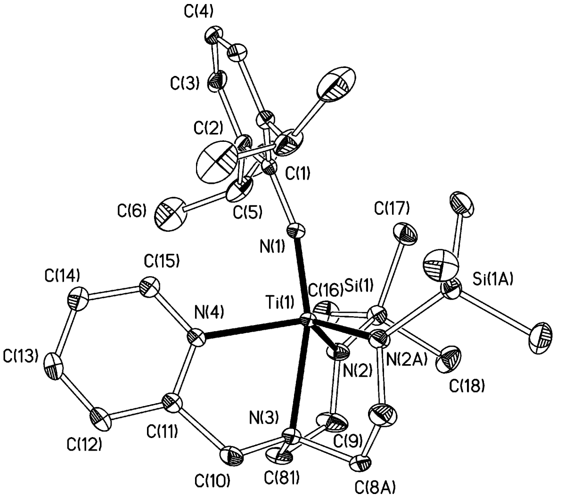

Figure 3. Displacement ellipsoid plot (25% probability) of Ti(NAr)(N$_2$NN′) (**15**). H atoms omitted for clarity. Atoms carrying the suffix 'A' are related to their counterparts by the symmetry operator [*x*, *y*, $^3/_2 - z$].

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Ti(NAr)(N$_2$NN′) (15)[a]

Ti(1)−N(1)	1.769(2)	Ti(1)−N(3)	2.291(2)
Ti(1)−N(2)	1.992(1)	Ti(1)−N(4)	2.227(2)
N(1)−Ti(1)−N(2)	108.35(4)	N(1)−Ti(1)−N(4)	92.13(7)
N(2)−Ti(1)−N(2A)	112.67(8)	N(2)−Ti(1)−N(4)	116.38(4)
N(1)−Ti(1)−N(3)	163.77(7)	N(3)−Ti(1)−N(4)	71.64(6)
N(2)−Ti(1)−N(3)	79.94(4)	Ti(1)−N(1)−C(1)	164.9(1)

[a] Atoms carrying the suffix 'A' are related to their counterparts by the symmetry operator [*x*, *y*, $^3/_2 - z$].

We have shown previously[20] that the readily prepared compounds Ti(NR)Cl$_2$(py)$_3$[21] are useful reagents in the synthesis of new titanium imido compounds. Reaction of Ti(N^{t}Bu)Cl$_2$(py)$_3$ or Ti(NAr)Cl$_2$(py)$_3$ (Ar = 2,6-C$_6$H$_3$^{i}-Pr$_2$) with Li$_2$N$_2$NN′ in benzene gave the five-coordinate imido complexes Ti(NR)(N$_2$NN′) (R = ^{t}Bu (**14**) or Ar (**15**)) in ca. 60% isolated yield. The NMR spectra were consistent with the C_s symmetric structures illustrated in Scheme 3 and confirmed by X-ray diffraction for **15** as shown in Figure 3. Selected bond distances and angles are listed in Table 3.

Molecules of **15** lie across crystallographic mirror planes that pass through the atoms Ti(1), N(1), N(3), and N(4). Disorder associated with the methylene linkages about N(3) was satisfactorily modeled. The geometry at Ti(1) is distorted trigonal bipyramidal with N(1) and N(3) occupying the apical positions. The Ti(1)−N(1)−C(1) angle of 164.9(1)° is typical for a formally "linear" imido group with N(1) being formally sp hybridized and, in principle, capable of acting as a four-electron donor. The bonding in related diamide-donor supported trigonal bipyramidal imido complexes has been analyzed in detail recently, as discussed below.[12] The Ti−N$_{amine}$ and Ti−N$_{amide}$ distances are within the usual ranges for such linkages,[22] whereas Ti(1)−N(1) is rather long at 1.769(2) Å. The range for terminal Ti=NAr bonds in the Cambridge Structural Database[22] is 1.697(7)−1.756(5) Å (av 1.727 Å for 20 examples). The long Ti=NAr bond in **15** is attributed to steric repulsions between the Ar and SiMe$_3$ groups.

Titanium and zirconium imido complexes M(NR)(py)(N$_2$N′) (N$_2$N′ = Me$_3$SiN(CH$_2$CH$_2$SiMe$_3$)$_2$[19c] or (2-C$_5$H$_4$N)C(Me)(CH$_2$NSiMe$_3$)$_2$[23]) related to **15** have been structurally characterized previously. In these trigonal bipyramidal complexes the imido and amido ligands all occupy the *equatorial* coordination sites while the neutral donors lie in the axial positions. An analogous geometry was found for the tantalum *tert*-butyl imido complex Ta(N^{t}Bu)Me{(2-C$_5$H$_4$N)C(Me)(CH$_2$NSiMe$_3$)$_2$}. However, the isoelectronic phenyl imido cation [W(NPh)Me{(2-C$_5$H$_4$N)C(Me)(CH$_2$NSiMe$_3$)$_2$}]$^+$ had a trigonal pyramidal geometry with equatorial amido groups but an *axial* imido ligand.[12] DFT calculations on model complexes M(NR)(X){HC(2-C$_5$H$_4$N)(CH$_2$SiH$_3$)$_2$} showed an unambiguous electronic preference for the imido ligand to occupy the axial sites (thereby allowing for optimal π-donation from the amido and imido nitrogens).[12] However, inclusion of significant steric bulk on the N atoms was shown to invert the site preference. The geometry found for **15** is therefore the electronically preferred one, i.e., with an axial imido ligand. However, this is clearly associated with unfavorable steric repulsion, which cannot be relieved due to the enforcing nature of the tetradentate N$_2$NN′ ligand.

Zirconium imido complexes of N$_2$NN′ have also been prepared (Scheme 3). Reaction of Li$_2$N$_2$NN′ with the imido synthon Zr$_2$(μ-NAr)$_2$Cl$_4$(THF)$_4$[24] in a manner analogous to that used for **14** and **15** gave a complex mixture of products. However, reaction of in situ generated Zr(CH$_2$SiMe$_3$)$_2$(N$_2$NN′) (**4**) with ArNH$_2$ (1 equiv) afforded the target imido compound Zr(NAr)(N$_2$NN′) (**16**) as an orange, sparingly soluble solid in low yield. The corresponding NMR tube scale reaction in C$_6$D$_6$ identified SiMe$_4$ as the expected side-product. Weakly diffracting crystals of **16** were found to have a unit cell very similar to that of **15**, but the diffraction data were too weak for a satisfactory refinement to be carried out. Nonetheless, on the basis of the available data it is likely that **16** has the five-coordinate monomeric structure shown in Scheme 3.

Attempts to prepare a *tert*-butyl imido compound by reaction of ZrCl$_2$(N$_2$NN′) **1** with 2 equiv of LiNH^{t}Bu gave the six-coordinate bis(*tert*-butyl amide) complex **17** in 49% yield. The compound does not eliminate ^{t}BuNH$_2$ on heating at 70 °C for extended periods in C$_6$D$_6$ either on its own or in the presence of pyridine. Reaction of ZrMe$_2$(N$_2$NN′) (**2**) with ^{t}BuNH$_2$ (1 equiv) in C$_6$D$_6$ in a manner akin to that employed for **16** gave only **17** (ca. 30% yield based on **2**, the remainder remaining unreacted) after 24 h. The corresponding reaction of in situ generated **4** also failed to produce an imido complex. Analogous results have been found previously in the reactions of zirconium dichloride or dialkyl compounds with less sterically demanding lithiated amides or

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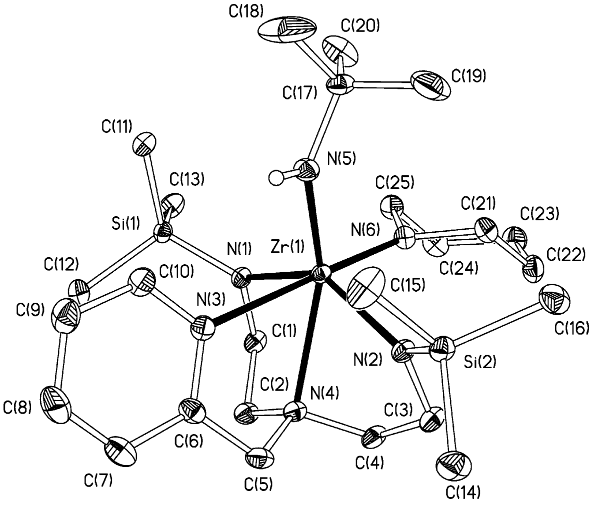


Figure 4. Displacement ellipsoid plot (25% probability) of $Zr(NH^tBu)(NC_5H_{10})(N_2NN')$ (**19**). C-bound H atoms omitted for clarity. H atom bound to N(5) drawn as a sphere of arbitrary radius.

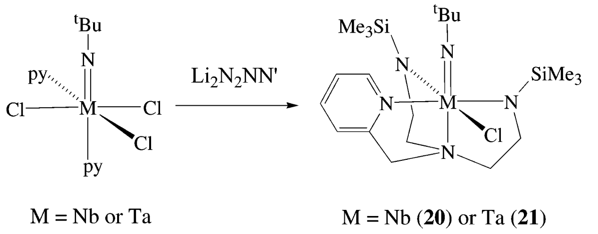
primary amines.[25] However, when the reaction between **4** and $^tBuNH_2$ (1 equiv) was carried out in the presence of pyridine, the dark red, six-coordinate imido complex $Zr(N^tBu)(py)(N_2NN')$ (**18**) was obtained in 73% yield. The C_s symmetrical structure proposed for **18** in Scheme 3 is based on the available NMR data (e.g., equivalent $SiMe_3$ groups). The presence of coordinated pyridine is also clearly indicated by the NMR data, and NOE experiments established the relative arrangements of the N^tBu, N_2NN', and pyridine ligands.

Although the use of pyridine in **18** allows access to this terminal imido compound, it still reacts readily with primary amines to form tetrakis(amido) derivatives. Thus addition of $^tBuNH_2$ (1 equiv) to a C_6D_6 solution of **18** quantitatively afforded **17** and free pyridine. This type of reaction has been seen previously for zirconium imido compounds.[25a,26] An analogous reaction between **18** and piperidine gave the mixed amide complex $Zr(NH^tBu)(NC_5H_{10})(N_2NN')$ (**19**) as the single isomer illustrated in Scheme 3 and confirmed by X-ray crystallography (see below). Compound **19** was made on a preparative scale in 52% yield from the "one-pot" reaction of in situ generated **4** with $^tBuNH_2$, piperidine, and pyridine.

The molecular structure of **19** is shown in Figure 4, and selected bond distances and angles are listed in Table 4. The overall geometry is analogous to that found for $ZrX_2(N_2NN')$ (X = Cl, NMe_2,[10b] CH_2Ph (**3**, Figure 1), and $ZrCl(CH_2Ph)(N_2NN')$ (**6**, Figure 2)). The N-*H* atom of the ^tBuNH ligand was found from a Fourier difference map and positionally and isotropically refined. The Zr(1)−N(1) and Zr(1)−N(2) distances are experimentally identical to the corresponding distances in $Zr(NMe_2)_2(N_2NN')$.[10b] Zr(1)−N(5) is marginally shorter than Zr(1)−N(6) (Δ = 0.016(3) Å), and both of these distances are shorter than those to N(1) and N(2). The trends in $Zr-N_{amide}$ distances is the same as in $Zr(NMe_2)_2(N_2NN')$. As proposed previously,[10b] the relative orientation of the substituents at the trigonal planar (sp^2 hybridized) atoms N(5) and N(6) can be rationalized in terms of maximizing $N(2p_\pi) \rightarrow Zr(4d_\pi)$ donation.[10b]

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $Zr(NH^tBu)(NC_5H_{10})(N_2NN')$ (19)

Zr(1)−N(1)	2.160(1)	Zr(1)−N(4)	2.452(1)
Zr(1)−N(2)	2.168(1)	Zr(1)−N(5)	2.075(2)
Zr(1)−N(3)	2.520(2)	Zr(1)−N(6)	2.091(2)
N(1)−Zr(1)−N(2)	141.83(6)	N(3)−Zr(1)−N(5)	83.45(6)
N(1)−Zr(1)−N(3)	84.02(5)	N(4)−Zr(1)−N(5)	150.14(6)
N(2)−Zr(1)−N(3)	88.59(5)	N(1)−Zr(1)−N(6)	90.53(6)
N(1)−Zr(1)−N(4)	73.40(5)	N(2)−Zr(1)−N(6)	94.20(6)
N(2)−Zr(1)−N(4)	69.18(5)	N(3)−Zr(1)−N(6)	174.01(6)
N(3)−Zr(1)−N(4)	67.63(5)	N(4)−Zr(1)−N(6)	108.45(6)
N(1)−Zr(1)−N(5)	112.04(6)	N(5)−Zr(1)−N(6)	100.96(7)
N(2)−Zr(1)−N(5)	104.17(6)		



(1)

We have previously reported[19b] the synthesis and solid-state structures of the group 5 diamide-donor supported imido compounds $M(NR)Cl\{(2\text{-}C_5H_4N)C(Me)(CH_2NSiMe_3)_2\}$ (M = Nb or Ta; R = ^tBu or Ar), which were prepared from $Li_2[(2\text{-}C_5H_4N)C(Me)(CH_2NSiMe_3)_2]$ and the appropriate imido reagent $M(NR)Cl_3(py)_2$.[27] In contrast, reaction between $Li_2[Me_3SiN(CH_2CH_2NSiMe_3)_2]$ and $Nb(N^tBu)Cl_3(py)_2$ gave a mixture of diamide-amine ligand degradation and ill-defined dimeric imido compounds. For the purposes of comparison with these previous studies and the new N_2NN'-supported imido chemistry described in Scheme 3 we carried out the reactions summarized in eq 1.

Reaction of Li_2N_2NN' with $M(N^tBu)Cl_3(py)_2$ in benzene followed by crystallization from pentane afforded the six-coordinate imido complexes $M(N^tBu)Cl(N_2NN')$ (M = Nb (**20**) or Ta (**21**)) as yellow or brown solids in ca. 30% isolated yield (eq 1). The low isolated yield is attributed to the rather high solubility of these compounds in pentane since the NMR tube scale reactions (C_6D_6) were quantitative. The NMR spectra for the two compounds were virtually identical and support the C_1 symmetrical structures illustrated in eq 1 (e.g., inequivalent $SiMe_3$ groups and 10 independent multiplet resonances (each of relative integration 1 H for the methylene hydrogens). The solid-state structure of **21** is shown in Figure 5, and selected bond distances and angles are listed in Table 5. There are two crystallographically independent molecules of **21** in the asymmetric unit but no substantial differences between them.

The structure of **21** in the solid state agrees with that assigned on the basis of the solution NMR data. The geometry at Ta(1) is approximately octahedral, and the metal−ligand distances are within previously reported ranges.[22] It is of particular interest to compare this structure with that of $Ta(N^tBu)Cl\{(2\text{-}C_5H_4N)C(Me)(CH_2NSiMe_3)_2\}$,[19b] in which the imide and amide donors are

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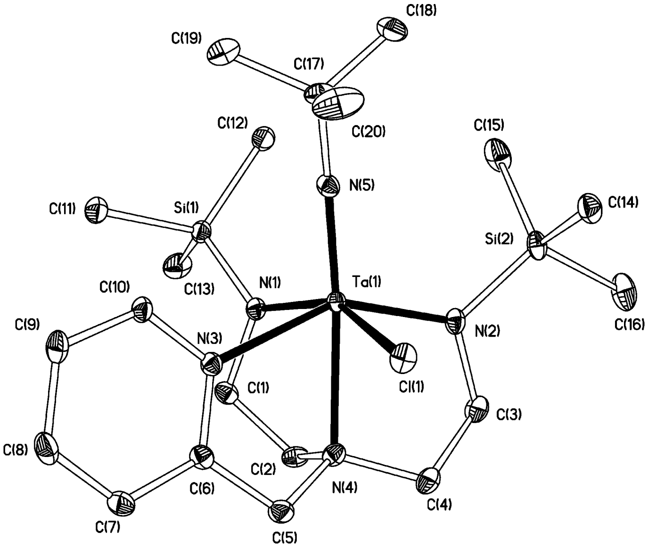


Figure 5. Displacement ellipsoid plot (25% probability) of one of the two crystallographically independent molecules of Ta(N^{t}Bu)Cl(N$_2$NN′) (**21**). H atoms omitted for clarity.

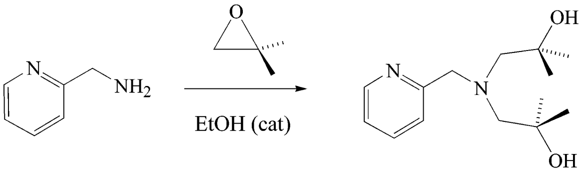
Table 5. Selected Bond Lengths (Å) and Angles (deg) for Ta(N^{t}Bu)Cl(N$_2$NN′) (21)^a

Ta(1)−Cl(1)	2.5500(9)	[2.515(1)]
Ta(1)−N(1)	2.055(3)	[2.055(3)]
Ta(1)−N(2)	2.029(3)	[2.034(3)]
Ta(1)−N(3)	2.274(3)	[2.309(3)]
Ta(1)−N(4)	2.363(3)	[2.379(3)]
Ta(1)−N(5)	1.783(3)	[1.791(3)]
Cl(1)−Ta(1)−N(1)	153.77(9)	[153.48(9)]
Cl(1)−Ta(1)−N(2)	88.88(9)	[90.4(1)]
N(1)−Ta(1)−N(2)	104.0(1)	[103.6(1)]
Cl(1)−Ta(1)−N(3)	75.30(8)	[75.09(8)]
N(1)−Ta(1)−N(3)	82.0(1)	[81.2(1)]
N(2)−Ta(1)−N(3)	147.5(1)	[146.9(1)]
Cl(1)−Ta(1)−N(4)	82.17(8)	[83.03(8)]
N(1)−Ta(1)−N(4)	78.4(1)	[77.9(1)]
N(2)−Ta(1)−N(4)	78.2(1)	[78.4(1)]
N(3)−Ta(1)−N(4)	71.7(1)	[70.5(1)]
Cl(1)−Ta(1)−N(5)	93.8(1)	[93.4(1)]
N(1)−Ta(1)−N(5)	103.3(1)	[103.7(1)]
N(2)−Ta(1)−N(5)	108.4(1)	[106.9(1)]
N(3)−Ta(1)−N(5)	101.0(1)	[103.6(1)]
N(4)−Ta(1)−N(5)	172.3(1)	[173.7(1)]
Ta(1)−N(5)−C(17)	165.5(3)	[165.0(3)]

[a] Values in brackets are for the other crystallographically independent molecule in the asymmetric unit.

also all *cis* to one another. The Ta−Cl, Ta−N$_{amine}$, and Ta−Cl distances in **21** and Ta(N^{t}Bu)Cl{(2-C$_5$H$_4$N)C(Me)(CH$_2$NSiMe$_3$)$_2$} are very similar. In contrast, the Ta=N^{t}Bu distances in **21** (1.783(3) and 1.791(3) Å) are somewhat shorter than in the previous compound (1.822(4) Å). It is not clear why **20** and **21** adopt nonsymmetrical structures while all the zirconium compounds [Zr(A)(B)(N$_2$NN′)]$^{n+}$ described above with two different coligands A and B (i.e., **6**, **7**, **8**, **12**$^+$, **19**, and (especially) **18**) have C_s symmetry.

Group 4 Complexes of O$_2$NN′. In a previous paper[10b] on the zirconium and hafnium complexes MX$_2$(N$_2$NN′) (X = Cl or NMe$_2$) we described how we had been unable to prepare six-coordinate titanium analogues TiX$_2$(N$_2$NN′). This was tentatively attributed to the possible difficulties in placing six ligands around Ti at the shorter metal−ligand bond lengths required for this 3d metal. The instability of the zirconium complexes Zr(CH$_2$R)$_2$(N$_2$NN′) (R = SiMe$_3$ (**4**) or CMe$_3$ (**5**)) may also stem from increased crowding in these silylamido systems. To test these ideas, we have developed a bis(alkoxide) analogue of N$_2$NN′, namely, O$_2$NN′ (O$_2$NN′ = (2-C$_5$H$_4$N)CH$_2$N(CH$_2$CMe$_2$O)$_2$), in which the NSiMe$_3$ group is replaced by O. Polydentate ligands with two anionic oxygen donors are extremely well established in early transition metal chemistry,[4−6,8] as are the related phenoxide-imine ligands (monoanionic N,O donors).[7] Interestingly, although dianionic O$_2$N$_2$ donor atom ligands with phenoxide groups are very well established in group 4,[5−6,8] the corresponding bis(alkoxide)-diamine systems are underdeveloped (tridentate O$_2$N donor bis(alkoxide)-monoamine ligand systems are, however, better known[9]).



(2)

H$_2$O$_2$NN′ (**22**)

Our initial efforts focused on the known[28] protio ligand (2-C$_5$H$_4$N)CH$_2$N(CH$_2$CH$_2$OH)$_2$ used previously in vanadium[28a] and nickel chemistry.[28b] However, reaction of this with a number of titanium and zirconium precursors of the type MX$_2$R$_2$ (X or R = alkyl, halide, or NMe$_2$) gave rather insoluble and intractable products. Reasoning that the O atoms in (2-C$_5$H$_4$N)CH$_2$N(CH$_2$CH$_2$OH)$_2$ are too sterically unprotected, we moved our attention to the new ligand system O$_2$NN′, in which a *gem*-dimethyl group is positioned next to each O (making the ligand a little like a bis(*tert*-butoxide) system). The protio ligand H$_2$O$_2$NN′ (**22**) was prepared from 2-aminomethyl pyridine and isobutylene oxide in the presence of a catalytic quantity of ethanol (eq 2) and isolated as a white powder in ca. 50% yield after column chromatography and high-vacuum sublimation.

H$_2$O$_2$NN′ (**22**) was structurally characterized. The molecular structure is shown in Figure 6, and selected intra- and intermolecular distances are listed in Table 6. The associated distances and angles are within the usual ranges.[22] The O-bound H atoms were located from Fourier difference maps and positionally refined. Molecules of H$_2$O$_2$NN′ form eight-membered intramolecular hydrogen-bonded rings (via O(1)−H(1)···O(2)), and each H$_2$O$_2$NN′ is part of a supramolecular chain motif propagating along the crystallographic *b* axis via hydrogen bonds between O(1) of one molecule and H(2) of its neighbor. Neither N atom is involved in a supramolecular interaction. The ^{1}H NMR spectrum of H$_2$O$_2$NN′ in CD$_2$Cl$_2$ at 20 °C showed (in addition to pyridyl and O*H* signals) resonances for a single methyl group environment (relative integral 12 H) and two methylene environments (2 and 4 H for (2-C$_5$H$_4$N)C*H*$_2$N and N(C*H*$_2$Me$_2$OH)$_2$, respectively), indicating that no intramolecular order is maintained (at least on the NMR time scale) at this temperature. Cooling to −90 °C led to significant broadening of the N(C*H*$_2$Me$_2$OH)$_2$ meth-

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[28] (a) Crans, D. C.; Keramidas, A. D.; Amin, S. S.; Anderson, O. P.; Miller, S. M. *J. Chem. Soc., Dalton. Trans.* **1997**, 2799. (b) Saalfrank, R. W.; Bernt, I.; Hampel, F. *Chem. Eur. J.* **2001**, *7*, 2770.

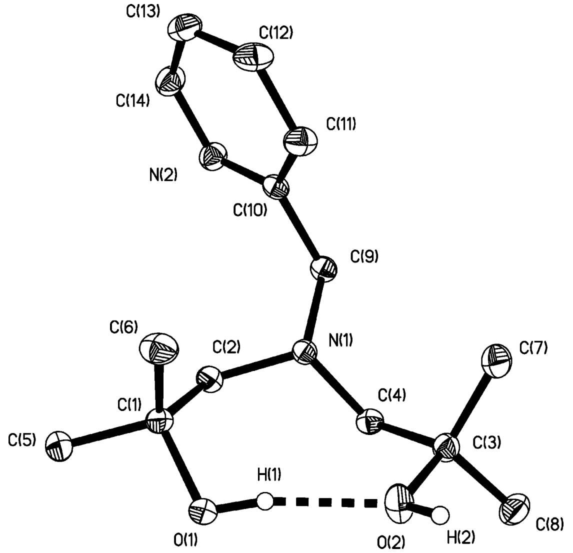


Figure 6. Displacement ellipsoid plot (25% probability) of H_2O_2NN' (**22**). C-bound H atoms omitted for clarity. H atoms bound to O drawn as spheres of arbitrary radius.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for H_2O_2NN' (22)[a]

N(1)−C(2)	1.469(2)	N(1)−C(4)	1.473(2)
N(1)−C(9)	1.470(2)	N(2)−C(10)	1.339(2)
N(2)−C(14)	1.347(2)	O(1)−C(1)	1.438(2)
O(1)−H(1)	0.88(2)	O(1)···H(2A)	1.88(2)
O(2)−C(3)	1.440(2)	O(2)···H(1)	1.83(2)
O(2)−H(2)	0.88(2)		
C(2)−N(1)−C(4)	114.2(1)	C(2)−N(1)−C(9)	111.9(1)
C(4)−N(1)−C(9)	110.5(1)	C(10)−N(2)−C(14)	117.39(13)
C(1)−O(1)−H(1)	109.0(12)	C(1)−O(1)−H(2A)	128.7(6)
H(1)−O(1)−H(2A)	102.5(14)	C(3)−O(2)−H(2)	110.4(13)
O(1)−H(1)···O(2)	167(2)	O(1B)···H(2)−O(2)	169(2)

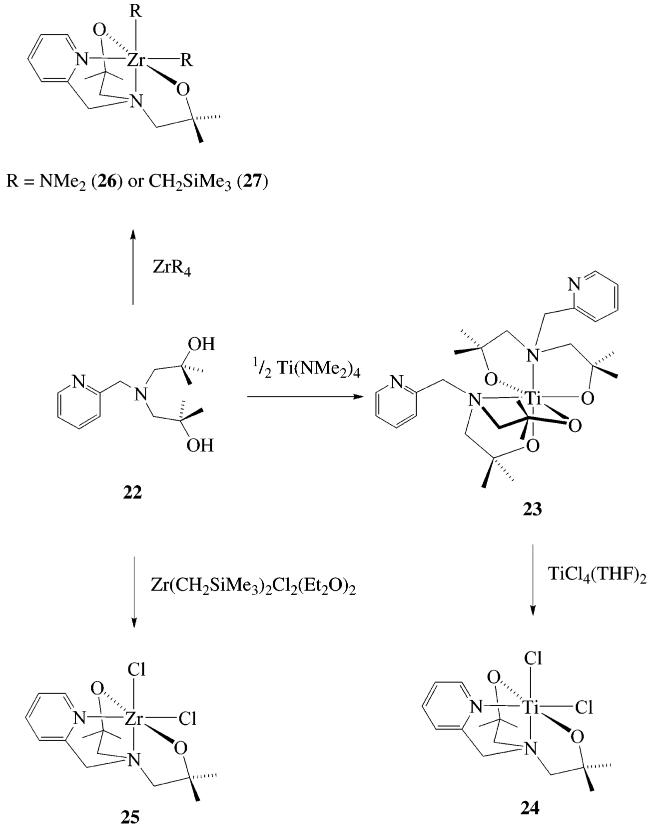
[a] Atoms carrying the suffixes 'A' and 'B' are related to their counterparts by the symmetry operator $[^3/_2 - x, y + {}^1/_2, {}^3/_2 - z]$ and $[^3/_2 - x, y - {}^1/_2, {}^3/_2 - z]$, respectively.

ylene signal and splitting of the $N(CH_2Me_2OH)_2$ methyl resonance to two broad resonances, each of relative integral 6 H. This is consistent with a greater degree of ordering of the intramolecular H bonding at low temperature.

Attempts to prepare Li_2O_2NN' or other alkali metal bis(alkoxide) salts by reaction of H_2O_2NN' with ^nBuLi, MeLi, NaH, or KH gave decomposition products, and so all complexation reactions needed to take place using only the protio ligand. The synthesis and proposed structures of the new neutral organometallic and coordination complexes of O_2NN' are shown in Scheme 4.

Reaction of $Ti(NMe_2)_4$ with H_2O_2NN' (1 equiv) gave ca. 50% conversion to the white homoleptic compound $Ti(O_2NN')_2$ (**23**) with ca. 50% of the $Ti(NMe_2)_4$ remaining unreacted. The preference for formation of **23** over the desired product $Ti(NMe_2)_2(O_2NN')$ persisted regardless of the method of addition, solvent, or reaction conditions. Reaction of $Ti(NMe_2)_4$ with H_2O_2NN' (2 equiv) gave **23** in ca. 80% isolated yield. Compound **23** is fluxional at room temperature, giving rise to broad NMR spectra. On cooling to −80 °C, a sharp, low-temperature limit ^1H spectrum was obtained which is consistent with the C_2 symmetric structure (equivalent O_2NN' ligands) illustrated in Scheme 4. The two CH_2CMe_2O "arms" of each ligand are inequivalent, and the methylene H atoms and CMe_2 methyl groups of each are also inequivalent. The shifts of the pyridyl group are rather similar to those in H_2O_2NN' itself, suggesting that it is not coordinated. The structure proposed for **23** is analogous to that found by X-ray diffraction for the homologous bis(alkoxide)-methylamine complex $Ti\{MeN(CH_2CH_2O)_2\}_2$, isolated from the reaction of amorphous α-titanic acid with $MeN(CH_2CH_2OH)_2$.[9i]

Scheme 4. Synthesis of Group 4 Dichloride, Bis(amide), and Dialkyl Complexes of O_2NN'



The redistribution reaction between **23** and $TiCl_4(THF)_2$ in benzene gave the sparingly soluble dichloride complex $TiCl_2(O_2NN')$ (**24**) as a white solid in 90% isolated yield. The NMR spectrum of **24** shows C_s symmetry with equivalent "arms" (featuring diastereotopic CH_2 and CMe_2 groups as expected). The EI mass spectrum of **24** showed a parent ion with the appropriate isotope distribution. The zirconium analogue of **24** was prepared in a similar way to that used for $ZrCl_2(N_2NN')$ (**1**), namely, by reaction of the protio ligand with $ZrCl_2(CH_2SiMe_3)_2(Et_2O)_2$.[29] The compound $ZrCl_2(O_2NN')$ (**25**) was isolated in 52% yield, and the NMR and other data were analogous to those of **24**. Protonolysis routes were also used for the synthesis of $Zr(NMe_2)_2(O_2NN')$ (**26**) and $Zr(CH_2SiMe_3)_2(O_2NN')$ (**27**) from $Zr(NMe_2)_4$ and $Zr(CH_2SiMe_3)_4$, respectively. The expected side products $SiMe_4$ and $HNMe_2$ were identified in NMR tube scale experiments. In contrast to $Zr(CH_2SiMe_3)_2(N_2NN')$ (**4**), which decomposes at room temperature over several hours, the dialkyl compound **27** appears to be indefinitely stable in solution at room temperature and has been crystallographically characterized. The molecular structure is shown in Figure 7, and selected bond

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(29) Brand, H.; Capriotti, J. A.; Arnold, J. *Organometallics* **1994**, *13*, 4469.

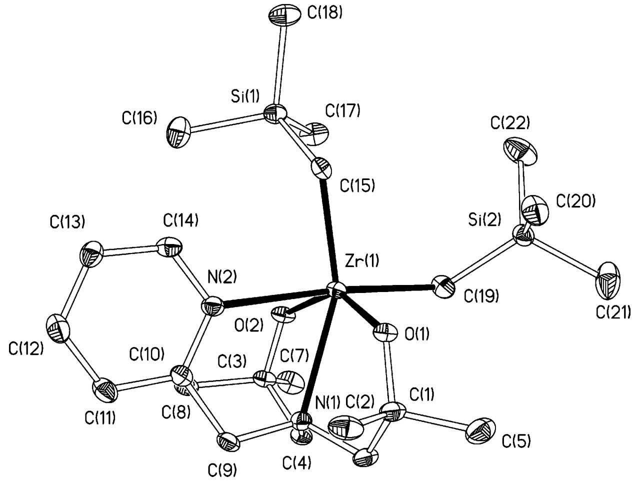


Figure 7. Displacement ellipsoid plot (30% probability) of one of the two crystallographically independent molecules of $Zr(CH_2SiMe_3)_2(O_2NN')$ (**27**). H atoms omitted for clarity.

Table 7. Selected Bond Lengths (Å) and Angles (deg) for $Zr(CH_2SiMe_3)_2(O_2NN')$ (27)[a]

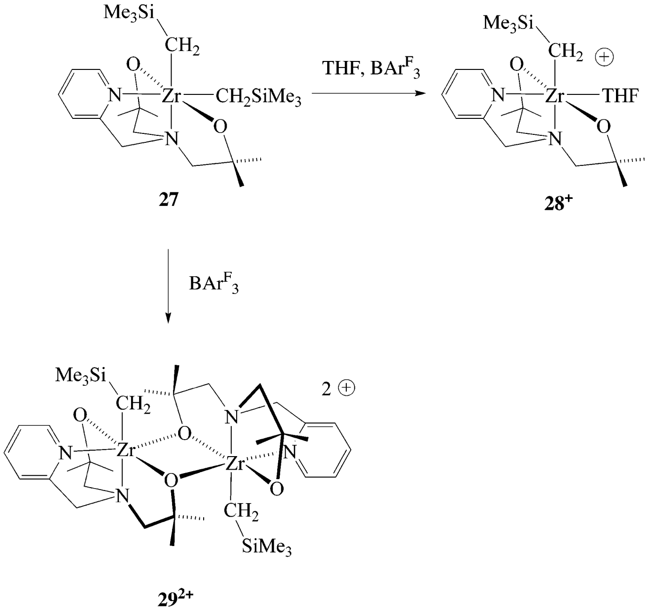
Zr(1)−N(1)	2.482(3)	[2.479(3)]
Zr(1)−N(2)	2.514(3)	[2.516(3)]
Zr(1)−O(1)	1.983(3)	[1.981(3)]
Zr(1)−O(2)	1.985(3)	[1.978(3)]
Zr(1)−C(15)	2.261(4)	[2.271(4)]
Zr(1)−C(19)	2.295(4)	[2.293(4)]
N(1)−Zr(1)−N(2)	68.30(11)	[68.3(1)]
N(1)−Zr(1)−O(1)	72.03(11)	[72.22(11)]
N(2)−Zr(1)−O(1)	85.66(11)	[81.95(11)]
N(1)−Zr(1)−O(2)	71.98(11)	[72.01(11)]
N(2)−Zr(1)−O(2)	85.49(11)	[88.60(11)]
O(1)−Zr(1)−O(2)	143.69(11)	[144.00(11)]
N(1)−Zr(1)−C(15)	154.25(13)	[154.70(13)]
N(2)−Zr(1)−C(15)	85.96(13)	[86.77(13)]
O(1)−Zr(1)−C(15)	106.95(13)	[109.61(13)]
O(2)−Zr(1)−C(15)	107.44(13)	[104.39(13)]
N(1)−Zr(1)−C(19)	106.69(13)	[102.76(14)]
N(2)−Zr(1)−C(19)	174.77(14)	[170.52(14)]
O(1)−Zr(1)−C(19)	91.35(14)	[92.45(14)]
O(2)−Zr(1)−C(19)	94.45(14)	[91.53(14)]
C(15)−Zr(1)−C(19)	99.03(15)	[102.37(16)]
Zr(1)−C(15)−Si(1)	124.0(2)	[120.9(2)]
Zr(1)−C(19)−Si(2)	124.7(2)	[125.8(2)]
Zr(1)−O(1)−C(1)	130.5(2)	[130.7(2)]
Zr(1)−O(2)−C(3)	129.9(2)	[129.7(2)]

[a] The values in brackets are for the other crystallographically independent molecule in the asymmetric unit.

distances and angles are listed in Table 7. There are two crystallographically independent molecules of **27** in the asymmetric unit with no substantial differences between them.

Molecules of **27** have approximately octahedral metal centers with Zr−N, −O, and −C distances within the usual ranges.[22] The overall coordination environment is analogous to both the previously described bis(phenolate)-diamine complexes $ZrX_2\{(2\text{-}C_5H_4N)CH_2N(2\text{-}O\text{-}3,5\text{-}C_6H_2R_2)_2\}$ (X = Cl, NMe_2, alkyl; R = ^{t}Bu or Me)[8j,l] and $Zr(CH_2Ph)_2(N_2NN')$ (**3**). The formal replacement of the CH_2NSiMe_3 groups of N_2NN' by $-CMe_2O$ in O_2NN' has clearly provided for a more open metal center. Surprisingly, the Zr−N_{amine} distances in **3** are both somewhat shorter than the corresponding values in **27** despite the apparent greater crowding in the former. The CH_2−Zr−CH_2 angle in **27** (av 100.7°) is more acute than that in **3** (87.09(9)°), which can be attributed to several factors, including the bulkier nature of N_2NN' vs O_2NN' and $SiMe_3$ vs Ph and the presence of the additional Zr···C_{ipso} interaction in **3**. In contrast to **3**, there are no acute Zr−CH_2−R angles (range 120.9(2)−125.8(2)°) in **27**.

Scheme 5. Synthesis of Cationic Zirconium Complexes of O_2NN' (anions omitted for clarity)

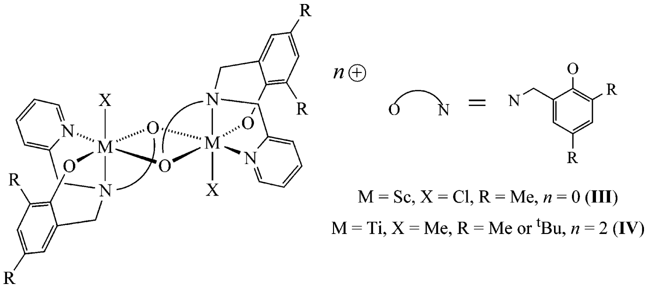


Scheme 5 summarizes the reactions of **27** with BAr^F_3 to form alkyl zirconium cations. In the presence of THF, dichloromethane solutions of **27** react with BAr^F_3 to form $[Zr(CH_2SiMe_3)(THF)(O_2NN')][Me_3SiCH_2BAr^F_3]$ (**28**-$Me_3SiCH_2BAr^F_3$) in 87% isolated yield. The NMR data for the $[Me_3SiCH_2BAr^F_3]^-$ anion show that it is noncoordinating. The $[Zr(CH_2SiMe_3)(THF)(O_2NN')]^+$ cation (**28**$^+$) is proposed to have the C_s symmetrical structure illustrated in Scheme 5. The relative positions of the CH_2SiMe_3, THF, and pyridyl groups were determined by NOE experiments. The base-stabilized cation **28**$^+$ is analogous to $[ZrMe(THF)(O_2NN')]^+$ (**12**$^+$, Scheme 2) and to previously described bis(phenolate)-diamine monoalkyl cations, for example, $[Zr(CH_2Ph)(THF)\{(2\text{-}C_5H_4N)CH_2N(2\text{-}O\text{-}3,5\text{-}C_6H_2R_2)_2\}]^+$.[8j]

Reaction of **27** with BAr^F_3 in dichloromethane in the absence of THF gave the compound **29**-$Me_3SiCH_2BAr^F_3$ as a white solid in 90% yield. In addition to resonances for a noncoordinating $[Me_3SiCH_2BAr^F_3]^-$ anion, the NMR spectra showed the formation of a C_1 symmetric species "$[Zr(CH_2SiMe_3)(O_2NN')]^+$". The methylene H atoms of the alkyl ligand appear as a pair of mutually coupled doublets, and the methyl groups and methylene H atoms of O_2NN' are all inequivalent. On the basis of these data and selected NOE experiments it is proposed that **29**-$Me_3SiCH_2BAr^F_3$ contains the bimetallic cation $[Zr_2(CH_2SiMe_3)_2(O_2NN')_2]^{2+}$ (Scheme 5). The dication has six-coordinate Zr centers linked by bridging alkoxide O atoms (each O_2NN' has one bridging and one nonbridging CH_2CMe_2O "arm").

Compounds with $Zr_2(\mu\text{-}O)_2$ cores are structurally well established.[22] The structure proposed for **29**$^{2+}$ can, in particular, be compared to recently reported[8c] dimeric neutral or dicationic complexes $Sc_2Cl_2\{(2\text{-}C_5H_4N)CH_2N(2\text{-}O\text{-}3,5\text{-}C_6H_2Me_2)_2\}_2$ (**III**, structurally characterized) and $[Ti_2Me_2\{(2\text{-}C_5H_4N)CH_2N(2\text{-}O\text{-}3,5\text{-}C_6H_2R_2)_2\}_2]^{2+}$ (**IV**, R =

Me or ^tBu). Whereas the titanium dication $[Ti_2Me_2\{(2\text{-}C_5H_4N)CH_2N(2\text{-}O\text{-}3,5\text{-}C_6H_2R_2)_2\}_2]^{2+}$ is very fluxional on the NMR time scale at room temperature (the fluxional process being frozen out at −80 °C), the dizirconium complex **29**$^{2+}$ is not. This is attributed to the reduced steric crowding about the μ-O atoms in the later (despite the presence of the neighboring CMe_2 units) and the larger radius of Zr. The discandium complex **III** was static on the NMR time scale at room temperature, there being much less Coulombic repulsion between the metal centers in this case.



M = Sc, X = Cl, R = Me, *n* = 0 (**III**)

M = Ti, X = Me, R = Me or ^tBu, *n* = 2 (**IV**)

Addition of ethylene (1 bar) to NMR tube samples of **29**-$Me_3SiCH_2BAr^F_3$ gave no polymerization activity (the same observation was made[8c] for solutions of $[Ti_2Me_2\{(2\text{-}C_5H_4N)CH_2N(2\text{-}O\text{-}3,5\text{-}C_6H_2{}^tBu_2)_2\}_2]^{2+}$), indicating that in these O_2NN'-supported systems the formation of alkoxide-bridged dimers is a potent catalyst deactivation pathway. Unsurprisingly, in the light of this, none of the compounds $MX_2(O_2NN')$ (M = Ti or Zr; X = Cl or CH_2SiMe_3) showed any significant ethylene polymerization capability when activated with either methyl aluminoxane or (for **27**) BAr^F_3 or $[CPh_3][BAr^F_4]$ (toluene solvent, 5 bar ethylene pressure, room temperature).

Conclusions

The N_2NN' ligand provides a useful support for a range of organometallic and imido complexes of certain group 4 and 5 metals, except for when bulky alkyl groups are involved. As seen in other silylamide-supported systems, however, monoalkyl cations undergo intramolecular cyclometalation via $SiMe_3$ group C−H bond activation. The new O_2NN' ligand allows for the syntheses of six-coordinate titanium dichloride and bis(dimethylamide) derivatives that were not accessible for N_2NN'. Furthermore, bulkier dialkyl zirconium derivatives are apparently more stable with the bis(alkoxide)-diamine ligand. The formation of cationic μ-alkoxide-bridged dimers probably accounts for (or at least contributes to) the lack of any significant ethylene polymerization activity with the O_2NN'-supported systems.

Experimental Section

General Methods and Instrumentation. All manipulations were carried out using standard Schlenk line or drybox techniques under an atmosphere of argon or of dinitrogen. Protio- and deutero-solvents were predried over activated 4 Å molecular sieves and were refluxed over the appropriate drying agent, distilled, and stored under dinitrogen in Teflon valve ampules. NMR samples were prepared under dinitrogen in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. ^1H, $^{13}C\{^1H\}$, ^{13}C, and ^{19}F NMR spectra were recorded on Varian Mercury-VX 300 and Varian Unity Plus 500 spectrometers. ^1H and ^{13}C assignments were confirmed with the use of DEPT-135 and two-dimensional $^1H-^1H$ and $^{13}C-^1H$ NMR experiments. ^1H and ^{13}C spectra were referenced internally to residual protio-solvent (^1H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane (δ = 0 ppm). ^{19}F and ^{11}B spectra were referenced externally to $CFCl_3$ and $BF_3{\cdot}Et_2O$, respectively. Chemical shifts are quoted in δ (ppm) and coupling constants in hertz. Infrared spectra were prepared as Nujol mulls and were recorded on Perkin-Elmer 1600 and 1710 series FTIR spectrometers; data are quoted in wavenumbers (cm^{-1}). Mass spectra were recorded by the mass spectrometry services of the University of Oxford Department of Chemistry, and elemental analyses by the analytical services of the University of Oxford Inorganic Chemistry Laboratory.

Literature Preparations and Other Starting Materials. The compounds H_2N_2NN',[10b] Li_2N_2NN',[10b] $ZrCl_2(N_2NN')$ (**1**),[10b] $Ti(NR)Cl_2(py)_3$ (R = ^tBu or Ar),[21] $Zr(CH_2SiMe_3)_4$,[30] $Zr(CH_2CMe_3)_4$,[31] $Zr(CH_2SiMe_3)_2Cl_2(Et_2O)_2$,[29] $M(NMe_2)_4$ (M = Ti or Zr),[32] $TiCl_4(THF)_2$,[33] $LiCH_2SiMe_3$,[34] and $M(N^tBu)Cl_3(py)_2$ (M = Nb or Ta)[27] were prepared according to published methods. Samples of BAr^F_3 were provided by DSM Research. Pyridine, $^tBuNH_2$, $ArNH_2$, and piperidine were dried over the appropriate drying agents and distilled under reduced pressure. All other compounds and reagents were purchased and used without further purification.

$ZrMe_2(N_2NN')$ (2). To a solution of $ZrCl_2(N_2NN')$ (**1**) (490 mg, 0.98 mmol) in benzene (20 mL) was added dropwise a solution of MeLi (1.6 M in Et_2O, 0.62 mL, 0.98 mmol) in benzene (5 mL). After stirring for 12 h another equivalent of MeLi (1.6 M in Et_2O, 0.62 mL, 0.98 mmol), in benzene (5 mL), was added dropwise. The mixture was stirred for a further 4 h, after which time the volatiles were removed under reduced pressure, giving crude $ZrMe_2(N_2NN')$ (**2**) as a light brown solid. This was extracted into pentane (3 × 15 mL) and filtered, and the combined extracts were concentrated to 5 mL. Cooling the solution to −30 °C produced **2** as a white solid, which was washed with cold pentane and dried in vacuo. Yield: 397 mg (88%).

^1H NMR (500.0 MHz, 293 K, C_6D_6): δ 8.59 (1 H, d, ^3J 5.0 Hz, 6-C_5H_4N), 6.77 (1 H, dd, ^3J 8.0, 7.0 Hz, 4-C_5H_4N), 6.38 (1 H, dd, ^3J 5.0, 7.0 Hz, 5-C_5H_4N), 6.31 (1 H, d, ^3J 8.0 Hz, 3-C_5H_4N), 3.43 (2 H, m, NCH_2CH_2NSi), 3.29 (2 H, s, $C_5H_4NCH_2$), 3.09 (2 H, m, NCH_2CH_2NSi), 2.54 (2 H, m, NCH_2CH_2NSi), 2.09 (2 H, m, NCH_2CH_2NSi), 0.79 (2 H, s, $ZrCH_3$), 0.70 (2 H, s, $ZrCH_3$), 0.36 (18 H, s, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (125.7 MHz, 293 K, C_6D_6): δ 158.5 (2-C_5H_4N), 150.1 (6-C_5H_4N), 137.8 (4-C_5H_4N), 122.9 (5-C_5H_4N), 121.8 (3-C_5H_4N), 58.3 ($C_5H_4NCH_2$), 57.9 (NCH_2CH_2NSi), 48.0 (NCH_2CH_2NSi), 41.8 ($ZrCH_3$), 36.4 ($ZrCH_3$), 1.3 ($Si(CH_3)_3$). IR (CsBr plates, Nujol): ν 1604 (m), 1572 (w), 1303 (w), 1280 (w), 1243 (s), 1154 (w), 1074 (s), 1035 (w), 1008 (w), 942 (m), 916 (m), 834 (s), 804 (m), 757 (m), 731 (w), 678 (w), 594 (w), 560 (w), 535 (w), 484 (w) cm^{-1}. EI-MS: *m/z* 441 (28%), $[M - CH_3]^+$; 425 (100%), $[M - 2CH_3, H]^+$. Anal. Found (calcd for $C_{18}H_{38}N_4Si_2Zr$): C, 46.0 (47.2); H, 8.1 (8.4); N, 11.8 (12.2).

$Zr(CH_2Ph)_2(N_2NN')$ (3). To a yellow solution of $ZrCl(CH_2Ph)(N_2NN')$ (**6**) (204 mg, 0.37 mmol) in benzene (20 mL) cooled to 5 °C was added $PhCH_2MgCl$ (1.0 M in Et_2O, 368 μL, 0.37 mmol) in benzene (5 mL). The mixture was allowed to warm to room temperature and stirred for 18 h, giving an opaque, dark orange solution. The volatiles were removed under reduced pressure, yielding an orange solid, which was triturated with pentane and dried in vacuo to afford pale yellow **3**. Yield: 140 mg (62%).

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^{1}H NMR (500.0 MHz, 293 K, C_6D_6): δ 8.14 (1 H, d, ^3J 5.5 Hz, 6-C_5H_4N), 7.35 (2 H, d, ^3J 8.5 Hz, *o*-C_6H_5), 7.30 (2 H, t, ^3J 7.5, 14 Hz, *m*-C_6H_5), 7.11 (2 H, t, ^3J 8.5, 6 Hz, *m*-C_6H_5), 7.06 (2 H, d, ^3J 7.5 Hz, *o*-C_6H_5), 6.85 (2 H, m, *p*-C_6H_5), 6.66 (1 H, dd, ^3J 8.0, 7.5 Hz, 4-C_5H_4N), 6.23 (1 H, dd, ^3J 5.5, 7.5 Hz, 5-C_5H_4N), 6.19 (1 H, d, ^3J 8.0 Hz, 3-C_5H_4N), 3.28 (2 H, m, $NCH_2C\mathit{H}_2NSi$), 3.15 (2 H, s, $C_6H_5C\mathit{H}_2$), 3.06 (2 H, s, $C_6H_5C\mathit{H}_2$), 2.94 (2 H, s, $C_5H_4NC\mathit{H}_2$), 2.91 (2 H, m, $NCH_2C\mathit{H}_2NSi$), 2.06 (2 H, m, $NC\mathit{H}_2CH_2NSi$), 1.76 (2 H, m, $NC\mathit{H}_2CH_2NSi$), 0.30 (18 Hs, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (125.7 MHz, 293 K, C_6D_6): δ 157.4 (2-C_5H_4N), 151.8 (*i*-C_6H_5), 151.4 (6-C_5H_4N), 150.4 (*i*-C_6H_5), 137.7 (4-C_5H_4N), 128.8 (*o*-C_6H_5), 127.0 (*m*-C_6H_5), 122.3 (5-C_5H_4N), 122.2 (3-C_5H_4N), 120.6 (*o*-, *m*-C_6H_5), 118.6 (2 × overlapping *p*-C_6H_5), 73.1 ($C_6H_5\mathit{C}H_2$), 65.3 ($C_6H_5\mathit{C}H_2$), 58.1 ($C_5H_4N\mathit{C}H_2$), 56.7 ($N\mathit{C}H_2CH_2NSi$), 48.1 ($NCH_2\mathit{C}H_2NSi$), 2.0 ($Si(CH_3)_3$). IR (CsBr plates, Nujol): ν 1733 (w), 1605 (w), 1591 (m), 1572 (w), 1302 (w), 1259 (m), 1247 (m), 1206 (w), 1073 (w), 1017 (w), 942 (w), 902 (w), 835 (s), 802 (w), 746 (m), 725 (m), 697 (w), 678 (w), 670 (w), 447 (w) cm^{-1}. EI-MS: *m/z* 505 (25%), $[M - 2CH_3, Si(CH_3)_3]^+$; 367 (7%), $[M - Si(CH_3)_3, CH_2C_6H_5, C_6H_5]^+$. Anal. Found (calcd for $C_{30}H_{46}N_4Si_2Zr$): C, 59.4 (59.1); H, 7.8 (7.6); N, 8.8 (9.2).

NMR Tube Scale Synthesis of $Zr(CH_2SiMe_3)_2(N_2NN')$ (4). A solution of H_2N_2NN' (18 mg, 0.053 mmol) in C_6D_6 (ca. 0.75 mL) was added to a sample of $Zr(CH_2SiMe_3)_4$ (20 mg, 0.045 mmol), resulting in the immediate formation of an orange-red solution. The NMR data were consistent with the quantitative formation of **4** and 2 equiv of $SiMe_4$. **4** subsequently decomposed to a complex mixture of products over 6 h. ^{1}H NMR (500.0 MHz, 293 K, C_6D_6): δ 8.61 (1 H, d, ^3J 5.5 Hz, 6-C_5H_4N), 6.87 (1 H, dd, ^3J 8.0, 7.5 Hz, 4-C_5H_4N), 6.53 (1 H, dd, ^3J 5.5, 7.5 Hz, 5-C_5H_4N), 6.48 (1 H, d, ^3J 8.0 Hz, 3-C_5H_4N), 3.47 (2 H, s, $C_5H_4NC\mathit{H}_2$), 3.41 (2 H, m,$NCH_2C\mathit{H}_2NSi$), 3.33 (2 H, m,$NCH_2C\mathit{H}_2NSi$), 2.59 (2 H, m,$NC\mathit{H}_2CH_2NSi$), 2.39 (2 H, m,$NC\mathit{H}_2CH_2NSi$), 0.84 (2 H, s, $C\mathit{H}_2Si(CH_3)_3$), 0.58 (2 H, s, $C\mathit{H}_2Si(CH_3)_3$), 0.31 (18 H, s, $NSi(CH_3)_3$), 0.24 (9 H, s, $CH_2Si(C\mathit{H}_3)_3$), 0.22 (9 H, s, $CH_2Si(C\mathit{H}_3)_3$). $^{13}C\{^1H\}$ NMR (125.7 MHz, 293 K, C_6D_6): δ 156.5 (2-C_5H_4N), 150.6 (6-C_5H_4N), 137.3 (4-C_5H_4N), 123.1 (5-C_5H_4N), 122.7 (3-C_5H_4N), 57.1 ($N\mathit{C}H_2CH_2NSi$), 54.2 ($\mathit{C}H_2Si(CH_3)_3$), 54.2 ($\mathit{C}H_2Si(CH_3)_3$), 51.1 ($C_5H_4N\mathit{C}H_2$), 48.0 ($NCH_2\mathit{C}H_2NSi$), 2.5 ($CH_2Si(\mathit{C}H_3)_3$), 2.4 ($CH_2Si(\mathit{C}H_3)_3$), 0.5 ($NSi(CH_3)_3$).

NMR Tube Scale Synthesis of $Zr(CH_2{}^tBu)_2(N_2NN')$ (5). A colorless solution of $Zr(CH_2{}^tBu)_4$ (22 mg, 0.059 mmol) in C_6D_6 (ca. 0.75 mL) was added to H_2N_2NN' (20 mg, 0.059 mmol), producing an immediate orange coloration. The NMR data were consistent with the quantitative formation of **5** and 2 equiv of CMe_4. **5** subsequently decomposed to a complex mixture of products over 6 h.

^{1}H NMR (500.0 MHz, 293 K, C_6D_6): δ 8.38 (1 H, d, ^3J 4.0 Hz, 6-C_5H_4N), 6.94 (1 H, dd, ^3J 6.0, 8.0 Hz, 4-C_5H_4N), 6.67 (1 H, dd, ^3J 4.0, 8.0 Hz, 5-C_5H_4N), 6.58 (1 H, d, ^3J 6.0 Hz, 3-C_5H_4N), 3.98 (2 H, s, $C_5H_4NC\mathit{H}_2$), 3.94 (2 H, m, $NCH_2C\mathit{H}_2NSi$), 3.33 (2 H, m, $NCH_2C\mathit{H}_2NSi$), 3.00 (2 H, m, $NC\mathit{H}_2CH_2NSi$), 2.57 (2 H, m, $NC\mathit{H}_2CH_2NSi$), 1.33 (2 H, s, $C\mathit{H}_2C(CH_3)_3$), 1.28 (2 H, s, $C\mathit{H}_2C(CH_3)_3$), 1.15 (18 Hs, $C(CH_3)_3$), 0.46 (18 Hs, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (125.7 MHz, 293 K, C_6D_6): δ 153.8 (2-C_5H_4N), 150.0 (6-C_5H_4N), 136.1 (4-C_5H_4N), 125.4 (5-C_5H_4N), 122.5 (3-C_5H_4N), 83.8 ($\mathit{C}H_2C(CH_3)_3$), 77.4 ($\mathit{C}H_2C(CH_3)_3$), 56.7 ($N\mathit{C}H_2CH_2NSi$), 48.5 ($NCH_2\mathit{C}H_2NSi$), 48.1 ($C_5H_4N\mathit{C}H_2$), 34.3 ($\mathit{C}(CH_3)_3$), 32.2 ($\mathit{C}(CH_3)_3$), 23.2 ($C(\mathit{C}H_3)_3$), 20.0 ($C(\mathit{C}H_3)_3$), 0.13 ($Si(CH_3)_3$).

$ZrCl(CH_2Ph)(N_2NN')$ (6). To a solution of $ZrCl_2(N_2NN')$ (**1**) (500 mg, 1.0 mmol) in benzene (30 mL) cooled to 5 °C was added dropwise a solution of $PhCH_2MgCl$ (1.0 M in Et_2O, 1.0 mL, 1.0 mmol) in benzene (5 mL). The mixture immediately turned slightly orange and was allowed to warm to room temperature before being stirred for a further 16 h. The volatiles were removed under reduced pressure, and the resulting yellow solid was extracted into benzene (60 mL). The yellow extract was filtered, and the volatiles were removed under reduced pressure to give **6** as a yellow solid. Yield: 486 mg (87%).

^{1}H NMR (500.0 MHz, 293 K, C_6D_6): δ 9.26 (1 H, d, ^3J 5.0 Hz, 6-C_5H_4N), 7.28 (4 H, m, *o*-, *m*-C_6H_5), 6.84 (1 H, t, ^3J 6.5 Hz, *p*-C_6H_5), 6.72 (1 H, dd, ^3J 7.5, 7.5 Hz, 4-C_5H_4N), 6.37 (1 H, dd, ^3J 5.0, 7.5 Hz, 5-C_5H_4N), 6.20 (1 H, d, ^3J 7.5 Hz, 3-C_5H_4N), 3.33 (2 H, s, $C_6H_5C\mathit{H}_2$), 3.32 (2 H, m, $NCH_2C\mathit{H}_2NSi$), 3.03 (2 H, s, $C_5H_4NC\mathit{H}_2$), 2.90 (2 H, m, $NCH_2C\mathit{H}_2NSi$), 2.15 (2 H, m, $NC\mathit{H}_2CH_2NSi$), 2.09 (2 H, m, $NC\mathit{H}_2CH_2NSi$), 0.32 (18 H, s, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (125.7 MHz, 293 K, C_6D_6): δ 157.5 (2-C_5H_4N), 151.4 (*i*-C_6H_5), 150.5 (6-C_5H_4N), 138.4 (4-C_5H_4N), 129.3 (*o*-C_6H_5), 128.3 (*m*-C_6H_5), 122.9 (5-C_5H_4N), 121.5 (3-C_5H_4N), 118.7 (*p*-C_6H_5), 64.7 ($C_6H_5\mathit{C}H_2$), 57.5 ($C_5H_4N\mathit{C}H_2$), 57.2 ($N\mathit{C}H_2CH_2NSi$), 48.7 ($NCH_2\mathit{C}H_2NSi$), 2.1 ($Si(CH_3)_3$). IR (CsBr plates, Nujol): ν 1604 (m), 1589 (m), 1570 (w), 1300 (w), 1206 (m), 1175 (w), 1157 (w), 1083 (s), 1015 (m), 946 (s), 925 (w), 902 (s), 873 (w), 839 (s), 799 (m), 790 (m), 747 (m), 730 (w), 694 (m), 679 (w), 648 (w), 633 (w), 594 (m), 579 (m) cm^{-1}. EI-MS: *m/z* 552 (5%), $[M]^+$; 517 (21%), $[M - Cl]^+$; 461 (35%), $[M - C_6H_5]^+$. Anal. Found (calcd for $C_{23}H_{39}ClN_4Si_2Zr$): C, 49.5 (49.8); H, 7.2 (7.1); N, 9.2 (10.1).

$ZrCl(CH_2SiMe_3)(N_2NN')$ (7). To a yellow solution of $ZrCl_2(N_2NN')$ (**1**) (113 mg, 0.23 mmol) in benzene (10 mL) was added dropwise a solution of $ClMgCH_2SiMe_3$ (1.0 M in Et_2O, 215 μL, 0.22 mmol) in benzene (5 mL), resulting in the immediate formation of a white precipitate. After stirring for 15 min the volatiles were removed under reduced pressure, producing a yellow solid, which was washed with pentane (20 mL) before being extracted into benzene (3 × 20 mL). The combined yellow extracts were filtered and the volatiles removed under reduced pressure to afford **7** as a white solid. Yield: 117 mg (97%).

^{1}H NMR (300.1 MHz, 293 K, C_6D_6): δ 9.16 (1 H, d, ^3J 5.5 Hz, (6-C_5H_4N), 6.82 (1 H, dd, ^3J 7.8, 7.8 Hz, (4-C_5H_4N), 6.44 (1 H, dd, ^3J 5.5, 7.8 Hz, (5-C_5H_4N), 6.36 (1 H, d, ^3J 7.8 Hz, (3-C_5H_4N), 3.49 (2 H, m, $NCH_2C\mathit{H}_2NSi$), 3.29 (2 H, s, $C_5H_4NC\mathit{H}_2$), 3.09 (2 H, m, $NCH_2C\mathit{H}_2NSi$), 2.82 (2 H, m, $NC\mathit{H}_2CH_2NSi$), 2.23 (2 H, m, $NC\mathit{H}_2CH_2NSi$), 1.18 (2 H, s, $C\mathit{H}_2Si(CH_3)_3$), 0.39 (9 H, s, $CH_2Si(C\mathit{H}_3)_3$), 0.35 (18 H, s, $NSi(CH_3)_3$). $^{13}C\{^1H\}$ NMR (75.5 MHz, 293 K, C_6D_6): δ 157.0 (2-C_5H_4N), 150.8 (6-C_5H_4N), 138.1 (4-C_5H_4N), 123.0 (5-C_5H_4N), 121.3 (3-C_5H_4N), 59.7 ($C_5H_4N\mathit{C}H_2$), 59.2 ($N\mathit{C}H_2CH_2NSi$), 53.0 ($\mathit{C}H_2Si(CH_3)_3$), 50.0 ($NCH_2\mathit{C}H_2NSi$), 4.0 ($CH_2Si(CH_3)_3$), 1.9 ($NSi(CH_3)_3$). IR (CsBr plates, Nujol): ν 1644 (w), 1605 (s), 1572 (m), 1402 (w), 1350 (w), 1306 (m), 1283 (m), 1156 (m), 1137 (m), 1106 (w), 1083 (s), 1036 (m), 1013 (w), 988 (w), 965 (w), 946 (w), 899 (w), 801 (w), 727 (w), 627 (s), 645 (m), 632 (m), 596 (s), 562 (s), 507 (s), 485 (w), 445 (m), 425 (m) cm^{-1}. Anal. Found (calcd for $C_{20}H_{43}ClN_4Si_3Zr$): C, 43.5 (43.6); H, 7.7 (7.9); N, 10.2 (10.2).

$ZrMe(CH_2Ph)(N_2NN')$ (8). To a yellow solution of $ZrCl(CH_2Ph)(N_2NN')$ (**6**) (206 mg, 0.37 mmol) in benzene (20 mL) cooled to 5 °C was added MeMgBr (1.4 M in toluene/thf, 265 μL, 0.37 mmol) in benzene (5 mL). The mixture was allowed to warm to room temperature and stirred for 16 h to give an opaque orange-brown solution. The volatiles were removed under reduced pressure, yielding a light brown solid. The solid was extracted into benzene (15 mL) and filtered to give an orange solution. The volatiles were removed under reduced pressure, yielding **8** as a yellow solid. Yield: 162 mg (82%).

^{1}H NMR (500.0 MHz, 293 K, C_6D_6): δ 8.60 (1 H, d, ^3J 5.5 Hz, 6-C_5H_4N), 7.35 (2 H, d, ^3J 7.0 Hz, *o*-C_6H_5), 7.29 (2 H, dd, ^3J 7.0, 7.5 Hz, *m*-C_6H_5), 6.84 (1 H, t, ^3J 7.5 Hz, *p*-C_6H_5), 6.76 (1 H, dd, ^3J 7.5, 7.5 Hz, 4-C_5H_4N), 6.37 (1 H, dd, ^3J 5.5, 7.5 Hz, 5-C_5H_4N), 6.29 (1 H, d, ^3J 7.5 Hz, 3-C_5H_4N), 3.29 (2 H, m, $NCH_2C\mathit{H}_2NSi$), 3.21 (2 H, s, $C_6H_5C\mathit{H}_2$), 3.08 (2 H, s, $C_5H_4NC\mathit{H}_2$), 2.91 (2 H, m, $NCH_2C\mathit{H}_2NSi$), 2.10 (2 H, m, $NC\mathit{H}_2CH_2NSi$), 1.83 (2 H, m, $NC\mathit{H}_2CH_2NSi$), 0.73 (3 H, s, $ZrCH_3$), 0.32 (18 H, s, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (125.7 MHz, 293 K, C_6D_6): δ 158.6 (2-C_5H_4N), 150.6 (6-C_5H_4N), 150.2 (*i*-C_6H_5), 138.0 (4-

C_5H_4N), 128.6 (*o*-C_6H_5), 127.7 (*m*-C_6H_5), 122.8 (5-C_5H_4N), 121.9 (3-C_5H_4N), 118.2 (*p*-C_6H_5), 63.7 ($C_6H_5\textit{C}H_2$), 58.0 ($C_5H_4N\textit{C}H_2$), 57.0 ($N\textit{C}H_2CH_2NSi$), 48.3 ($NCH_2\textit{C}H_2NSi$), 44.5 ($ZrCH_3$), 1.8 ($Si(CH_3)_3$). IR (CsBr plates, Nujol): ν 1654 (m), 1604 (s), 1304 (m), 1280 (w), 1250 (s), 1209 (s), 1174 (w), 1159 (w), 1142 (w), 1112 (w), 1082 (m), 1072 (s), 1036 (w), 1025 (w), 1010 (w), 1000 (w), 943 (s), 906 (s), 835 (s), 779 (w), 764 (w), 747 (m), 730 (w), 697 (m), 675 (w), 633 (m), 593 (w), 584 (w), 561 (w), 541 (w), 520 (w), 452 (m) cm^{-1}. EI-MS: *m/z* 441 (20%), $[M - CH_2C_6H_5^+]$; 425 (96%), $[M - CH_2C_6H_5, H, CH_3]^+$. Anal. Found (calcd for $C_{24}H_{42}N_4Si_2Zr$): C, 53.7 (54.0); H, 7.8 (7.9); N, 10.2 (10.5).

ZrCl{(2-NC$_5$(6-C$_3$H$_5$)H$_4$)CH$_2$N(CH$_2$CH$_2$NSiMe$_3$)$_2$} (9). To a yellow solution of $ZrCl_2(N_2NN')$ (**1**) (194 mg, 0.39 mmol) in benzene (5 mL) was added dropwise a solution of $ClMgCH_2CHCH_2$ (2.0 M in thf, 194 μL, 0.39 mmol) in benzene (3 mL). After stirring for 75 min the mixture had become cloudy and brown-orange in color. The volatiles were removed under reduced pressure, and the resulting brown oil was extracted into pentane (30 mL). The extract was filtered and the volatiles were removed under reduced pressure to give analytically pure **9** as a yellow oil, which could not be crystallized. Yield: 145 mg (74%).

^1H NMR (300.1 MHz, 293 K, C_6D_6): δ 6.06 (1 H, m, $C_5H_4(CH_2C\textit{H}CH_2)N$), 6.02 (1 H, dd, $^3J = 5.4, 8.8$ Hz, 4-$C_5H_4(CH_2CHCH_2)N$), 5.36 (1 H, m, $^3J = 8.8, 5.9$ Hz, 5-$C_5H_4(CH_2CHCH_2)N$), 5.20 (1 H, m, $C_5H_4(CH_2CHC\textit{H}_2)N$), 5.05 (1 H, m, 6-$C_5H_4(CH_2CHCH_2)N$), 4.98 (1 H, m, $C_5H_4(CH_2CHC\textit{H}_2)N$), 4.79 (1 H, d, $^3J = 5.4$ Hz, 3-$C_5H_4(CH_2CHCH_2)N$), 3.38 (2 H, m, $NCH_2C\textit{H}_2NSi$), 3.12 (1 H, d, $^2J = 13.2$ Hz, $C_5H_4(CH_2CHCH_2)NC\textit{H}_2$), 2.85 (2 H, m, $NCH_2C\textit{H}_2NSi$), 2.78 (1 H, d, $^2J = 13.2$ Hz, $C_5H_4(CH_2CHCH_2)NC\textit{H}_2$), 2.47 (3 H, m, $NC\textit{H}_2CH_2NSi$, $C_5H_4(C\textit{H}_2CHCH_2)N$), 2.10 (3 H, m, $NC\textit{H}_2CH_2NSi$, $C_5H_4(C\textit{H}_2CHCH_2)N$), 0.33 (9 H, s, $Si(CH_3)_3$), 0.29 (9 H, s, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (75.5 MHz, 293 K, C_6D_6): δ 148.1 (2-$C_5H_4(CH_2CHCH_2)N$), 136.4 ($C_5H_4(CH_2\textit{C}HCH_2)N$), 123.2 (4-$C_5H_4(CH_2CHCH_2)N$), 118.9 (5-$C_5H_4(CH_2CHCH_2)N$), 117.5 ($C_5H_4(CH_2CH\textit{C}H_2)N$), 95.5 (3-$C_5H_4(CH_2CHCH_2)N$), 60.1 ($C_5H_4(CH_2CHCH_2)N\textit{C}H_2$), 60.1 ($N\textit{C}H_2CH_2NSi$), 59.5 ($N\textit{C}H_2CH_2NSi$), 58.0 (6-$C_5H_4(CH_2CHCH_2)N$), 48.0 ($NCH_2\textit{C}H_2NSi$), 47.7 ($NCH_2\textit{C}H_2NSi$), 40.8 ($C_5H_4(\textit{C}H_2CHCH_2)N$), 1.5 ($Si(CH_3)_3$), 1.3 ($Si(CH_3)_3$). IR (CsBr plates): ν 3072 (w), 3036 (w), 2951 (s), 2900 (w), 2854 (m), 1634 (m), 1607 (m), 1560 (s), 1465 (w), 1445 (m), 1407 (m), 1374 (m), 1354 (w), 1308 (m), 1247 (s), 1201 (w), 1157 (w), 1122 (w), 1072 (m), 1022 (w), 992 (m), 916 (s), 869 (w), 836 (m), 807 (w), 758 (w), 747 (m), 706 (w), 680 (m), 624 (w), 599 (w), 570 (w), 450 (w) cm^{-1}. EI-MS: *m/z* 502 (15%) $[M]^+$; 429 (29%) $[M - Si(CH_3)_3]^+$. Anal. Found (calcd for $C_{19}H_{39}ClN_4Si_2Zr$): C, 46.3 (45.3); H, 7.0 (7.4); N, 11.3 (11.1).

[Zr{(2-NC$_5$H$_4$)CH$_2$N(CH$_2$CH$_2$NSiMe$_3$)(CH$_2$CH$_2$NSiMe$_2$CH$_2$−)}][MeBAr^F$_3$] (10-MeBAr^F$_3$). To a solution of $ZrMe_2(N_2NN')$ (**2**) (187 mg, 0.41 mmol) in benzene (5 mL) was added $BAr^F{}_3$ in benzene (5 mL), resulting in the immediate formation of a red oil. The oil was isolated, washed with benzene (3 × 5 mL), and dried in vacuo to afford **10**-$MeBAr^F{}_3$ as a white solid. Yield: 235 mg (60%).

^1H NMR (500.0 MHz, 293 K, CD_2Cl_2): δ 9.20 (1 H, d, ^3J 6.0 Hz, 6-C_5H_4N), 8.24 (1 H, dd, ^3J 8.0, 7.5 Hz, 4-C_5H_4N), 7.76 (1 H, dd, ^3J 7.5, 6.0 Hz, 5-C_5H_4N), 7.69 (1 H, d, ^3J 8.0 Hz, 3-C_5H_4N), 4.32 (2 H, s, $C_5H_4NC\textit{H}_2$), 3.93 (1 H, m, $NCH_2C\textit{H}_2NSi$), 3.79 (1 H, m, $NCH_2C\textit{H}_2NSi$), 3.79 (1 H, m, $NCH_2C\textit{H}_2NSi$), 3.61 (1 H, m, $NCH_2C\textit{H}_2NSi$), 3.54 (1 H, m, $NC\textit{H}_2CH_2NSi$), 3.32 (1 H, m, $NC\textit{H}_2CH_2NSi$), 3.24 (1 H, m, $NC\textit{H}_2CH_2NSi$), 3.02 (1 H, m, $NC\textit{H}_2CH_2NSi$), 1.39 (1 H, d, $^2J = 15.5$ Hz, $ZrCH_2$), 1.10 (1 H, d, $^2J = 15.5$ Hz, $ZrCH_2$), 0.44 (3 H, br s, BCH_3), 0.43 (3 H, s, $Si(CH_3)_2$), 0.00 (3 H, s, $Si(CH_3)_2$), −0.02 (9 H, s, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (125.7 MHz, 293 K, CD_2Cl_2): δ 159.3 (2-C_5H_4N), 152.5 (6-C_5H_4N), 148.7 (*o*-C_6F_5, ^1J 234 Hz), 143.7 (4-C_5H_4N), 137.8 (*p*-C_6F_5, ^1J 248 Hz), 136.8 (*m*-C_6F_5, ^1J 264 Hz), 126.2 (5-C_5H_4N), 124.8 (3-C_5H_4N), 60.0 ($N\textit{C}H_2CH_2NSi$), 59.5 ($ZrCH_2$), 58.7 ($C_5H_4N\textit{C}H_2$), 56.1 ($N\textit{C}H_2CH_2NSi$), 52.6 ($NCH_2\textit{C}H_2NSi$), 45.0 ($NCH_2\textit{C}H_2NSi$), 10.3 (BCH_3), 7.6 ($SiCH_3$), 3.2 ($SiCH_3$), 0.8 ($Si(CH_3)_3$). ^{19}F NMR (470.4 MHz, 293 K, CD_2Cl_2): δ −133.4 (6 F, d, ^3J 21.4 Hz, *o*-C_6F_5), −165.2 (3 F, t, ^3J 21.4 Hz, *p*-C_6F_5), −167.9 (6 F, dd, ^3J 21.4 Hz, *m*-C_6F_5). ^{11}B NMR (160.4 MHz, 293 K, CD_2Cl_2): δ −14.73 ($[MeB(C_6F_5)_3]^-$). IR (CsBr plates, Nujol): ν 1641 (m), 1610 (m), 1510 (s), 1304 (w), 1260 (m), 1086 (s), 1054 (w), 1040 (w), 1018 (w), 995 (w), 979 (w), 966 (w), 952 (w), 936 (w), 922 (w), 876 (w), 840 (s), 766 (w), 748 (w), 724 (w), 685 (w), 660 (w), 647 (w), 619 (w), 604 (w), 588 (w), 570 (w), 541 (w), 522 (w), 474 (w), 430 (w) cm^{-1}. Anal. Found (calcd for $C_{35}H_{34}BF_{15}N_4Si_2Zr$): C, 44.7 (44.1); H, 4.0 (3.6); N, 5.7 (5.9); B, 1.1 (1.1).

[ZrMe(THF)(N$_2$NN′)][MeBAr^F$_3$] (12-MeBAr^F$_3$). To a colorless solution of $ZrMe_2(N_2NN')$ (**2**) (111 mg, 0.24 mmol) and THF (ca. 0.5 mL) in benzene (5 mL) was added a solution of $BAr^F{}_3$ (124 mg, 24 mmol) in benzene (10 mL), resulting in the immediate formation of an orange-brown solution. The mixture was stirred for 15 min, after which time the volatiles were removed under reduced pressure, yielding **12**-$MeBAr^F{}_3$ as a brown oil, which could not be crystallized. Yield: 247 mg (98%).

^1H NMR (300.0 MHz, 293 K, CD_2Cl_2): δ 8.84 (1 H, d, ^3J 6.6 Hz, 6-C_5H_4N), 8.04 (1 H, dd, ^3J 7.8, 7.5 Hz, 4-C_5H_4N), 7.55 (2 H, m, 3-C_5H_4N, 5-C_5H_4N), 4.31 (4 H, br s, 2,5-C_4H_8O), 4.13 (2 H, s, $C_5H_4NC\textit{H}_2$), 3.76 (2 H, m, $NCH_2C\textit{H}_2NSi$), 3.37 (4 H, m, $NCH_2C\textit{H}_2NSi$, $NC\textit{H}_2CH_2NSi$), 2.85 (2 H, m, $NC\textit{H}_2CH_2NSi$), 2.18 (3 H, br s, 3,4-C_4H_8O), 1.92 (1 H, br s, 3,4-C_4H_8O), 0.52 (3 H, s, $ZrCH_3$), 0.48 (3 H, br s, BCH_3), 0.0518 H, s, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (75.5 MHz, 293 K, CD_2Cl_2): δ 159.4 (2-C_5H_4N), 151.4 (6-C_5H_4N), 148.7 (*o*-C_6F_5, ^1J 228 Hz), 141.8 (4-C_5H_4N), 137.7 (*p*-C_6F_5, ^1J 238 Hz), 137.0 (*m*-C_6F_5, ^1J 238 Hz), 125.1 (5-C_5H_4N), 124.6 (3-C_5H_4N), 74.6 (2,5-C_4H_8O), 58.1 ($N\textit{C}H_2CH_2NSi$), 56.5 ($C_5H_4N\textit{C}H_2$), 49.4 ($NCH_2\textit{C}H_2NSi$), 48.0 (3,4-C_4H_8O), 25.8 ($ZrCH_3$), 10.6 (BCH_3), 0.9 ($Si(CH_3)_3$). ^{19}F NMR (282.3 MHz, 293 K, CD_2Cl_2): δ −133.6 (6 F, d, ^3J 21.5 Hz, *o*-C_6F_5), −165.6 (3 F, t, ^3J 21.7 Hz, *p*-C_6F_5), −168.2 (6 F, m, ^3J 21.7, 21.5 Hz, *m*-C_6F_5). ^{11}B NMR (96.3 MHz, 293 K, CD_2Cl_2): δ −14.9 ($[MeBAr^F{}_3]^-$). IR (CsBr plates, Nujol): ν 2613 (w), 2588 (w), 2538 (w), 2082 (w), 2006 (w), 1933 (w), 1871 (w), 1641 (s), 1611 (s), 1572 (m), 1554 (w), 1515 (m), 1505 (w), 1306 (m), 1261 (s), 1163 (m), 1142 (m), 1099 (s), 1044 (w), 898 (w), 802 (w), 780 (w), 687 (m), 661 (s), 647 (w), 602 (s), 568 (s), 529 (w), 459 (s), 436 (w), 423 (w) cm^{-1}. Anal. Found (calcd for $C_{40}H_{46}BF_{15}N_4OSi_2Zr\cdot 0.3C_6H_6$): C, 46.9 (47.2); H, 4.8 (4.5); N, 5.1 (5.3).

[ZrCl(N$_2$NN′)][PhCH$_2$BAr^F$_3$] (13-PhCH$_2$BAr^F$_3$). To a yellow suspension of $ZrCl(CH_2Ph)(N_2NN')$ (**6**) (426 mg, 0.77 mmol) in benzene (15 mL) cooled to 5 °C was added dropwise a solution of $BAr^F{}_3$ (393 mg, 0.77 mmol) in benzene (15 mL), resulting immediately in a loss of color intensity of the solution. The solution was stirred for 10 min, after which time the volatiles were removed under reduced pressure from the mixture (cooled to freezing), yielding **13**-$PhCH_2BAr^F{}_3$ as a white solid. Yield: 769 mg (94%).

^1H NMR (500.0 MHz, 293 K, CD_2Cl_2): δ 9.19 (1 H, d, ^3J 5.5 Hz, 6-C_5H_4N), 8.16 (1 H, dd, ^3J 8.5, 7.5 Hz, 4-C_5H_4N), 7.66 (1 H, dd, ^3J 8.5, 5.5 Hz, 5-C_5H_4N), 7.57 (1 H, d, ^3J 7.5 Hz, 3-C_5H_4N), 6.97 (2 H, dd, ^3J 7.0, 7.5 Hz, *m*-C_6H_5), 6.87 (1 H, t, ^3J 7.5 Hz, *p*-C_6H_5), 6.84 (2 H, d, ^3J 7.0 Hz, *o*-C_6H_5), 4.20 (2 H, s, $C_5H_4NC\textit{H}_2$), 3.91 (2 H, m, $NCH_2C\textit{H}_2NSi$), 3.60 (2 H, m, $NCH_2C\textit{H}_2NSi$), 3.50 (2 H, m, $NC\textit{H}_2CH_2NSi$), 3.01 (2 H, m, $NC\textit{H}_2CH_2NSi$), 2.89 (2 H, br s, $C_6H_5C\textit{H}_2$), 0.27 (18, H, s, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (125.7 MHz, 293 K, CD_2Cl_2): δ 159.2 (2-C_5H_4N), 152.4 (*i*-C_6H_5), 149.0 (6-C_5H_4N), 148.6 (*o*-C_6F_5, ^1J 226 Hz), 144.3 (4-C_5H_4N), 138.0 (*p*-C_6F_5, ^1J 245 Hz), 136.8 (*m*-C_6F_5, ^1J 237 Hz), 129.1 (*o*-C_6H_5), 127.2 (*m*-C_6H_5), 126.2 (5-C_5H_4N), 125.2 (3-C_5H_4N), 122.8 (*p*-C_6H_5), 60.2 ($N\textit{C}H_2CH_2NSi$), 59.4 ($C_5H_4N\textit{C}H_2$), 49.2 ($NCH_2\textit{C}H_2NSi$), 32.0 ($C_6H_5\textit{C}H_2$), 0.6 ($Si(CH_3)_3$). ^{19}F NMR (282.3 MHz, 293 K, CD_2Cl_2): δ −131.5 (6 F, d, ^3J 20.3 Hz, *o*-C_6F_5), −165.0 (3 F, t, ^3J 20.0 Hz, *p*-C_6F_5), −167.9 (6 F, m, ^3J 20.3, 20.0 Hz, *m*-C_6F_5). ^{11}B NMR (160.4 MHz, 293 K, CD_2Cl_2): δ −10.51 ($[PhCH_2B(C_6F_5)_3]^-$). IR (CsBr plates, Nujol): ν 1641 (w), 1612 (w), 1511 (m), 1307 (w), 1259 (m), 1213 (w), 1082 (m), 1026 (w), 982 (m), 930 (w), 894 (w), 840 (m), 800 (w), 755 (w), 723 (w), 704 (w), 681 (w), 651 (w), 634 (w), 606 (w), 570 (w), 550 (w), 528 (w) cm^{-1}. Anal. Found (calcd for $\mathrm{C_{41}H_{39}BClF_{15}N_4Si_2Zr}$): C, 46.0 (46.2); H, 3.8 (3.7); N, 5.3 (5.3).

Ti(N^{t}Bu)(N$_2$NN′) (14). To a solution of $\mathrm{Li_2N_2NN'}$ (339 mg, 0.97 mmol) in benzene (30 mL) cooled to 5 °C was added a solution of $\mathrm{Ti(N^tBu)Cl_2(py)_3}$ (368 mg, 0.83 mmol) in benzene (20 mL). The mixture was allowed to warm to room temperature and stirred for a further 90 min. The volatiles were removed under reduced pressure, leaving an orange-red solid, which was extracted into pentane (40 mL). The resulting red solution was filtered and concentrated to 20 mL, at which point the formation of a yellow crystalline solid began. The mixture was cooled to −30 °C for 2 days, and the resulting yellow solid was isolated and dried in vacuo affording **14**. Yield: 232 mg (61%).

^{1}H NMR (300.1 MHz, 293 K, $\mathrm{C_6D_6}$): δ 9.68 (1 H, d, ^3J 5.5 Hz, 6-$\mathrm{C_5H_4N}$), 6.71 (1 H, dd, ^3J 7.7, 7.7 Hz, 4-$\mathrm{C_5H_4N}$), 6.42 (1 H, dd, ^3J 5.5, 7.7 Hz, 5-$\mathrm{C_5H_4N}$), 6.12 (1 H, d, ^3J 7.7 Hz, 3-$\mathrm{C_5H_4N}$), 3.64 (2 H, m, $\mathrm{NCH_2C}H_2\mathrm{NSi}$), 3.38 (2 H, m, $\mathrm{NCH_2C}H_2\mathrm{NSi}$), 2.97 (2 H, s, $\mathrm{C_5H_4NC}H_2$), 2.47 (2 H, m, $\mathrm{NC}H_2\mathrm{CH_2NSi}$), 1.98 (2 H, m, $\mathrm{NC}H_2\mathrm{CH_2NSi}$), 1.69 (9 H, s, $\mathrm{C(CH_3)_3}$), 0.69 (18 H, s, $\mathrm{Si(CH_3)_3}$). ^{13}C{^{1}H} NMR (75.5 MHz, 293 K, $\mathrm{C_6D_6}$): δ 159.9 (2-$\mathrm{C_5H_4N}$), 155.7 (6-$\mathrm{C_5H_4N}$), 139.3 (4-$\mathrm{C_5H_4N}$), 122.1 (5-$\mathrm{C_5H_4N}$), 122.1 (3-$\mathrm{C_5H_4N}$), 65.4 ($C\mathrm{(CH_3)_3}$), 57.0 ($\mathrm{C_5H_4N}C\mathrm{H_2}$), 56.2 ($\mathrm{N}C\mathrm{H_2CH_2NSi}$), 49.1 ($\mathrm{NCH_2}C\mathrm{H_2NSi}$), 34.8 ($\mathrm{C(}C\mathrm{H_3)_3}$), 4.4 ($\mathrm{Si(CH_3)_3}$). IR (CsBr plates, Nujol): ν 1608 (m), 1571 (w), 1299 (w), 1235 (m), 1155 (w), 1096 (m), 1042 (w), 1018 (w), 937 (m), 836 (m), 757 (m), 682 (w), 592 (m), 552 (w), 531 (m), 457 (m) cm^{-1}. EI-MS: *m/z* 455 (11%), [M]$^+$; 440 (25%), [M − $\mathrm{CH_3}$]$^+$. Anal. Found (calcd for $\mathrm{C_{20}H_{41}N_5Si_2Ti}$): C, 52.5 (52.7); H, 8.9 (9.1); N, 15.0 (15.4).

Ti(NAr)(N$_2$NN′) (15). To a mixture of solid $\mathrm{Ti(N\text{-}2,6\text{-}C_6H_3{}^iPr_2)Cl_2(py)_3}$ (298 mg, 0.56 mmol) and $\mathrm{Li_2N_2NN'}$ (197 mg, 0.56 mmol) cooled to −78 °C was added benzene (10 mL). The mixture was allowed to warm to room temperature and stirred for a further 12 h. The volatiles were removed under reduced pressure, and the resulting orange solid was extracted into $\mathrm{CH_2Cl_2}$ (ca. 30 mL). The orange solution was filtered, and the volatiles were removed under reduced pressure to yield **15** as a red-orange solid. Yield: 183 mg (58%).

^{1}H NMR (500.0 MHz, 293 K, $\mathrm{CD_2Cl_2}$): δ 9.23 (1 H, d, ^3J 5.5 Hz, 6-$\mathrm{C_5H_4N}$), 7.88 (1 H, dd, ^3J 6.5, 7.5 Hz, 4-$\mathrm{C_5H_4N}$), 7.38 (1 H, d, ^3J 6.5 Hz, 3-$\mathrm{C_5H_4N}$), 7.34 (1 H, dd, ^3J 5.5, 7.5 Hz, 5-$\mathrm{C_5H_4N}$), 7.00 (2 H, d, ^3J 7.5 Hz, *m*-$\mathrm{C_6H_3}$), 6.70 (1 H, t, ^3J 7.5 Hz, *p*-$\mathrm{C_6H_3}$), 4.12 (2 H, m, ^3J 7.0 Hz, $\mathrm{C}H\mathrm{(CH_3)_2}$), 4.10 (2 H, s, $\mathrm{C_5H_4NC}H_2$), 3.77 (2 H, m, $\mathrm{NCH_2C}H_2\mathrm{NSi}$), 3.50 (2 H, m, $\mathrm{NCH_2C}H_2\mathrm{NSi}$), 3.10 (2 H, m, $\mathrm{NC}H_2\mathrm{CH_2NSi}$), 2.69 (2 H, m, $\mathrm{NC}H_2\mathrm{CH_2NSi}$), 1.15 (12 H, d, ^3J 7.0 Hz, $\mathrm{CH(C}H_3\mathrm{)_2}$), 0.22 (18 H, s, $\mathrm{Si(CH_3)_3}$). ^{13}C{^{1}H} NMR (125.7 MHz, 293 K, $\mathrm{CD_2Cl_2}$): δ 159.5 (2-$\mathrm{C_5H_4N}$), 154.8 (6-$\mathrm{C_5H_4N}$), 143.0 (*o*-$\mathrm{C_6H_3}$), 140.6 (4-$\mathrm{C_5H_4N}$), 123.7 (5-$\mathrm{C_5H_4N}$), 122.8 (3-$\mathrm{C_5H_4N}$), 122.8 (*m*-$\mathrm{C_6H_3}$), 117.6 (*p*-$\mathrm{C_6H_3}$), 59.6 ($\mathrm{N}C\mathrm{H_2CH_2NSi}$), 59.5 ($\mathrm{C_5H_4N}C\mathrm{H_2}$), 48.3 ($\mathrm{NCH_2}C\mathrm{H_2NSi}$), 27.5 ($C\mathrm{H(CH_3)_2}$), 24.9 ($\mathrm{CH(}C\mathrm{H_3)_2}$), 2.3 ($\mathrm{Si(CH_3)_3}$). IR (CsBr plates, Nujol): ν 1608 (m), 1417 (m), 1328 (m), 1269 (m), 1241 (m), 1161 (w), 1141 (w), 1069 (w), 1032 (w), 1020 (w), 957 (w), 933 (s), 893 (w), 873 (m), 837 (s), 804 (m), 758 (m), 682 (w), 593 (w), 553 (w) cm^{-1}. EI-MS: *m/z* 559 (30%), [M]$^+$; 544 (10%), [M − $\mathrm{CH_3}$]$^+$; 384 (65%), [M − NAr]$^+$. Anal. Found (calcd for $\mathrm{C_{28}H_{49}N_5Si_2Ti}$): C, 59.8 (60.1); H, 8.4 (8.8); N, 12.2 (12.5).

Zr(NAr)(N$_2$NN′) (16). To a yellow solution of $\mathrm{ZrCl_2(N_2NN')}$ (**1**) (163 mg, 0.33 mmol) in benzene (10 mL) was added dropwise a solution of $\mathrm{LiCH_2SiMe_3}$ (62 mg, 0.65 mmol) in benzene (10 mL). After complete addition the resulting opaque orange mixture was stirred for 5 min before being filtered. A solution of $\mathrm{ArNH_2}$ (58 mg, 62 μL, 0.33 mmol) in benzene (5 mL) was added to the solution and the mixture stirred at room temperature for 20 h to give a brown opaque mixture. The volatiles were removed under reduced pressure, and the resulting brown solid was washed with $\mathrm{CH_2Cl_2}$ (3 × 5 mL), giving **16** as an orange solid. Yield: 55 mg (27%).

^{1}H NMR (500.0 MHz, 293 K, $\mathrm{CD_2Cl_2}$): δ 9.18 (1 H, d, ^3J 5.0 Hz, 6-$\mathrm{C_5H_4N}$), 8.00 (1 H, dd, ^3J 7.5, 7.0 Hz, 4-$\mathrm{C_5H_4N}$), 7.49 (1 H, d, ^3J 7.5 Hz, 3-$\mathrm{C_5H_4N}$), 7.45 (1 H, dd, ^3J 5.0, 7.0 Hz, 5-$\mathrm{C_5H_4N}$), 6.87 (2 H, d, ^3J 7.5 Hz, *m*-$\mathrm{C_6H_3}$), 6.46 (1 H, t, ^3J 7.5 Hz, *p*-$\mathrm{C_6H_3}$), 4.14 (2 H, s, $\mathrm{C_5H_4NC}H_2$), 4.06 (2 H, m, ^3J 6.8 Hz, $\mathrm{C}H\mathrm{(CH_3)_2}$), 3.68 (2 H, m, $\mathrm{NCH_2C}H_2\mathrm{NSi}$), 3.41 (2 H, m, $\mathrm{NCH_2C}H_2\mathrm{NSi}$), 3.18 (2 H, m, $\mathrm{NC}H_2\mathrm{CH_2NSi}$), 2.68 (2 H, m, $\mathrm{NC}H_2\mathrm{CH_2NSi}$), 1.08 (12 H, d, ^3J 6.8 Hz, $\mathrm{CH(C}H_3\mathrm{)_2}$), 0.06 (18 H, s, $\mathrm{Si(CH_3)_3}$). The compound was too insoluble to obtain ^{13}C NMR data. IR (CsBr plates, Nujol): ν 1607 (m), 1580 (w), 1568 (w), 1416 (m), 1338 (m), 1277 (w), 1255 (w), 1241 (w), 1161 (w), 1139 (w), 1108 (w), 1098 (w), 1071 (m), 1053 (w), 1029 (w), 1000 (w), 926 (s), 869 (m), 836 (s), 797 (m), 754 (m), 724 (w), 680 (w), 649 (w), 635 (w), 624 (w), 606 (w), 587 (m), 543 (m), 454 (w), 430 (m) cm^{-1}. EI-MS: *m/z* 571 (18%), [M − $\mathrm{2CH_3}$]$^+$; 557 (10%), [M − $\mathrm{CH(CH_3)_2}$, H]$^+$; 543 (20%), [M − $\mathrm{CH_3}$, $\mathrm{CH(CH_3)_2}$]$^+$; 515 (18%), [M − 2 $\mathrm{CH(CH_3)_2}$]$^+$. Anal. Found (calcd for $\mathrm{C_{28}H_{49}N_5Si_2Zr}$): C, 55.5 (55.8); H, 7.9 (8.2); N, 10.9 (11.6).

Zr(NH^{t}Bu)$_2$(N$_2$NN′) (17). To a yellow solution of $\mathrm{ZrCl_2(N_2NN')}$ (**6**) (219 mg, 0.44 mmol) in benzene (20 mL) was added a colorless solution of $\mathrm{LiNH^tBu}$ in benzene (20 mL). The mixture was stirred at room temperature for 6 h, after which time the mixture attained an orange-red color and a small amount of precipitate formed. After filtering, the solid was washed with benzene (2 × 5 mL), and the volatiles of the combined filtrates were removed under reduced pressure. The resulting solid was triturated with pentane to give **17** as an orange-red solid. Yield: 122 mg (49%).

^{1}H NMR (300.1 MHz, 293 K, $\mathrm{C_6D_6}$): δ 8.89 (1 H, d, ^3J 5.4 Hz, 6-$\mathrm{C_5H_4N}$), 6.82 (1 H, dd, ^3J 7.8, 7.5 Hz, 4-$\mathrm{C_5H_4N}$), 6.49 (1 H, dd, ^3J 5.4, 7.5 Hz, 5-$\mathrm{C_5H_4N}$), 6.30 (1 H, d, ^3J 7.8 Hz, 3-$\mathrm{C_5H_4N}$), 5.22 (1 H, br s, NH), 4.22 (1 H, br s, NH), 3.67 (2 H, m, $\mathrm{NCH_2C}H_2\mathrm{NSi}$), 3.27 (2 H, s, $\mathrm{C_5H_4NC}H_2$), 3.17 (2 H, m, $\mathrm{NC}H_2\mathrm{CH_2NSi}$), 3.09 (2 H, m, $\mathrm{NCH_2C}H_2\mathrm{NSi}$), 2.13 (2 H, m, $\mathrm{NC}H_2\mathrm{CH_2NSi}$), 1.68 (9 H, s, $\mathrm{C(CH_3)_3}$), 1.50 (9 H, s, $\mathrm{C(CH_3)_3}$), 0.16 (18 H, s, $\mathrm{Si(CH_3)_3}$). ^{13}C{^{1}H} NMR (75.5 MHz, 293 K, $\mathrm{C_6D_6}$): δ 158.8 (2-$\mathrm{C_5H_4N}$), 149.2 (6-$\mathrm{C_5H_4N}$), 137.8 (4-$\mathrm{C_5H_4N}$), 122.5 (5-$\mathrm{C_5H_4N}$), 122.5 (3-$\mathrm{C_5H_4N}$), 59.8 ($\mathrm{C_5H_4N}C\mathrm{H_2}$), 58.0 ($\mathrm{N}C\mathrm{H_2CH_2NSi}$), 54.7 ($C\mathrm{(CH_3)_3}$), 54.4 ($C\mathrm{(CH_3)_3}$), 46.2 ($\mathrm{NCH_2}C\mathrm{H_2NSi}$), 35.9 ($\mathrm{C(}C\mathrm{H_3)_3}$), 35.1 ($\mathrm{C(}C\mathrm{H_3)_3}$), 1.5 ($\mathrm{Si(CH_3)_3}$). IR (CsBr plates, Nujol): ν 1604 (m), 1572 (w), 1364 (m), 1307 (w), 1254 (w), 1240 (m), 1214 (m), 1154 (w), 1065 (m), 985 (w), 967 (w), 944 (w), 910 (m), 897 (m), 832 (s), 774 (w), 756 (m), 726 (w), 677 (w), 584 (w) cm^{-1}. EI-MS: *m/z* 523 (5%), [M − 3 $\mathrm{CH_3}$, H]$^+$; 497 (3%), [M − $\mathrm{Si(CH_3)_3}$]$^+$. A satisfactory elemental analysis could not be obtained.

Zr(N^{t}Bu)(py)(N$_2$NN′) (18). To a yellow solution of $\mathrm{ZrCl_2(N_2NN')}$ (**1**) (241 mg, 0.48 mmol) in benzene (10 mL) was added 2 equiv of $\mathrm{LiCH_2SiMe_3}$ (91 mg, 0.97 mmol) in benzene (5 mL). The mixture was stirred for 5 min, after which time pyridine (1 mL) and a solution of $\mathrm{^tBuNH_2}$ (31.8 mg, 0.43 mmol) in benzene (5 mL) was added. The mixture was stirred for 6 h before the volatiles were removed under reduced pressure, yielding a dark red product, which was subsequently extracted into pentane (2 × 15 mL). The red pentane solution was filtered, concentrated to ca. 5 mL, and then cooled to −30 °C, resulting in the formation of a dark red solid, which was isolated and dried in vacuo, affording **18**. Yield: 183 mg (73%).

^{1}H NMR (300.1 MHz, 293 K, $\mathrm{C_6D_6}$): δ 9.86 (1 H, d, ^3J 5.4 Hz, 6-$\mathrm{C_5H_4N}$), 9.16 (2 H, br m, *o*-$\mathrm{C_5H_5N}$), 6.91 (1 H, tt, *p*-$\mathrm{C_5H_5N}$), 6.81 (1 H, td, ^3J 7.8, 7.8 Hz, 4-$\mathrm{C_5H_4N}$), 6.72 (2 H, t, *m*-$\mathrm{C_5H_5N}$), 6.55 (1 H, t, ^3J 5.4, 7.8 Hz, 5-$\mathrm{C_5H_4N}$), 6.28 (1 H, d, ^3J 7.8 Hz, 3-$\mathrm{C_5H_4N}$), 3.33 (4 H, m, $\mathrm{NCH_2C}H_2\mathrm{NSi}$), 3.26 (2 H, s, $\mathrm{C_5H_4NC}H_2$), 2.55 (2 H, m, $\mathrm{NC}H_2\mathrm{CH_2NSi}$), 2.08 (2 H, m, $\mathrm{NC}H_2\mathrm{CH_2NSi}$), 1.60 (9 H, s, $\mathrm{C(CH_3)_3}$), 0.52 (18 H, s, $\mathrm{Si(CH_3)_3}$). ^{13}C{^{1}H} NMR (75.5 MHz, 293 K, $\mathrm{C_6D_6}$): δ 159.1 (2-$\mathrm{C_5H_4N}$), 155.4 (6-$\mathrm{C_5H_4N}$), 152.2 (*o*-$\mathrm{C_5H_5N}$), 138.2 (4-$\mathrm{C_5H_4N}$), 137.1 (*p*-$\mathrm{C_5H_5N}$), 123.6 (*m*-$\mathrm{C_5H_5N}$), 121.8 (5-$\mathrm{C_5H_4N}$), 121.5 (3-$\mathrm{C_5H_4N}$), 60.6 ($C\mathrm{(CH_3)_3}$), 57.9 ($\mathrm{C_5H_4N}C\mathrm{H_2}$, $\mathrm{N}C\mathrm{H_2CH_2NSi}$), 46.9 ($\mathrm{NCH_2}$-

CH_2NSi), 36.0 ($C(CH_3)_3$), 3.8 ($Si(CH_3)_3$). IR (CsBr plates, Nujol): ν 1603 (s), 1571 (m), 1341 (w), 1305 (m), 1341 (s), 1214 (w), 1153 (m), 1133 (w), 1085 (w), 1069 (w), 1049 (w), 1037 (w), 1019 (w), 1011 (w), 993 (w), 969 (w), 942 (w), 919 (w), 899 (w), 834 (s), 754 (m), 726 (w), 701 (m), 676 (m), 628 (m), 612 (w), 578 (w), 558 (m), 522 (w), 508 (w), 483 (w), 443 (m), 421 (w), 403 (w) cm^{-1}. EI-MS: *m/z* 576 (27%), $[M]^+$; 505 (10%), $[M - NC(CH_3)_3]^+$. Anal. Found (calcd for $C_{25}H_{46}N_6Si_2Zr$): C, 51.8 (51.9); H, 8.4 (8.0); N, 14.9 (14.5).

$Zr(NH^tBu)(NC_5H_{10})(N_2NN')$ (19). To a yellow solution of $ZrCl_2(N_2NN')$ (**1**) (208 mg, 0.42 mmol) in benzene (5 mL) was added a colorless solution of $LiCH_2SiMe_3$ (65 mg, 0.83 mmol) in benzene (5 mL), resulting in the formation of a precipitate and an orange solution. The mixture was allowed to stir for 15 min before a solution of $^tBuNH_2$ (30 mg, 0.42 mmol) and piperidine (200 mg, 2.3 mmol) in pyridine (5 mL) was added dropwise. After complete addition the solution darkened while becoming clear. The solution was stirred for 4 h, after which time the volatiles were removed under reduced pressure and the resulting brown product was extracted into pentane (30 mL). After filtering, the red pentane solution was concentrated to 5 mL and cooled to −30 °C, resulting in the formation of **19** as a red, crystalline solid. Yield: 127 mg (52%).

^1H NMR (300.1 MHz, 298 K, C_6D_6): δ 8.78 (1 H, d, ^3J 5.1 Hz, 6-C_5H_4N), 6.75 (1 H, td, ^3J 8.1, 8.2 Hz, 4-C_5H_4N), 6.41 (1 H, td, ^3J 5.1, 8.2 Hz, 5-C_5H_4N), 6.22 (1 H, d, ^3J 8.1 Hz, 3-C_5H_4N), 4.22 (1 H, br s, NH), 3.93 (4 H, br m, 2,6-NC_5H_{10}), 3.67 (2 H, m, NCH_2CH_2NSi), 3.20 (2 H, s, $C_5H_4NCH_2$), 3.11 (4 H, m, NCH_2CH_2NSi, NCH_2CH_2NSi), 2.09 (2 H, m, NCH_2CH_2-NSi), 1.67 (6 H, br m, 3,4,5-NC_5H_{10}), 1.61 (9 H, s, $C(CH_3)_3$), 0.12 (18 H, s, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR data (75.5 MHz, 298 K, C_6D_6): δ 158.9 (2-C_5H_4N), 149.2 (6-C_5H_4N), 137.7 (4-C_5H_4N), 122.6 (5-C_5H_4N), 122.4 (3-C_5H_4N), 59.3 ($C_5H_4NCH_2$), 57.4 (NCH_2CH_2NSi), 57.0 (2,6-NC_5H_{10}), 56.9 (NCH_2CH_2NSi), 44.8 ($C(CH_3)_3$), 35.8 ($C(CH_3)_3$), 31.0 (4-NC_5H_{10}), 27.0 (3,5-NC_5H_{10}), 2.4 ($Si(CH_3)_3$). IR (CsBr plates, Nujol): ν 1645 (w), 1604 (s), 1571 (m), 1422 (w), 1358 (m), 1305 (m), 1254 (w), 1239 (w), 1202 (m), 1167 (w), 1155 (w), 1148 (w), 1129 (w), 1093 (m), 1078 (w), 1063 (w), 1041 (w), 1027 (w), 1011 (w), 995 (m), 969 (m), 942 (w), 911 (w), 775 (m), 756 (w), 741 (w), 726 (w), 676 (m), 666 (m), 633 (w), 622 (s), 584 (m), 564 (s), 493 (s), 468 (w), 448 (m), 420 (w), 406 (m) cm^{-1}. EI-MS: *m/z* 582 (6%), $[M]^+$; 510 (2%), $[M - NH^tBu]^+$. Anal. Found (calcd for $C_{25}H_{52}N_6Si_2Zr$): C, 51.6 (51.4); H, 9.1 (9.0); N, 14.7 (14.4).

$Nb(N^tBu)Cl(N_2NN')$ (20). To a yellow solution of $Nb(N^tBu)Cl_3(py)_2$ (326 mg, 0.71 mmol) in benzene (30 mL) was added dropwise a solution of Li_2N_2NN' (250 mg, 0.71 mmol) in benzene (40 mL), immediately resulting in a darkening of the coloration. The solution was stirred for 16 h, after which time the volatiles were removed under reduced pressure, yielding an orange-brown solid. The remaining solid was extracted into pentane (40 mL), filtered, concentrated to ca. 10 mL, and cooled to −80 °C to give **20** as a yellow solid. Yield: 114 mg (30%).

^1H NMR (300.1 MHz, 293 K, C_6D_6): δ 8.86 (1 H, d, ^3J 4.9 Hz, 6-C_5H_4N), 6.71 (1 H, dd, ^3J 7.2, 8.2 Hz, 4-C_5H_4N), 6.34 (1 H, dd, ^3J 4.9, 8.2 Hz, 5-C_5H_4N), 6.26 (1 H, d, ^3J 7.2 Hz, 3-C_5H_4N), 4.73 (1 H, d, ^2J 14.9 Hz, $C_5H_4NCH_2$), 3.70 (3 H, m, NCH_2CH_2NSi), 3.12 (1 H, m, NCH_2CH_2NSi), 2.90 (1 H, d, ^2J 14.9 Hz, $C_5H_4NCH_2$), 2.82 (1 H, m, NCH_2CH_2NSi), 2.30 (1 H, m, NCH_2CH_2NSi), 2.12 (1 H, m, NCH_2CH_2NSi), 2.00 (1 H, m, NCH_2CH_2NSi), 1.76 (9 H, s, $C(CH_3)_3$), 0.63 (9 H, s, $Si(CH_3)_3$), 0.37 (9 H, s, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (75.5 MHz, 293 K, C_6D_6): δ 159.9 (2-C_5H_4N), 150.5 (6-C_5H_4N), 137.3 (4-C_5H_4N), 122.0 (5-C_5H_4N), 121.3 (3-C_5H_4N), 66.5 ($C(CH_3)_3$), 64.5 ($C_5H_4NCH_2$), 59.9 (NCH_2CH_2NSi), 59.5 (NCH_2CH_2NSi), 53.2 (NCH_2CH_2NSi), 50.2 (NCH_2CH_2NSi), 32.6 ($C(CH_3)_3$), 3.0 ($Si(CH_3)_3$), 3.0 ($Si(CH_3)_3$). IR (CsBr plates, Nujol): ν 1606 (m), 1292 (w), 1243 (m), 1156 (w), 1113 (w), 1075 (m), 1018 (w), 930 (m), 864 (m), 837 (m), 776 (m), 724 (w), 685 (w), 592 (m), 549 (m), 442 (m) cm^{-1}. EI-MS: *m/z* 535 (32%), $[M]^+$; 500 (7%), $[M - Cl]^+$; 463 (11%), $[M - CH_3, C(CH_3)_3]^+$. Anal. Found (calcd for $C_{20}H_{41}ClN_5NbSi_2$): C, 44.4 (44.8); H, 7.3 (7.7); N, 12.7 (13.1).

$Ta(N^tBu)Cl(N_2NN')$ (21). To a green-yellow solution of $Ta(N^tBu)Cl_3(py)_2$ (430 mg, 0.83 mmol) in benzene (20 mL) cooled to 5 °C was added a solution of Li_2N_2NN' (291 mg, 0.83 mmol) in benzene (20 mL). The reaction was allowed to warm to room temperature and stirred for a further 16 h, giving an orange-brown opaque mixture. The volatiles were removed under reduced pressure, and the resulting solid was extracted into pentane. The solution was filtered and concentrated to ca. 5 mL, and upon cooling to −30 °C, a brown crystalline solid formed. This was isolated and dried in vacuo to afford **21**. Yield: 150 mg (29%).

^1H NMR (500.0 MHz, 293 K, C_6D_6): δ 9.00 (1 H, d, ^3J 5.0, Hz, 6-C_5H_4N), 6.71 (1 H, dd, ^3J 8.0, 7.5 Hz, 4-C_5H_4N), 6.34 (1 H, dd, ^3J 5.0, 7.5 Hz, 5-C_5H_4N), 6.26 (1 H, d, ^3J 8.0 Hz, 3-C_5H_4N), 4.64 (1 H, d, ^2J 15.1 Hz, $C_5H_4NCH_2$), 3.86 (1 H, m, NCH_2CH_2NSi), 3.80 (1 H, m, NCH_2CH_2NSi), 3.61 (1 H, m, NCH_2CH_2NSi), 3.35 (1 H, m, NCH_2CH_2NSi), 2.90 (1 H, d, ^2J 15.1 Hz, $C_5H_4NCH_2$), 2.80 (1 H, m, NCH_2CH_2NSi), 2.29 (1 H, m, NCH_2CH_2NSi), 2.19 (1 H, m, NCH_2CH_2NSi), 1.99 (1 H, m, NCH_2CH_2NSi), 1.74 (9 H, s, $C(CH_3)_3$), 0.59 (9 H, s, $Si(CH_3)_3$), 0.32 (9 H, s, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (125.7 MHz, 293 K, C_6D_6): δ 160.3 (2-C_5H_4N), 150.8 (6-C_5H_4N), 137.7 (4-C_5H_4N), 122.3 (5-C_5H_4N), 121.5 (3-C_5H_4N), 65.1 ($C(CH_3)_3$), 64.9 ($C_5H_4NCH_2$), 60.5 (NCH_2CH_2NSi), 59.8 (NCH_2CH_2NSi), 52.2 (NCH_2CH_2NSi), 49.1 (NCH_2CH_2NSi), 34.1 ($C(CH_3)_3$), 3.4 ($Si(CH_3)_3$), 3.2 ($Si(CH_3)_3$). IR (CsBr plates, Nujol): ν 1610 (s), 1571 (w), 1355 (m), 1294 (w), 1250 (m), 1212 (w), 1158 (m), 1141 (w), 1132 (w), 1110 (w), 1077 (m), 1055 (w), 1033 (m), 1023 (m), 936 (m), 868 (m), 839 (m), 789 (w), 760 (w), 726 (m), 686 (m), 650 (m), 634 (m), 589 (m), 551 (m), 527 (m), 470 (w) cm^{-1}. EI-MS: *m/z* 623 (58%), $[M]^+$; 608 (57%), $[M - CH_3]^+$; 552 (11%), $[M - NC(CH_3)_3]^+$; 521 (95%), $[M - N^tBu, 2\ CH_3, H]^+$. Anal. Found (calcd for $C_{20}H_{41}ClN_5Si_2Ta$): C, 38.4 (38.5); H, 6.6 (6.6); N, 11.0 (11.2).

H_2O_2NN' (22). 2-Aminomethylpyridine (5.0 g, 46.2 mmol) was added dropwise to isobutylene oxide (9.84 g, 136.7 mmol) with stirring in a thick-walled Teflon valve ampule. A catalytic amount of ethanol (3 mL) was added to the resulting yellow solution, which was frozen using liquid nitrogen and the headspace evacuated. The solution was stirred at 75 °C for 5 days. The volatiles were removed under reduced pressure to give a dark brown solid (13 g), which was purified in 5 g portions by column chromatography on silica (250 g, elution gradient CH_2Cl_2/EtOH, 100:0 to 95:5). Final purification was achieved by sublimation (80−100 °C, $0.5-1 \times 10^{-6}$ mbar) to give **22** as a white powder. Yield: 5.50 g (47%).

^1H NMR (300.1 MHz, 183 K, CD_2Cl_2): δ 8.48 (1 H, d, ^3J 4.0 Hz, 6-C_5H_4N), 7.66 (1 H, app.t, app.^3J 9.0 Hz, 4-C_5H_4N), 7.37 (1 H, d, ^3J 7.0 Hz, 3-C_5H_4N), 7.16 (1 H, app t, app.^3J 6.0 Hz, 5-C_5H_4N), 6.53 (2 H, br s, NCH_2CMe_2OH), 3.95 (2 H, s, $NCH_2C_5H_4N$), 2.65 (4 H, br s, NCH_2CMe_2OH), 1.16 (6 H, s, NCH_2CMe_2OH (“b”)), 0.96 (6 H, s, NCH_2CMe_2OH (“a”)). $^{13}C\{^1H\}$ NMR (75.5 MHz, 183 K, CD_2Cl_2): δ 159.0 (2-C_5H_4N), 147.8 (6-C_5H_4N), 135.9 (4-C_5H_4N), 121.7 (3-C_5H_4N), 121.2 (5-C_5H_4N), 71.2 (NCH_2CMe_2OH), 67.5 (NCH_2CMe_2OH), 63.7 ($NCH_2C_5H_4N$), 27.2 (NCH_2CMe_2OH (“a”)), 26.3 (NCH_2CMe_2OH (“b”)). The arbitrary designations “a” and “b” refer to the chemically distinct methyl groups. IR (KBr plates, Nujol): ν 3217 (br s), 1591 (w), 1568 (w), 1261 (w), 1200 (w), 1154 (w), 1126 (w), 1101 (m), 1084 (m), 1047 (w), 1023 (w), 995 (w), 972 (w), 935 (w), 907 (w), 855 (w), 800 (w), 766 (w), 723 (w), 645 (w), 622 (w), 583 (w), 488 (w) cm^{-1}. EI-MS: *m/z* 252 (23%), $[M]^+$; 192 (97%), $[M - CMe_2OH]^+$; 162 (97), $[M - CMe_2OH, - 2Me]^+$; 134 (68%), $[M - 2CMe_2OH, + H]^+$; 92 (100%), $[CH_2C_5H_4N + H]^+$; 91 (80%), $[CH_2C_5H_4N]^+$. Anal. Found (calcd for $C_{14}H_{24}N_2O$): C, 66.6 (66.6); H, 9.7 (9.6); N, 11.2 (11.1).

$Ti(O_2NN')_2$ (23). To a stirred solution of $Ti(NMe_2)_4$ (0.329 g, 1.47 mmol) in benzene (20 mL), cooled to 7 °C, was added dropwise a solution of H_2O_2NN' (**22**) (0.734 g, 2.93 mmol) in benzene (20 mL). The solution was allowed to warm to room temperature and was stirred for 16 h. The volatiles were removed under reduced pressure to give a highly soluble waxy white solid, which was washed with pentane (25 mL) at 7 °C and dried in vacuo to give Ti(O$_2$NN′)$_2$ (**23**) as a free-flowing white powder. Yield: 0.643 g (80%).

^{1}H NMR (300.1 MHz, 193 K, CD$_2$Cl$_2$): δ 8.50 (2 H, dd, ^3J 5.5 Hz, ^4J 2.0 Hz, 6-C$_5$H$_4$N), 7.69 (2 H, app td, app. ^3J 7.5 Hz, ^4J 2.0 Hz, 4-C$_5$H$_4$N), 7.29−7.20 (4 H, overlapping m, 3-, 5-C$_5$H$_4$N), 4.42 (2 H, d, ^2J 14.5 Hz, NCH_2C$_5$H$_4$N), 3.99 (2 H, d, ^2J 14.5 Hz, NCH_2C$_5$H$_4$N), 3.28 (2 H, d, ^2J 14.0 Hz, NCH_2CMe$_2$O ("a")), 3.01 (2 H, d, ^2J 13.0 Hz, NCH_2CMe$_2$O ("b")), 2.60 (2 H, d, ^2J 13.0 Hz, NCH_2CMe$_2$O ("b")), 2.53 (2 H, d, ^2J 14.0 Hz, NCH_2CMe$_2$O ("a")), 1.61 (6 H, s, NCH$_2$CMe_2O), 1.32 (6 H, s, NCH$_2$CMe_2O), 1.05 (12 H, overlapping 2 × s, NCH$_2$CMe_2O). ^{13}C{^{1}H} NMR (75.5 MHz, 193 K, CD$_2$Cl$_2$): δ 156.1 (2-C$_5$H$_4$N), 148.4 (6-C$_5$H$_4$N), 135.4 (4-C$_5$H$_4$N), 125.0 (5-C$_5$H$_4$N), 121.8 (3-C$_5$H$_4$N), 81.0 (NCH$_2$$CMe_2$O), 80.9 (NCH$_2$$CMe_2$O), 70.0 (N$CH_2CMe_2$O ("b")), 64.8 (N$CH_2C_5H_4$N), 63.8 (N$CH_2CMe_2$O ("a")), 31.0 (NCH$_2CMe_2$O), 29.9 (NCH$_2CMe_2$O), 29.5 (NCH$_2CMe_2$O), 27.6 (NCH$_2CMe_2$O). The arbitrary designations "a" and "b" refer to the chemically distinct "arms".

IR (KBr plates, Nujol): ν 1588 (w), 1572 (w), 1302 (w), 1262 (w), 1209 (w), 1156 (w), 1079 (w), 992 (w), 954 (w), 918 (w), 852 (w), 799 (w), 772 (w), 723 (w), 652 (w), 633 (w), 603 (w), 583 (w), 551 (w), 474 (w), 442 (w) cm^{-1}. EI-MS: m/z 490 (13%), [M − CMe$_2$OH, + H]$^+$; 398 (100%) [M − CMe$_2$OH, − CH$_2$C$_5$H$_4$N, + H]$^+$; 298 (68%), [M − C$_5$H$_4$N(CH$_2$)N(CH$_2$CMe$_2$O)]$^+$; 93 (76%), [CH$_2$C$_5$H$_4$N + H]$^+$; 92 (65%), [CH$_2$C$_5$H$_4$N]$^+$. Anal. Found (calcd for C$_{28}$H$_{44}$N$_4$O$_4$Ti): C, 61.0 (61.3); H, 8.1 (8.1); N, 10.2 (10.2).

TiCl$_2$(O$_2$NN′) (24). To a stirred slurry of TiCl$_4$(THF)$_2$ (0.274 g, 8.20 mmol) in benzene (25 mL) cooled to 7 °C was added dropwise a solution of Ti(O$_2$NN′)$_2$ (**23**) (0.450 g, 8.20 mmol) in benzene (20 mL). The solution was allowed to warm to room temperature and was stirred for a further 3 h (on warming, a yellow wax was formed and was triturated by the stirring). The volatiles were removed under reduced pressure to give the crude product as a white powder, which was washed with pentane (60 mL) and dried in vacuo to give **24**. Yield: 0.540 g (90%).

^{1}H NMR (300.1 MHz, 293 K, pyridine-d_5): δ 9.37 (1 H, d, ^3J 6.0 Hz, 6-C$_5$H$_4$N), 7.80 (1 H, dd, ^3J 7.5 Hz, ^3J 6.9 Hz, 4-C$_5$H$_4$N), 7.38 (1 H, d, ^3J 7.5 Hz, 3-C$_5$H$_4$N), 7.24 (1 H, dd, ^3J 7.0 Hz, ^3J 6.0 Hz, 5-C$_5$H$_4$N), 4.89 (2 H, s, NCH_2C$_5$H$_4$N), 3.78 (2 H, d, ^2J 12.0 Hz, NCH_2CMe$_2$O), 3.51 (2 H, d, ^2J 12.0 Hz, NCH_2CMe$_2$O), 1.48 (6 H, s, NCH$_2$CMe_2O), 1.03 (6 H, s, NCH$_2$CMe_2O). ^{13}C{^{1}H} NMR (75.5 MHz, 293 K, pyridine-d_5): δ 159.6 (2-C$_5$H$_4$N), 140.7 (6-C$_5$H$_4$N), 129.2 (4-C$_5$H$_4$N), 124.8 (5-C$_5$H$_4$N), 122.6 (3-C$_5$H$_4$N), 90.7 (NCH$_2$$CMe_2$O), 78.6 (N$CH_2CMe_2$O), 68.4 (N$CH_2C_5H_4$N), 29.7 (NCH$_2CMe_2$O), 28.8 (NCH$_2CMe_2$O). IR (CsBr plates, Nujol): ν 1608 (w), 1573 (w), 1291 (w), 1262 (w), 1225 (w), 1207 (w), 1173 (w), 1151 (m), 1092 (w), 1079 (w), 1061 (w), 1022 (w), 975 (m), 946 (m), 906 (w), 830 (w), 803 (w), 786 (w), 765 (w), 721 (w), 686 (w), 656 (m), 611 (m), 528 (w), 503 (w), 468 (w), 413 (m) cm^{-1}. EI-MS: m/z 368 (1%), [M]$^+$; 333 (3%), [M − Cl]$^+$. Anal. Found (calcd for C$_{14}$H$_{22}$Cl$_2$N$_2$O$_2$Ti): C, 45.8 (45.6); H, 6.2 (6.0); N, 7.4 (7.6).

ZrCl$_2$(O$_2$NN′) (25). A solution of H$_2$O$_2$NN′ (**22**) (0.36 g, 1.4 mmol) in benzene (15 mL) was added dropwise to ZrCl$_2$(CH$_2$SiMe$_3$)$_2$(Et$_2$O)$_2$ (0.70 g, 1.4 mmol) in benzene (20 mL) with cooling using an ice/water bath. The mixture was allowed to warm to room temperature and stirred overnight. A white precipitate progressively appeared. The volatiles were removed under reduced pressure, and the resulting powder was extracted into 60 mL of dichloromethane. Filtration and evaporation of the solvent gave **25** as a white powder. Yield: 0.30 g (52%).

^{1}H NMR (500.0 MHz, 293 K, C$_6$D$_6$): δ 9.12 (1 H, d, ^3J 6.0 Hz, 6-C$_5$H$_4$N), 6.68 (1 H, ddd, ^3J 7.2 and 8.1 Hz, ^4J 1.7 Hz, 4-C$_5$H$_4$N), 6.17 (1 H, dd, ^3J 4.9, 7.2 Hz, 5-C$_5$H$_4$N), 6.09 (1 H, d, ^3J 8.1 Hz, 3-C$_5$H$_4$N), 3.68 (2 H, s, NC$_5$H$_4$NCH_2), 3.05 (2 H, d, ^2J 12.7 Hz, NCH_2CMe$_2$), 2.44 (2 H, d, ^2J 12.7 Hz, NCH_2CMe$_2$), 1.31 (6 H, s, CMe_2), 0.7 (6 H, s, CMe_2). The compound is too soluble in C$_6$D$_6$ and CD$_2$Cl$_2$ to record ^{13}C{^{1}H} NMR data. IR (Nujol mull, KBr plates): ν 1608 (w), 1572 (w), 1296 (w), 1261 (w), 1207 (w), 1174 (m), 1158 (m), 1079 (m), 1059 (w), 1019 (m), 983 (m), 948 (w), 801 (w), 767 (w), 684 (w), 641 (w), 617 (w) cm^{-1}. Anal. Found (calcd for C$_{14}$H$_{22}$Cl$_2$N$_2$O$_2$Zr): C, 48.2 (48.8); H, 5.4 (5.4); N, 6.5 (6.8); Cl, 16.5, (17.2).

Zr(NMe$_2$)$_2$(O$_2$NN′) (26). A solution of H$_2$O$_2$NN′ (**22**) (220 mg, 0.87 mmol) in benzene (20 mL) was added dropwise to Zr(NMe$_2$)$_4$ (233 mg, 0.87 mmol) in benzene (15 mL) with stirring and cooling using an ice/water bath. This produced an immediate darkening in color to give a bright orange solution by the end of the addition. The solution was stirred at room temperature for ca. 30 min, which produced no further color change, and the volatiles were subsquently removed under reduced pressure to leave a red solid, which was recrystallized from pentane to give **26** as an orange solid. Yield: 129 mg (34%).

^{1}H NMR (500. MHz, 293 K, C$_6$D$_6$): δ 8.61 (1 H, d, ^3J 5.5 Hz, 6-C$_5$H$_4$N), 6.82 (1 H, dd, ^3J 8.4 Hz, ^3J 7.7 Hz, 4-C$_5$H$_4$N), 6.46 (1 H, dd, ^3J 7.7 Hz, ^3J 5.5 Hz,5-C$_5$H$_4$N), 6.21 (1 H, d, ^3J 8.4 Hz, 3-C$_5$H$_4$N), 3.74 (2 H, s, C$_5$H$_4$NCH_2), 3.68 (6 H, s, NMe$_2$ *cis* or *trans* to C$_5$H$_4$N), 3.40 (6 H, s, NMe$_2$ *trans* or *cis* to C$_5$H$_4$N), 2.89 (2 H, d, ^2J = 12.3 Hz, NCH_2CMe$_2$), 2.53 (2 H, d, ^2J = 12.3 Hz, NCH_2CMe$_2$), 1.32 (6 H, s, CMe_2), 0.79 (6 H, s, CMe_2). ^{13}C{^{1}H} NMR (75.5 MHz, 293 K, C$_6$D$_6$): δ 160.1 (2-C$_5$H$_4$N), 151.3 (6-C$_5$H$_4$N), 137.7 (4-C$_5$H$_4$N), 122.7 (5-C$_5$H$_4$N), 119.9 (3-C$_5$H$_4$N), 79.5 (CMe$_2$), 76.2 (NCH$_2$CMe$_2$), 65.9 (C$_5$H$_4$NCH$_2$), 47.9 (NMe$_2$ *cis* or *trans* to C$_5$H$_4$N), 43.9 (NMe$_2$ *trans* or *cis* to C$_5$H$_4$N), 32.6 (CMe_2), 29.0 (CMe_2). IR (CsBr plates, Nujol): ν cm^{-1} 2746 (m), 1632 (w), 1602 (w), 1572 (w), 1300 (w), 1286 (w), 1261 (w), 1238 (w), 1221 (w), 1202 (w), 1182 (m), 1160 (m), 1129 (w), 1091 (m), 1051 (w), 1013 (w), 996 (m), 981 (m), 953 (m), 902 (w), 846 (w), 816 (w), 799 (w), 767 (m), 725 (m), 682 (w), 634 (w), 611 (w), 585 (w), 556 (m), 521 (w). Anal. Found (calcd for C$_{18}$H$_{34}$N$_4$O$_2$Zr): C, 50.1 (50.3); H, 7.8 (8.0); N, 12.8 (13.0).

Zr(CH$_2$SiMe$_3$)$_2$(O$_2$NN′) (27). A solution of H$_2$O$_2$NN′ (**22**) (0.254 g, 1 mmol) in benzene (20 mL) was added dropwise to Zr(CH$_2$SiMe$_3$)$_4$ (0.441 g, 1 mmol) in benzene (20 mL) with cooling using an ice/water bath. The mixture was allowed to warm to room temperature and was stirred overnight. The volatiles were subsequently removed under reduced pressure, and the resulting solids were extracted into 80 mL of dry pentane. The orange solution was filtered, concentrated to 60 mL, and cooled to −30 °C to give **27** as pale orange crystals. Yield: 0.356 g (69%).

^{1}H NMR (500.0 MHz, 293 K, C$_6$D$_6$): δ 8.59 (1 H, d, ^3J 5.3 Hz, 6-C$_5$H$_4$N), 6.83 (1 H, ddd, ^3J 7.6, 8.0 Hz, ^4J 1.7 Hz, 4-C$_5$H$_4$N), 6.42 (1 H, dd, ^3J 5.3, 7.6 Hz, 5-C$_5$H$_4$N), 6.19 (1 H, d, ^3J 8.0 Hz, 3-C$_5$H$_4$N), 3.60 (2 H, s, NC$_5$H$_4$NCH_2), 2.43 (2 H, Part A of an AB system, ^2J 12.8 Hz, NCH_2CMe$_2$), 2.37 (2 H, Part B of an AB system, ^2J 12.8 Hz, NCH_2CMe$_2$), 1.24 (6 H, s, CMe_2), 0.70 (6 H, s, CMe_2), 0.55 (9 H, s, CH$_2$SiMe_3 *cis* to pyridyl group), 0.55 (2 H, s, CH_2SiMe$_3$ *trans* to pyridyl group), 0.44 (9 H, s, CH$_2$SiMe_3 trans to pyridyl group), 0.26 (2 H, s, CH_2SiMe$_3$ *cis* to pyridyl group). ^{13}C{^{1}H} NMR (75.5 MHz, 293 K, C$_6$D$_6$): δ 160.3 (2-C$_5$H$_4$N), 150.2 (6-C$_5$H$_4$N), 138.1 (4-C$_5$H$_4$N), 122.4 (5-C$_5$H$_4$N), 120.3 (3-C$_5$H$_4$N), 80.8 (CMe$_2$), 76.5 (NCH$_2$CMe$_2$), 66.7 (NC$_5$H$_4$NCH$_2$), 47.6 (CH$_2$SiMe$_3$ *trans* to pyridyl group), 45.0 (CH$_2$SiMe$_3$ *cis* to pyridyl group), 32.4 (CMe_2), 29.1 (CMe_2), 4.6 (CH$_2$SiMe_3 *cis* to pyridyl group), 4.2 (CH$_2$SiMe_3 *trans* to pyridyl group). IR (Nujol mull): ν 1604 (w), 1574 (w), 1302 (w), 1287 (w), 1249 (w), 1238 (w), 1204 (w), 1185 (m), 1089 (w), 1060 (w), 1002 (w), 950 (w), 872 (m), 853 (m), 824 (w), 763 (m), 741 (w), 677 (w), 637 (w) cm^{-1}. MS-EI: m/z 499 (5%), [M − CH$_3$]$^+$; 427 (100%), [M − CH$_2$SiMe$_3$]$^+$. Anal. Found (calcd for C$_{22}$H$_{44}$N$_2$O$_2$Si$_2$Zr): C, 50.4; (51.2); H, 8.8 (8.6); N, 5.4 (5.4).

[Zr(CH$_2$SiMe$_3$)(THF)(O$_2$NN′)][Me$_3$SiCH$_2$BAr^F$_3$] (28-Me$_3$SiCH$_2$BAr^F$_3$). A solution of BAr^F$_3$ (0.070 g, 0.136 mmol) in

Table 8. X-ray Data Collection and Processing Parameters for $\mathrm{Zr(CH_2Ph)_2(N_2NN')}$ (3), $\mathrm{ZrCl(CH_2Ph)(N_2NN')}$ (6), $\mathrm{Ti(NAr)(N_2NN')}$ (15), $\mathrm{Zr(NH^tBu)(NC_5H_{10})(N_2NN')}$ (19), $\mathrm{Ta(N^tBu)Cl(N_2NN')}$ (21), $\mathrm{H_2O_2NN'}$ (22), and $\mathrm{Zr(CH_2SiMe_3)_2(O_2NN')}$ (27)

	3	**6**	**15**
empirical formula	$C_{30}H_{46}N_4Si_2Zr$	$C_{23}H_{39}ClN_4Si_2Zr$	$C_{28}H_{49}N_5Si_2Ti$
fw	610.12	554.44	559.8
temp/K	150	175	170
wavelength/Å	0.71073	0.71073	0.71073
space group	$P2_1/n$	$P4_2/n$	$Pbcm$
a/Å	13.296(1)	25.584(1)	9.8632(4)
b/Å	17.017(1)	25.584(1)	18.413(1)
c/Å	14.262(1)	8.459(1)	17.507(1)
α/deg	90	90	90
β/deg	94.792(5)	90	90
γ/deg	90	90	90
V/Å^3	3215.6(8)	5536.0(9)	3179.4(8)
Z	4	8	4
d(calcd)/Mg·m^{-3}	1.26	1.33	1.17
abs coeff/mm^{-1}	0.43	0.59	0.36
R indices R_1, R_w	$R_1 = 0.0564$	$R_1 = 0.0692$	$R_1 = 0.0574$
$[I > 3\sigma(I)]^a$	$R_w = 0.0424$	$R_w = 0.0647$	$R_w = 0.0434$

	19	**21**	**22**	**27**
empirical formula	$C_{25}H_{52}N_6Si_2Zr$	$C_{20}H_{41}ClN_5Si_2Ta$	$C_{14}H_{24}N_2O_2$	$C_{22}H_{44}N_2O_2Si_2Zr$
fw	584.12	624.16	252.36	5115.99
temp/K	150	175	150	150
wavelength/Å	0.71073	0.71073	0.71073	0.71073
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a/Å	9.586(1)	12.828(1)	14.8201(5	11.0613(2)
b/Å	16.247(1)	14.178(2)	6.2365(2)	13.2371(2)
c/Å	20.632(2)	31.148(3)	16.7248(7)	20.4745(4)
α/deg	90	90	90	107.2552(8)
β/deg	103.30(1)	100.19(3)	107.934(2)	95.4488(8)
γ/deg	90	90	90	95.4178(9)
V/Å^3	3127(1)	5576(1)	1470.7(1)	2826.21(9)
Z	4	8	4	4
d(calcd)/Mg·m^{-3}	1.24	1.49	1.14	1.21
abs coeff/mm^{-1}	0.44	4.09	0.076	0.49
R indices R_1, R_w	$R_1 = 0.0253$	$R_1 = 0.0246$	$R_1 = 0.0385$	$R_1 = 0.0355$
$[I > 3\sigma(I)]^a$	$R_w = 0.0260$	$R_w = 0.0293$	$R_w = 0.0400$	$R_w = 0.0349$

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = \sqrt{\{\sum w(|F_o| - |F_c|)^2/\sum(w|F_o|^2\}}$.

$\mathrm{CH_2Cl_2}$ (3 mL) was added at room temperature to $\mathrm{Zr(CH_2SiMe_3)_2(O_2NN')}$ (**27**) (0.071 g, 0.138 mmol) in $\mathrm{CH_2Cl_2}$ (4 mL) in the presence of THF (12 μL, 0.139 mmol). After 90 min at room temperature, the volatiles were removed under reduced pressure to yield **28**-$\mathrm{Me_3SiCH_2BAr^F_3}$ as a white powder. Yield: 0.13 g (87%).

^{1}H NMR (500.0 MHz, 293 K, $\mathrm{CD_2Cl_2}$): δ 8.94 (1 H, d, ^3J 5.2 Hz, 6-$\mathrm{C_5H_4N}$), 8.11 (1 H, ddd, ^3J 7.6, 8.0 Hz, ^4J 1.7 Hz, 4-$\mathrm{C_5H_4N}$), 7.62 (1 H, dd, ^3J 5.2, 7.6 Hz, 5-$\mathrm{C_5H_4N}$), 6.19 (1 H, d, ^3J 8.0 Hz, 3-$\mathrm{C_5H_4N}$), 4.41 (2 H, s, $\mathrm{NC_5H_4NC}\mathit{H}_2$), 4.38 (4 H, br m, $\mathrm{O(C}\mathit{H}_2\mathrm{CH_2)_2}$), 3.22 (2 H, part A of an AB system, ^2J 13.7 Hz, $\mathrm{NC}\mathit{H}_2\mathrm{CMe_2}$), 3.12 (2 H, part B of an AB system, ^2J 13.7 Hz, $\mathrm{NC}\mathit{H}_2\mathrm{CMe_2}$), 2.10 (4 H, br m, $\mathrm{O(CH_2C}\mathit{H}_2\mathrm{)_2}$), 1.33 (6 H, s, $\mathrm{C}\mathit{Me}_2$), 1.05 (6 H, s, $\mathrm{C}\mathit{Me}_2$), 0.51 (2 H, br s, $\mathrm{BC}\mathit{H}_2\mathrm{SiMe_3}$), 0.31 (2 H, s, $\mathrm{C}\mathit{H}_2\mathrm{SiMe_3}$ *cis* to pyridyl group), −0.08 (9 H, s, $\mathrm{CH_2Si}\mathit{Me}_3$ *cis* to pyridyl group), −0.39 (s, 2 H, $\mathrm{BCH_2Si}\mathit{Me}_3$). ^{13}C{^{1}H} NMR (125.7 MHz, 293 K, $\mathrm{CD_2Cl_2}$): δ 159.6 (2-$\mathrm{C_5H_4N}$), 151.5 (6-$\mathrm{C_5H_4N}$), 148.7 (^1J 232 Hz, *o*-$\mathrm{C_6F_5}$), 142.4 (4-$\mathrm{C_5H_4N}$), 137.9 (^1J 243 Hz, *p*-$\mathrm{C_6F_5}$), 136.7 (^1J 268 Hz, m−$\mathrm{C_6F_5}$), 128.9 (v br, B*C*), 125.1 (5-$\mathrm{C_5H_4N}$), 124.1 (3-$\mathrm{C_5H_4N}$), 82.6 ($\mathit{C}\mathrm{Me_2}$), 75.6 ($\mathrm{O(}\mathit{C}\mathrm{H_2CH_2)_2}$), 73.9 ($\mathrm{N}\mathit{C}\mathrm{H_2CMe_2}$), 64.3 ($\mathrm{NC_5H_4N}\mathit{C}\mathrm{H_2}$), 48.0 ($\mathit{C}\mathrm{H_2SiMe_3}$ *cis* to pyridyl group), 32.7 ($\mathrm{C}\mathit{Me}_2$), 30.4 ($\mathrm{C}\mathit{Me}_2$), 25.7 ($\mathrm{O(CH_2}\mathit{C}\mathrm{H_2)_2}$), 9.0 (v br, $\mathrm{B}\mathit{C}\mathrm{H_2SiMe_3}$), 2.7 ($\mathrm{CH_2Si}\mathit{Me}_3$ *cis* to pyridyl group), 1.1 ($\mathrm{CH_2Si}\mathit{Me}_3$ *trans* to pyridyl group). ^{19}F NMR (282 MHz, $\mathrm{CD_2Cl_2}$, 293 K): δ −132.17 (6 F, d, ^3J 19.8 Hz, *o*-$\mathrm{C_6F_5}$), −165.25 (3 F, t, ^3J 20.2 Hz, *p*-$\mathrm{C_6F_5}$), −167.91 (6 F, m, *m*-$\mathrm{C_6F_5}$). IR (Nujol mull, KBr plates): ν 1638 (m), 1612 (m), 1572 (w), 1559 (w), 1542 (w), 1510 (s), 1175 (m), 1127 (vw), 1079 (s), 861 (w), 827 (m), 782 (m), 767 (w), 670 (w), 627 (w) cm^{-1}. Anal. Found (calcd for $\mathrm{C_{44}H_{52}BF_{15}N_2O_3Si_2Zr\cdot 0.6CH_2Cl_2}$): C 46.2 (46.5), H 5.0 (4.7), N 2.6 (2.4).

$\mathrm{[Zr_2(CH_2SiMe_3)_2(O_2NN')_2][Me_3SiCH_2BAr^F_3]_2}$ (29-$\mathrm{Me_3SiCH_2BAr^F_3}$). A solution of $\mathrm{BAr^F_3}$ (0.099 g, 0.193 mmol) in benzene (15 mL) was added to $\mathrm{Zr(CH_2SiMe_3)_2(O_2NN')}$ (**27**) (0.100 g, 0.193 mmol) in benzene (15 mL) with cooling using an ice/water bath. The mixture was allowed to warm to room temperature, and the stirring was continued for a further 30 min. The volatiles were removed under reduced pressure to yield a colorless oily compound, which was triturated with $\mathrm{Et_2O}$. The compound **29** was obtained as a white powder after removal of the volatiles under reduced pressure. Yield: 0.11 g (90%).

^{1}H NMR (500.0 MHz, 293 K, $\mathrm{CD_2Cl_2}$): δ 8.86 (1 H, d, ^3J 5.2 Hz, 6-$\mathrm{C_5H_4N}$), 8.31 (1 H, ddd, ^3J 7.5, 8.1 Hz, ^4J 1.5 Hz, 4-$\mathrm{C_5H_4N}$), 7.90 (1 H, dd, ^3J 5.2, 7.5 Hz, 5-$\mathrm{C_5H_4N}$), 7.77 (1 H, d, ^3J 8.1 Hz, 3-$\mathrm{C_5H_4N}$), 4.94 (2 H, d, ^2J 16.4 Hz, $\mathrm{NC_5H_4NC}\mathit{H}_2$), 4.35 (2 H, d, ^2J 16.4 Hz, $\mathrm{NC_5H_4NC}\mathit{H}_2$), 3.85 (2 H, d, ^2J 14.4 Hz, $\mathrm{NC}\mathit{H}_2\mathrm{CMe_2}$), 3.58 (2 H, d, ^2J 14.4 Hz, $\mathrm{NC}\mathit{H}_2\mathrm{CMe_2}$), 3.07 (2 H, d, ^2J 14.3 Hz, $\mathrm{NC}\mathit{H}_2\mathrm{CMe_2}$), 2.73 (2 H, d, ^2J 14.3 Hz, $\mathrm{NC}\mathit{H}_2\mathrm{CMe_2}$), 1.84 (6 H, s, $\mathrm{C}\mathit{Me}_2$), 1.70 (6 H, s, $\mathrm{C}\mathit{Me}_2$), 1.49 (6 H, s, $\mathrm{C}\mathit{Me}_2$), 1.41 (6 H, s, $\mathrm{C}\mathit{Me}_2$), 0.87 (2 H, part A of an AB system, ^2J 11.7 Hz, $\mathrm{C}\mathit{H}_2\mathrm{SiMe_3}$), 0.80 (2 H, part B of an AB system, ^2J 11.7 Hz,$\mathrm{C}\mathit{H}_2\mathrm{SiMe_3}$), 0.51 (2 H, br s, $\mathrm{BC}\mathit{H}_2\mathrm{SiMe_3}$), −0.31 and −0.36 (2 × 9 H, 2 × s, $\mathrm{CH_2Si}\mathit{Me}_3$ and $\mathrm{BCH_2Si}\mathit{Me}_3$). ^{13}C{^{1}H} NMR (125.7 MHz, 293 K, $\mathrm{CD_2Cl_2}$): δ 155.9 (2-$\mathrm{C_5H_4N}$), 148.9 (6-$\mathrm{C_5H_4N}$), 148.5 (d, ^1J 242 Hz, o-$\mathrm{C_6F_5}$), 144.1 (4-$\mathrm{C_5H_4N}$), 138.6 (d, ^1J 245 Hz, *p*-$\mathrm{C_6F_5}$), 136.6 (d, ^1J 234 Hz, *m*-$\mathrm{C_6F_5}$), 126.2 (3-$\mathrm{C_5H_4N}$), 126.1 (5-$\mathrm{C_5H_4N}$), 88.1 ($\mathit{C}\mathrm{Me_2}$), 87.0 ($\mathit{C}\mathrm{Me_2}$), 75.2 ($\mathrm{N}\mathit{C}\mathrm{H_2CMe_2}$), 69.1 ($\mathrm{N}\mathit{C}\mathrm{H_2CMe_2}$), 67.4 ($\mathit{C}\mathrm{H_2SiMe_3}$), 63.5 ($\mathrm{NC_5H_4N}\mathit{C}\mathrm{H_2}$), 33.0 ($\mathrm{C}\mathit{Me}_2$), 32.9 ($\mathrm{C}\mathit{Me}_2$), 31.8 ($\mathrm{C}\mathit{Me}_2$), 29.8 ($\mathrm{C}\mathit{Me}_2$), 15.4 ($\mathrm{B}\mathit{C}\mathrm{H_2SiMe_3}$), 1.6 ($\mathrm{CH_2Si}\mathit{Me}_3$), 1.1 ($\mathrm{CH_2Si}\mathit{Me}_3$). ^{19}F NMR (282 MHz, 293 K, $\mathrm{CD_2Cl_2}$): δ −132.10 (6 F, d, ^3J, *o*-$\mathrm{C_6F_5}$), −165.06 (3 F, t, ^3J 20.6 Hz, *p*-$\mathrm{C_6F_5}$), −167.74 (6 F, m, *m*-$\mathrm{C_6F_5}$). IR (Nujol mull): ν 1646 (m), 1614 (m), 1571 (w), 1559 (w), 1542 (w), 1510 (s), 1305 (vw), 1128 (vw), 1079 (s), 910 (w), 848 (w), 828 (m), 768 (m), 687 (w), 644 (w), 625 (w) cm^{-1}. Anal. Found (calcd for $\mathrm{C_{40}H_{44}BF_{15}N_2O_2Si_2Zr}$): C, 46.9 (46.8); H, 4.8 (4.3); N, 2.8 (2.7).%.

Crystal Structure Determinations of $\mathrm{Zr(CH_2Ph)_2(N_2NN')}$ (3), $\mathrm{ZrCl(CH_2Ph)(N_2NN')}$ (6), $\mathrm{Ti(NAr)(N_2NN')}$ (15),

$Zr(NH^tBu)(NC_5H_{10})(N_2NN')$ (19), $Ta(N^tBu)Cl(N_2NN')$ (21), H_2O_2NN' (22), and $Zr(CH_2SiMe_3)_2(O_2NN')$ (27). Crystal data collection and processing parameters are given in Table 8. Crystals were mounted on a glass fiber using perfluoropolyether oil and cooled rapidly in a stream of cold N_2. Diffraction data were measured using an Enraf-Nonius DIP2000 or KappaCCD diffractometer. Intensity data were processed using the DENZO-SMN package.[35] The structures were solved using the direct-methods program SIR92,[36] which located all non-hydrogen atoms. Subsequent full-matrix least-squares refinement was carried out using the CRYSTALS program suite.[37] Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined. Hydrogen atoms were positioned geometrically with the exception of H(1) in **19** and the O-bound atoms in **22**, which were located from Fourier difference maps and positionally refined. Minor disorder in **6** and **15** was satisfactorily modeled. Weighting schemes were applied as appropriate. Full listings of atomic coordinates, bond lengths and angles, and displacement parameters have been deposited at the Cambridge Crystallographic Data Center. See Notice to Authors, Issue No. 1.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of $Zr(CH_2Ph)_2(N_2NN')$ (**3**), $ZrCl(CH_2Ph)(N_2NN')$ (**6**), $Ti(NAr)(N_2NN')$ (**15**), $Zr(NH^tBu)(NC_5H_{10})(N_2NN')$ (**19**), $Ta(N^tBu)Cl(N_2NN')$ (**21**), H_2O_2NN' (**22**), and $Zr(CH_2SiMe_3)_2(O_2NN')$ (**27**). This material is available free of charge via the Internet at http://pubs.acs.org.

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