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Synthesis of Group 4 $[(RN\text{-}o\text{-}C_6H_4)_2O]^{2-}$ complexes where R is $SiMe_3$ or 0.5 $Me_2SiCH_2CH_2SiMe_2$

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Abstract

Complexes that contain the $[(Me_3SiN\text{-}o\text{-}C_6H_4)_2O]^{2-}$ ligand ($[\mathbf{1}]^{2-}$) of the type $[\mathbf{1}]M(NMe_2)_2$, $[\mathbf{1}]MCl_2$, and $[\mathbf{1}]MMe_2$ have been prepared where M = Ti, Zr, or Hf. Although cations prepared by addition of $[Ph_3C][B(C_6F_5)_4]$ or $[PhNMe_2H][B(C_6F_5)_4]$ to $[\mathbf{1}]ZrMe_2$ or $[\mathbf{1}]HfMe_2$ could not be observed in NMR studies, addition of $[(\eta^5\text{-}C_5H_4Me)_2Fe][B(C_6H_5)_4]$ to $[\mathbf{1}]HfMe_2$ in the presence of THF led to isolation of $\{[\mathbf{1}]HfMe(THF)_2\}[B(C_6H_5)_4]$. An X-ray study showed the cation to be a distorted octahedron in which the $[\mathbf{1}]^{2-}$ ligand is in the *mer* arrangement and is significantly twisted from a planar NC_2OC_2N arrangement. The THF ligands are *trans* to one another. No well-behaved activity for the polymerization of 1-hexene could be observed with activated $[\mathbf{1}]ZrMe_2$, while $\{[\mathbf{1}]HfMe(THF)_2\}[B(C_6H_5)_4]$ was inactive. The reaction between $Li_2[O(o\text{-}C_6H_4NH)_2]$ and $Me_2ClSiCH_2CH_2SiMe_2Cl$ in THF produced a cyclic diamido/ether ligand $H_2[\mathbf{2}]$. The reaction between $H_2[\mathbf{2}]$ and $Zr(NMe_2)_4$ or ZrR_4 (R = CH_2Ph, CH_2SiMe_3) gave $[\mathbf{2}]Zr(NMe_2)_2(HNMe_2)$ and $Zr[\mathbf{2}]_2$, respectively. The dimethylamine in $[\mathbf{2}]Zr(NMe_2)_2(HNMe_2)$ could be replaced with pyridine or 2,4-lutidine to give $[\mathbf{2}]Zr(NMe_2)_2(L)$ (L = pyridine or 2,4-lutidine), which then could be converted into $[\mathbf{2}]ZrCl_2(L)$ with excess Me_3SiCl. The reaction between $[\mathbf{2}]ZrCl_2(py)$ and two equivalents of Me_3SiCH_2MgCl gave a bimetallic complex in which one of the trimethylsilyl methyl groups has been doubly C–H activated, as confirmed by X-ray crystallography.

Keywords: Titanium; Zirconium; Hafnium; Diamido; Polymerisation of hexene

1. Introduction

We recently reported the synthesis of zirconium dialkyl complexes that contain a variety of diamido/donor ligands such as $[(RN\text{-}o\text{-}C_6H_4)_2O]^{2-}$ (R = *t*-Bu [1–3] , *i*-Pr [4], or cyclohexyl [4]), $[(t\text{-}Bu\text{-}d_6\text{-}N\text{-}o\text{-}C_6H_4)_2S]^{2-}$ [5], $[(ArylNCH_2CH_2)_2O]^{2-}$ [6], $[(ArylNCH_2CH_2)_2S]^{2-}$ [6] , $[(ArylNSiMe_2CH_2)_2PPh]^{2-}$ [7], or $[(ArylNCH_2CH_2)_2NR]^{2-}$ (R = H or Me) [8], and the behavior of activated dialkyl complexes for the polymerization of 1-hexene. The activity of zirconium dimethyl complexes activated with $[PhNMe_2H][B(C_6F_5)_4]$ or $[Ph_3C][B(C_6F_5)_4]$ varied from living (at 0°C) in the case of $[(t\text{-}Bu\text{-}d_6\text{-}N\text{-}o\text{-}C_6H_4)_2O]ZrMe_2$ to little sustained activity in the case of complexes that contain sulfur or phosphorus donors. At the time we began this work zirconium complexes containing $[(Me_3SiNCH_2CH_2)_2N(SiMe_3)]^{2-}$ had been reported [9–12]. Therefore, we thought it would be informative to explore complexes that contain a trimethylsilyl analog of the most successful of our diamido/donor ligands, namely $[(t\text{-}BuN\text{-}o\text{-}C_6H_4)_2O]^{2-}$ [1–3] , as we could then directly compare the activity of Group 4 complexes that contain the $[(Me_3SiN\text{-}o\text{-}C_6H_4)_2O]^{2-}$ ligand ($[\mathbf{1}]^{2-}$) with catalysts that contain the $[(Me_3CN\text{-}o\text{-}C_6H_4)_2O]^{2-}$ ligand. We have postulated that an important feature of the successful living polymerization of 1-hexene using activated $[(t\text{-}Bu\text{-}d_6\text{-}N\text{-}o\text{-}C_6H_4)_2O]ZrMe_2$ is stabilization of crowded tetrahedral cationic intermediates in which the olefin inserts into the metal–carbon bond virtually exclusively in a 1,2 manner to give intermediates in which β elimination is slow. In order to encourage the formation of tetrahedral cationic zirconium alkyls we also have begun to explore diamido/donor ligands in which the donor cannot invert when bound to zirconium, namely those that contain N [8] or P [7] , and those in which the geometry of the diamido/donor complex is restricted as a conse-

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quence of tying the two arms together as part of a tetrahydrofuran ring [13]. A third potential method of encouraging formation of tetrahedral cationic zirconium alkyls is to tie the two amido substituents together. That is relatively easy in the case of silicon, as bis(chlorosilanes) are readily available. We report here the synthesis of Group 4 complexes that contain the $[(Me_3SiN\text{-}o\text{-}C_6H_4)_2O]^{2-}$ ligand ($[\mathbf{1}]^{2-}$), as well as several zirconium complexes that contain an analogous ligand ($[\mathbf{2}]^{2-}$) in which the two nitrogen centers are linked by a $Me_2SiCH_2CH_2SiMe_2$ chain.

2. Results

2.1. Synthesis of $[(Me_3SiN\text{-}o\text{-}C_6H_4)_2O]^{2-}$ complexes of Ti, Zr, and Hf

Addition of two equivalents of LiBu to an ether solution of $(H_2N\text{-}o\text{-}C_6H_4)_2O$ followed by two equivalents of Me_3SiCl yielded white crystalline $[(Me_3SiNH\text{-}o\text{-}C_6H_4)_2O]$ ($H_2[\mathbf{1}]$) in ~75% yield on a 10 g scale. Addition of two equivalents of LiBu to a solution of $H_2[\mathbf{1}]$ in ether, followed by $(NMe_2)_2TiCl_2$ gave orange crystalline $[\mathbf{1}]Ti(NMe_2)_2$ in ~55% yield (Eq. (1)).

$$(NMe_2)_2TiCl_2 \xrightarrow[\text{ether}]{Li_2[\mathbf{1}]} [\mathbf{1}]Ti(NMe_2)_2 \xrightarrow[\text{toluene, 110°C}]{\text{excess } Me_3SiCl} [\mathbf{1}]TiCl_2 \quad (1)$$

Subsequent cleavage of the dimethylamido ligands with Me_3SiCl gave purple–black $[\mathbf{1}]TiCl_2$ in 74% yield after 7 days at 110°C in a sealed Schlenk tube. We did not find conditions where the reaction between $Ti(NMe_2)_4$ and $H_2[\mathbf{1}]$ would produce $[\mathbf{1}]Ti(NMe_2)_2$ readily, nor conditions where the reaction between $TiCl_4$ and $Li_2[\mathbf{1}]$ would produce $[\mathbf{1}]TiCl_2$ readily. The analogous $[\mathbf{1}]ZrCl_2$ and $[\mathbf{1}]HfCl_2$ complexes can be prepared by the sequence of reactions shown in Eq. (2).

$$M(NMe_2)_4 \xrightarrow[-2Me_2NH]{+H_2[\mathbf{1}]} [\mathbf{1}]M(NMe_2)_2 \xrightarrow{\text{excess } Me_3SiCl} [\mathbf{1}]MCl_2 \quad (2)$$

M = Zr or Hf

All reactions are complete in 2 days or less at 22°C, those involving Zr being significantly faster than those involving Hf. H-NMR spectra of all $[\mathbf{1}]M(NMe_2)_2$ complexes contain a single sharp NMe_2 resonance, consistent with the dimethylamido ligands being equivalent and freely rotating about the M–NMe_2 bond on the NMR time scale in solution. Any $[\mathbf{1}]MCl_2$ complex could be a dimer containing bridging chlorides, judging from a single crystal X-ray study of $\{[(t\text{-}BuN\text{-}o\text{-}C_6H_4)_2O]ZrCl_2\}_2$ reported elsewhere [3].

The $[\mathbf{1}]MCl_2$ complexes are smoothly methylated by two equivalents of methyl Grignard reagent to give $[\mathbf{1}]MMe_2$ complexes. $[\mathbf{1}]TiMe_2$ is an orange microcrystalline solid, while the zirconium and hafnium analogs are colorless. Room temperature (r.t.) H-NMR spectra show a single resonance for the methyl groups and a single resonance for the TMS groups, consistent with C_{2v} or C_2 symmetry in solution on the NMR time-scale. Attempts to prepare $[\mathbf{1}]ZrEt_2$ by addition of an ethyl Grignard reagent to ether solutions of $[\mathbf{1}]ZrCl_2$ failed; the mixture darkened within minutes and H-NMR spectra of reaction aliquots at 25°C could not be interpreted.

Attempts to prepare cationic species by addition of $[Ph_3C][B(C_6F_5)_4]$ to $[\mathbf{1}]MMe_2$ complexes in chlorobenzene at 0°C led to complex mixtures that could not be identified. However, it was possible to isolate a cationic Hf species that contained two equivalents of THF with $[B(C_6H_5)_4]^-$ as the counter ion. Addition of $[(\eta^5\text{-}C_5H_4Me)_2Fe][B(C_6H_5)_4]$ to a THF solution of $[\mathbf{1}]HfMe_2$ at −25°C led to formation of $(\eta^5\text{-}C_5H_4Me)_2Fe$. Recrystallization of the crude mixture yielded a colorless product that was shown to be $\{[\mathbf{1}]HfMe(THF)_2\}[B(C_6H_5)_4]$ in an X-ray study (see below). Unfortunately, crystallization of $\{[\mathbf{1}]HfMe(THF)_2\}[B(C_6H_5)_4]$ was difficult and not entirely reproducible. Therefore, samples of pure $\{[\mathbf{1}]HfMe(THF)_2\}[B(C_6H_5)_4]$ could not be obtained. The complex and temperature dependent NMR spectra of the crude product mixture also suggested that more than one product (perhaps more than one isomer of $\{[\mathbf{1}]HfMe(THF)_2\}[B(C_6H_5)_4]$) was present, and possibly also that some fluxional process was taking place. Therefore we cannot be certain that a mixture of $(\eta^5\text{-}C_5H_4Me)_2Fe$ and $\{[\mathbf{1}]HfMe(THF)_2\}[B(C_6H_5)_4]$ is in fact produced initially. Complexes of the type $\{[(t\text{-}Bu\text{-}d_6\text{-}N\text{-}o\text{-}C_6H_4)_2O]HfMe(THF)_2\}BPh_4$ have been prepared and found to exist in the form of two isomers in solution, while $\{[(t\text{-}Bu\text{-}d_6\text{-}N\text{-}o\text{-}C_6H_4)_2O]ZrMe(THF)_2\}[B(C_6F_5)_4]$ and $\{[(t\text{-}Bu\text{-}d_6\text{-}N\text{-}o\text{-}C_6H_4)_2O]ZrMe(DME)][B(C_6F_5)_4]$ have been isolated and their structures determined in X-ray studies [3].

X-ray-quality crystals of $\{[\mathbf{1}]HfMe(THF)_2\}[B(C_6H_5)_4]$ were obtained by allowing diethyl ether vapor to diffuse into a concentrated chlorobenzene solution. Crystallographic details are listed in Table 1 and selected bond lengths and angles are listed in Table 2, while drawings are presented in Fig. 1 (a and b). (Only the cation is shown in Fig. 1; the $[B(C_6H_5)_4]^-$ anion is well separated from the cation and entirely normal.) The cation is a distorted octahedron in which the $[\mathbf{1}]^{2-}$ ligand is found in the *mer* arrangement and is significantly twisted from a planar NC_2OC_2N arrangement (Fig. 1(b)). The N(1)–Hf–N(2) angle is 141.23(12)°, which is characteristic of the structure of diamido/donor complexes in which the ligand has approximately the *mer* arrangement [3,6,8]. The twisting of the diamido/donor ligand also can be evaluated via the O/Hf/N/Si dihedral angles of 141 and 164°, and via the angle between the N(1)/Hf/O(1) and N(2)/Hf/O(1) planes (169°). The nitrogens are planar, but the sum of the angles at the oxygen of the $[\mathbf{1}]^{2-}$ ligand is only 351.6°. The THF ligands are nearly *trans* to one another (O(2)–Hf–O(3) = 176.25(9)°), while O(1) is approximately *trans* to C(13) (167.31(13)°). The ring of each THF ligand is tipped slightly away from each neighboring TMS group in response to steric demands. The two $Hf–O_{THF}$ bond lengths are ~0.1 Å shorter than the Hf–O(1) dative bond, in part because O(1) is likely to be a poorer σ-donor and a poorer π-donor, and because the ligand's relatively rigid conformation may not allow the Hf–O(1) bond length to adjust to what it otherwise could be. (The Zr–O bond lengths in two six-coordinate *mer* $[(i\text{-PrN-}o\text{-}C_6H_4)_2O]^{2-}$ complexes range from 2.33 to 2.37 Å [4].) The Hf–C(13) bond length (2.220(4) Å) is not unusual.

Table 1
Crystallographic data, collection parameters, and refinement parameters for $\{[\mathbf{1}]Hf(CH_3)(THF)_2\}[B(C_6H_5)_4]$ and $[\mathbf{2}][\mathbf{2'}]Zr_2(CH_2SiMe_3)_2$

Empirical formula	$C_{51}H_{65}BHfN_2O_3Si_2$	$C_{44}H_{68}N_4O_2Si_6Zr_2$
Formula weight	999.53	1036.00
Temperature (K)	185(2)	188(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	15.849(3)	13.328(4)
b (Å)	13.977(2)	14.964(4)
c (Å)	22.837(2)	18.212(3)
α (°)	90	100.217(12)
β (°)	106.458(13)	103.932(14)
γ (°)	90	114.90(2)
Volume ($Å^3$)	4851.9(12)	3032.9(13)
Z	4	2
D_{calc} ($Mg\ m^{-3}$)	1.368	1.134
Absorption coefficient (mm^{-1})	2.242	0.494
F(000)	2056	1080
Crystal size (mm)	0.42 × 0.26 × 0.18	0.28 × 0.24 × 0.13
θ Range for data collection (°)	1.34–23.26	1.58–23.26
Limiting indices	$-17 \le h \le 17$, $-8 \le k \le 15$, $-25 \le l \le 24$	$-14 \le h \le 14$, $-13 \le k \le 16$, $-20 \le l \le 16$
Reflections collected	19 232	12 202
Independent reflections	6953 ($R_{int} = 0.0348$)	8370 ($R_{int} = 0.0357$)
Absorption correction	Semi-empirical	None
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	6937/0/542	8361/0/523
Goodness-of-fit on *F*	1.121	0.936
Final *R* indices $[I > 2\sigma(I)]$	$R_1 = 0.0254$, $wR_2 = 0.0591$	$R_1 = 0.0431$, $wR_2 = 0.1174$
R indices (all data)	$R_1 = 0.0328$, $wR_2 = 0.0759$	$R_1 = 0.0548$, $wR_2 = 0.1415$
Largest difference peak and hole (e $Å^{-3}$)	0.525 and −0.499	0.546 and −0.455

Table 2
Selected bond lengths (Å) and angles (°) for $\{[(Me_3SiN\text{-}o\text{-}C_6H_4)_2O]Hf(CH_3)(THF)_2\}^+$

Bond lengths			
Hf–N(1)	2.118(3)	Hf–N(2)	2.122(3)
Hf–O(3)	2.165(2)	Hf–O(2)	2.172(2)
Hf–C(13)	2.220(4)	Hf–O(1)	2.289(3)
Bond angles			
N(l)–Hf–N(2)	141.23(12)	O(1)–Hf–O(3)	79.59(10)
N(l)–Hf–O(1)	71.77(10)	O(1)–Hf–C(13)	167.31(13)
N(l)–Hf–O(2)	87.93(10)	O(2)–Hf–O(3)	176.25(9)
N(l)–Hf–O(3)	89.65(10)	O(2)–Hf–C(13)	95.37(13)
N(l)–Hf–C(13)	105.61(13)	O(3)–Hf–C(13)	88.05(13)
N(2)–Hf–O(1)	70.99(11)	Si(l)–N(l)–Hf	125.9(2)
N(2)–Hf–O(2)	86.18(11)	Si(2)–N(2)–Hf	130.4(2)
N(2)–Hf–O(3)	93.93 (11)	C(7)–O(l)–C(1)	126.2(3)
N(2)–Hf–C(13)	113.08(14)	O(1)/Hf/N(1)/Si(1)	164
O(1)–Hf–O(2)	96.92(10)	O(1)/Hf/N(2)/Si(2)	141
		N(1)/Hf/O(1)/N(2)	169

We were somewhat surprised to find that a cation can be isolated in the presence of a $[B(C_6H_5)_4]^-$ anion (instead of a relatively poorly coordinating $[B(C_6F_5)_4]^-$

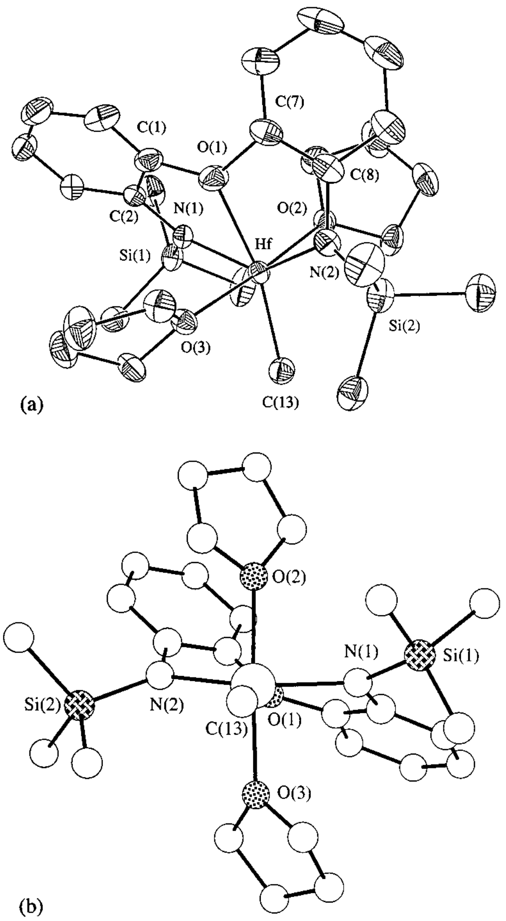
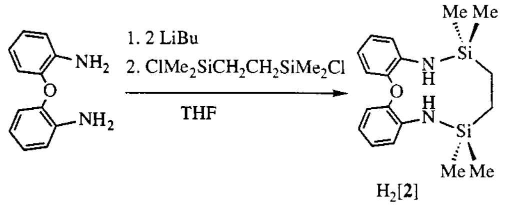


Fig. 1. (a) An ORTEP drawing of the structure of $\{[(Me_3SiN\text{-}o\text{-}C_6H_4)_2O]Hf(CH_3)(THF)_2\}^+$. (b) A CHEM 3D drawing of the structure of $\{[(Me_3SiN\text{-}o\text{-}C_6H_4)_2O]Hf(CH_3)(THF)_2\}^+$.

anion). However, the strongly coordinating THF ligands and resulting octahedral coordination geometry prevent binding of the $[B(C_6H_5)_4]^-$ anion to the metal and possible destructive reactions between the two [14]. The apparent instability of $\{[\mathbf{1}]HfMe(THF)_2\}[B(C_6H_5)_4]$ and our inability to obtain it in pure form might be the result of dissociation of one THF ligand and subsequent destructive reactions involving $[B(C_6H_5)_4]^-$.

2.2. Synthesis of $[(CH_2Me_2SiN\text{-}o\text{-}C_6H_4)_2O]^{2-}$ complexes of Zr

The reaction between $Li_2[O(o\text{-}C_6H_4NH)_2]$ and $ClMe_2SiCH_2CH_2SiMe_2Cl$ in THF in dilute solution gave crystalline $H_2[\mathbf{2}]$ in ~70% yield (Eq. (3)). $H_2[\mathbf{2}]$ exhibits one CH_2 and one SiMe resonance in both proton and C-NMR spectra, consistent with the presence of two mirror planes on the NMR time scale, as expected.



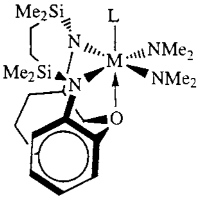
$H_2[\mathbf{2}]$ (3)

Attempts to react $Li_2[\mathbf{2}]$ with $ZrCl_4$ or $ZrCl_4(THF)_2$ under a variety of conditions did not yield any isolable complexes. However, the reaction between $H_2[\mathbf{2}]$ and $Zr(NMe_2)_4$ in pentane at r.t. yielded a dimethylamine adduct, $[\mathbf{2}]Zr(NMe_2)_2(HNMe_2)$, as colorless crystals in ~90% yield (Eq. (4)). The dimethylamine appears to coordinate to zirconium strongly since $[\mathbf{2}]Zr(NMe_2)_2(HNMe_2)$ is unchanged after being heated to 100°C for 1 day in vacuo (~30 mtorr). The dimethylamine can be replaced by pyridine or 2,4-lutidine to give related $[\mathbf{2}]Zr(NMe_2)_2(L)$ species (L = pyridine or 2,4-lutidine) in quantitative yield. Several attempts to convert $[\mathbf{2}]Zr(NMe_2)_2(HNMe_2)$ into $[\mathbf{2}]ZrCl_2$ by treatment with excess Me_3SiCl led to formation of $H_2[\mathbf{2}]$ (observed by H-NMR) and apparent decomposition. However, the analogous pyridine or 2,4-lutidine adducts can be converted readily to dichloride complexes in high yield (Eq. (5)).

$$H_2[\mathbf{2}] + Zr(NMe_2)_4 \xrightarrow[-\,HNMe_2]{\text{pentane}} [\mathbf{2}]Zr(NMe_2)_2(HNMe_2) \quad (4)$$

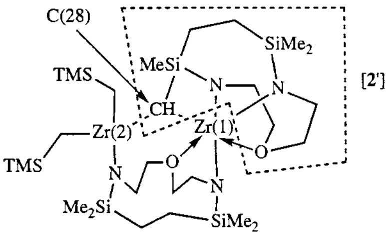
$$[\mathbf{2}]Zr(NMe_2)_2(L) + 2Me_3SiCl$$
$$\rightarrow [\mathbf{2}]ZrCl_2(L) + 2Me_3SiNMe_2 \quad (5)$$

H-NMR spectra of $[\mathbf{2}]Zr(NMe_2)_2(HNMe_2)$ exhibit a broad resonance centered at ~2.86 ppm that can be ascribed to the two dimethylamide ligands. This broad resonance becomes two resonances below −20°C and sharpens at higher temperatures ($T_c = 30$°C, $\Delta\nu_o = 238$ Hz). The pyridine and 2,4-lutidine complexes behave similarly. In $[\mathbf{2}]Zr(NMe_2)_2(py)$ the two dimethylamido resonances are found at 3.04 and 2.76 ppm at r.t., while in $[\mathbf{2}]Zr(NMe_2)_2(2,4\text{-lut})$ they are found at 3.19 and 2.71 ppm at r.t. All NMR data of $[\mathbf{2}]Zr(NMe_2)_2(L)$ species indicate that at all temperatures the TMS groups are equivalent, and that added L exchanges during the process in which the two dimethylamido methyl resonances exchange. Since the two amido nitrogens are linked together, we propose that the core is a pseudooctahedron in which the $[\mathbf{2}]^{2-}$ ligand is in a *fac* geometry, the two NMe_2 ligands are *cis* to one another and do not rotate about the Zr–N bonds on the NMR time scale, and the 'L' ligand is in a position *trans* to the oxygen donor, viz.



We also propose that the fluxional process consists of loss of L and exchange and rotation of the dimethylamido ligands about the M–N bond in the resulting five-coordinate species. It is not possible to say whether the dimethylamido ligands lie in the ZrN_4 plane, or whether the dimethylamido plane contains the L–Zr–O axis. In either case the methyl groups on each dimethylamido ligand would be inequivalent.

Reactions between $[\mathbf{2}]ZrCl_2(py)$ and one or two equivalents of MeMgCl, $PhCH_2MgCl$, or LiMe under a variety of conditions produced magnesium or lithium salts, but only mixtures of products, none of which could be identified. However, addition of two equivalents of Me_3SiCH_2MgCl to $[\mathbf{2}]ZrCl_2(py)$ in diethyl ether at −35°C yielded a pale yellow crystalline solid in ~50% yield. This crystalline product also could be obtained in ~70% yield in the reaction between $Li_2[\mathbf{2}]$ and $ZrCl_2(CH_2SiMe_3)_2$ in diethyl ether at −35°C. An X-ray study (Tables 1 and 3, Fig. 2) reveals this product to be a dimer that has the composition $[\mathbf{2}][\mathbf{2'}]Zr_2(CH_2SiMe_3)_2$, in which the $[\mathbf{2'}]^{4-}$ ligand is formed from a $[\mathbf{2}]^{2-}$ ligand by loss of two protons from C(28), thereby creating a bridging CH ligand between the two metal centers, as shown schematically below. (The phenylene rings are not shown.)



Metal center Zr(2) is pseudotetrahedral with bonds to the two trimethylsilyl ligands, the bridging methine

Table 3
Selected bond lengths (Å) and angles (°) in [**2**][**2′**]$Zr_2(CH_2SiMe_3)_2$

Bond lengths			
Zr(1)–N(1)	2.109(3)	Zr(1)–N(2)	2.114(3)
Zr(1)–N(3)	2.154(4)	Zr(1)–C(28)	2.236(4)
Zr(1)–O(1)	2.365(3)	Zr(1)–O(2)	2.374(3)
Zr(1)–Si(2)	2.884(2)	Zr(2)–N(4)	2.082(4)
Zr(2)–C(28)	2.141(4)	Zr(2)–C(5)	2.229(4)
Zr(2)–C(6)	2.253(4)	Zr(2)–C(22)	2.768(4)
Bond angles			
N(1)–Zr(1)–N(2)	95.85(13)	N(1)–Zr(1)–N(3)	100.97(14)
N(2)–Zr(1)–N(3)	146.96(13)	N(1)–Zr(1)–C(28)	104.3(2)
N(2)–Zr(1)–C(28)	75.70(14)	N(3)–Zr(1)–C(28)	125.99(14)
N(1)–Zr(1)–O(1)	155.31(12)	N(2)–Zr(1)–O(1)	82.09(11)
N(3)–Zr(1)–O(1)	70.80(11)	C(28)–Zr(1)–O(1)	99.01(13)
N(1)–Zr(1)–O(2)	73.82(12)	N(2)–Zr(1)–O(2)	71.61(11)
N(3)–Zr(1)–O(2)	86.01(12)	C(28)–Zr(1)–O(2)	146.80(12)
O(1)–Zr(1)–O(2)	82.27(9)	N(1)–Zr(1)–Si(2)	94.98(11)
N(2)–Zr(1)–Si(2)	36.66(9)	N(3)–Zr(l)–Si(2)	162.05(10)
C(28)–Zr(1)–Si(2)	40.34(10)	O(l)–Zr(1)–Si(2)	97.64(7)
O(2)–Zr(1)–Si(2)	106.47(7)	N(4)–Zr(2)–C(28)	105.7(2)
N(4)–Zr(2)–C(5)	114.1(2)	C(28)–Zr(2)–C(5)	106.5(2)
N(4)–Zr(2)–C(6)	117.7(2)	C(28)–Zr(2)–C(6)	107.9(2)
C(5)–Zr(2)–C(6)	104.4(2)	N(4)–Zr(2)–C(22)	30.47(12)
C(28)–Zr(2)–C(22)	96.83(14)	C(5)–Zr(2)–C(22)	143.38(14)
C(6)–Zr(2)–C(22)	94.47(14)		

carbon C(28), and N(4) of an intact [**2**]$^{2-}$ ligand that spans the two metal centers. (Carbon atom C(22) could be said to be weakly bound to the metal judging from the Zr–C(22) distance of 2.768 (4) Å).) Metal center Zr(1) is pseudooctahedral and contains the N(2)/Zr(1)/N(1)/O(2) core of the [**2′**]$^{4-}$ ligand in a *fac* arrangement. The N(1)–Zr–O(2) and N(2)–Zr–O(2) angles are 73.82(12) and 71.61(11)°, similar to what is found in {[**1**]HfMe$(THF)_2$}[$B(C_6H_5)_4$], but the N(2)–Zr–N(1) angle is only 95.85(13)°, perhaps in large part as consequence of the restrictions imposed by the $SiCH_2CH_2Si$ link between N(1) and N(2) and the formation of the Zr(1)/N(2)/Si(2)/C(28) ring. The Zr–O, Zr–N_{amide}, and Zr–C bond lengths are all typical of zirconium complexes that contain diamido/ether ligands [1,6,15] . The bond lengths between the bridging methine carbon and the two zirconium centers (2.236(4) and 2.141(4) Å) are typical of Zr–C single bonds. The Zr(1)–C(28)–Zr(2) angle (116.0(2)°), however, is ~22° larger than the Zr–C–Zr angle (93.9(5)°) in {*cyclo*-$ZrCHSiMe_2$-$NSiMe_3[N(SiMe_3)_2]$}$_2$, a complex that also contains a bridging methine connecting two zirconium centers and that is formed by double C–H activation upon thermolysis of $[(Me_3Si)_2N]_2ZrR_2$ ($R = Me$, Et, CH_2SiMe_3) complexes at 60°C 0.01 mm^{-1} [16]. The sum of bond angles around three of the amido nitrogens (N(1) = 357.2, N(3) = 358.7, N(4) = 355.5°) suggests that they are planar. However, the sum of the angles around N(2) is only 349.2°, which may result from the strain produced in the Zr(1)/N(2)/Si(2)/C(28) ring. The distance between Si(2) and Zr(1) (2.884(2) Å) is typical of compounds that contain M/N/Si/C rings [16,17] . The oxygen atoms O(1) and O(2) coordinate to Zr(1) with bond lengths of ~2.36–2.37 Å and an O(1)–Zr(1)–O(2) bond angle of 82°.

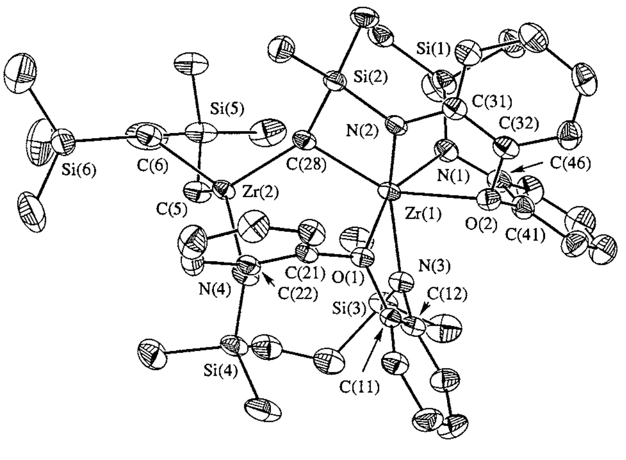
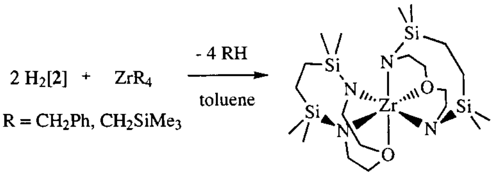


Fig. 2. An ORTEP drawing of the structure of [**2**][**2′**]$Zr_2(CH_2SiMe_3)_2$.

The NMR spectrum of [**2**][**2′**]$Zr_2(CH_2SiMe_3)_2$ is fully in accord with the X-ray structure. The most characteristic feature of the NMR spectra of this unsymmetric compound is a singlet at 5.42 ppm in the H-NMR spectrum and a doublet at 163.59 ppm ($^1J_{CH} = 106$ Hz) in the C-NMR spectrum for the bridging CH group. The analogous resonances in the thermolysis product of $[(Me_3Si)_2N]_2ZrR_2$ are found at 7.08 and 201.4 ppm [16] .

The reaction between [**2**]$ZrCl_2$(py) and two equivalents of $PhMe_2CCH_2MgCl$ gave an orange crystalline product in ~50% yield whose NMR spectra are analogous to those for [**2**][**2′**]$Zr_2(CH_2SiMe_3)_2$, in particular a singlet resonance at 4.88 ppm that can be ascribed to the proton in the bridging methine group. Elemental analysis further supports the proposal that this product can be formulated as an analog of [**2**][**2′**]$Zr_2(CH_2SiMe_3)_2$, namely [**2**][**2′**]$Zr_2(CH_2CPhMe_2)_2$. The failure to observe similar products when [**2**]$ZrCl_2$(py) is treated with methyl Grignard or methyllithium or with benzyl Grignard might be attributed to the relatively small size of these alkyls in comparison to trimethylsilylmethyl and neophyl, and competing decomposition reactions; details remain obscure.

Attempts to prepare dialkyl complexes of the type [**2**]ZrR_2 by adding H_2[**2**] to ZrR_4 ($R = CH_2Ph$, CH_2SiMe_3) in toluene or benzene led to 1:1 mixtures of ZrR_4 and a compound whose NMR spectra and elemental analyses are consistent with its formulation as Zr[**2**]$_2$. Addition of two equivalents of H_2[**2**] to ZrR_4 yielded Zr[**2**]$_2$ quantitatively. There is no evidence for formation of [**2**]ZrR_2, even if the reactions are conducted in diethyl ether or THF. Complex Zr[**2**]$_2$ shows four $SiCH_3$ resonances in both proton and C-NMR spectra plus twelve aromatic signals in the C-NMR spectrum, which suggests that the [**2**]$^{2-}$ ligand is bound to the metal in a *fac* manner with the oxygen donors *cis* to one another, as shown schematically in Eq. (6). If [**2**]ZrR_2 complexes are intermediates in these reactions, we could conclude that the volume of the [**2**]$^{2-}$ ligand is significantly smaller than the volume occupied by [**1**]$^{2-}$ in analogous [**1**]ZrR_2 complexes, so that further reaction of [**2**]ZrR_2 complexes with H_2[**2**] is fast. However, it is still possible that Zr[**2**]$_2$ forms without first forming [**2**]ZrR_2 intermediates.



Zr[2]$_2$ (6)

3. Discussion

We have shown that it is possible to prepare some Group 4 dialkyl complexes that contain the [(Me_3SiN-*o*-C_6H_4)O]$^{2-}$ ligand, but monoalkyl cationic versions apparently are not stable in the absence of coordinating solvents such as THF. Nevertheless, we were somewhat surprised that a crowded cationic monoalkyl pseudooctahedral complex that contains two coordinated THF ligands could be prepared, and that strong binding of THF to the metal could force the [(Me_3SiN-*o*-C_6H_4)O]$^{2-}$ ligand to adopt the twisted *mer* arrangement. Six-coordinate *mer* complexes are much more readily accessible when the substituents on the amido nitrogens are *i*-Pr [4], although an analogous zirconium cation in which the amido substituent is *t*-Bu can also be prepared [3], again presumably as a consequence of strong binding of THF to the cationic Zr center.

Dialkyl complexes that contain the [**2**]$^{2-}$ ligand appear to be dramatically less stable than those that contain the [**1**]$^{2-}$ ligand. We suggest that the lower stability of hypothetical [**2**]ZrR_2 species and (possibly) the rapid reaction of intermediate [**2**]ZrR_2 species with more H_2[**2**] to yield Zr[**2**]$_2$ can be ascribed a significant restriction of the N–Zr–N bond angle in *fac*-[**2**]$^{2-}$ complexes. However, we have assumed that the N–Zr–N angle in the *fac* coordinated ligand (95.85(13)°) in [**2**][**2′**]$Zr_2(CH_2SiMe_3)_2$ is an indication of what it might be in five-coordinate [**2**]ZrR_2. Almost certainly that will not be the case, although a comparison of the N–Hf–N angle in {[**1**]HfMe(THF)$_2$}-[B(C_6H_5)$_4$] with the N–Zr–N angle around Zr(1) in [**2**][**2′**]$Zr_2(CH_2SiMe_3)_2$ is compelling evidence that there will be a significant difference in the N–M–N angle in [**1**]$^{2-}$ and [**2**]$^{2-}$ complexes, since the metal in both of these complexes is six-coordinate. A smaller value for the N–Zr–N angle should lead to a stabilization of a *fac*-pseudooctahedral coordination geometry and (for steric reasons) to low stability of five-coordinate species toward intermolecular reactions. In contrast, a larger N–Zr–N angle for steric reasons also should discourage intermolecular CH activation in dialkyl species. It should be possible to connect the two amido substituents with a longer link, e.g. $Me_2Si(CH_2)_xSiMe_2$ where $x = 3$, 4, or 5, but we suspect that cations prepared from such species also will not be stable.

In this work we have been able to compare directly a successful catalyst that contains a *t*-butyl group on the amido nitrogen with an analogous complex that contains a trimethylsilyl group on the amido nitrogen. Since the latter fails, we conclude that if the development of active catalysts for α-olefin polymerization is the goal, then silylamido groups should not be incorporated in the design of diamido/donor ligands. Similar conclusions were reached in another recent paper in which zirconium complexes were prepared that contain diamido/phosphine ligands [7], although in that case no complex that contains a diamido/phosphine ligand (and no N–Si bond) has been shown to be an effective catalyst for polymerization of ordinary olefins.

4. Experimental

4.1. General procedures

All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by standard Schlenk techniques unless specified otherwise. Tetrahydrofuran and diethyl ether were sparged with nitrogen and passed through two columns of activated alumina. Toluene was distilled from sodium benzophenone ketyl. Pentane was sparged with nitrogen and passed through a column of activated alumina. All solvents were stored in the drybox over 4 Å molecular sieves. Molecular sieves and Celite were activated in vacuo (10^{-3} torr) for 24 h at 175 and 125°C, respectively.

NMR chemical shifts are listed as parts per million downfield from tetramethylsilane. Routine coupling constants are not reported. Spectra were obtained at 22°C in C_6D_6 unless otherwise noted. A standard variable temperature unit was used to control the probe temperature in variable temperature runs and temperatures are considered accurate to ± 1°C. NMR solvents were sparged with nitrogen and stored over 4 Å molecular sieves. Elemental analyses were performed by H.

Kolbe Microanalytical Laboratory, Mülheim an der Ruhr, Germany. X-ray data were collected on a Siemens SMART/CCD diffractometer with λ(Mo–K_α) = 0.71073 Å and solved using a full-matrix least-squares refinement on F^2. No absorption correction was applied. High-resolution mass spectroscopy were performed on a Finnigan MAT 8200 Sector Mass Spectrometer.

$O(o\text{-}C_6H_4NH_2)_2$ [18], $Zr(NMe_2)_4$ [19], $ZrCl_2(CH_2SiMe_3)_2$ [20], $Zr(CH_2SiMe_3)_4$ [21], $Zr(CH_2Ph)_4$ [22], and $TiCl(NMe_2)_2$ [23] were prepared according to literature procedures. All other chemicals were purchased from commercial suppliers and used as received.

4.2. $(Me_3SiNH\text{-}o\text{-}C_6H_4)_2O$ (H_2[**1**])

A solution of LiBu in hexane (51 ml, 1.6 M) was added to a solution of $(2\text{-}NH_2C_6H_4)_2O$ (8.08 g, 40.4 mmol) in THF (120 ml) at −25°C. The mixture was allowed to warm to r.t. and was stirred for 4 h. Me_3SiCl (11.3 ml, 89 mmol) was then added at −25°C and the solution was allowed to warm to r.t. After 8.5 h all volatile components were removed in vacuo and the residue was extracted with pentane (60 ml) over a period of ~15 min. A white solid was filtered off and washed with pentane (20 ml). The solution was concentrated in vacuo and stored at −25°C overnight to yield crystals of the colorless product; yield 10.61 g (76%): ^{1}H-NMR δ 6.88 (m, 6), 6.58 (m, 2), 4.21 (br s, 2, NH), 0.095 (s, 18, Si*Me*$_3$); ^{13}C-NMR δ 146.1, 139.8, 124.9, 119.2, 118.6, 116.5, 0.3 (Si*Me*$_3$). Anal. Calc. for $C_{18}H_{28}N_2OSi_2$: C, 62.74; H, 8.19; N, 8.13. Found: C, 63.11; H, 8.52; N, 7.99%.

4.3. [**1**]$Ti(NMe_2)_2$

A solution of LiBu in hexane (6.1 ml, 1.6 M) was added to a solution of H_2[**1**] (1.678 g, 4.88 mmol) in ether (30 ml) at −25°C. The solution was allowed to warm to r.t. After 4 h $Ti(NMe_2)_2Cl_2$ (1.01 g, 4.88 mmol) was added to this solution at −25°C. The mixture was allowed to warm to r.t. and was stirred for 22 h, during which time a white precipitate formed. All volatile components were removed in vacuo and the residue was extracted with pentane (40 ml) for 30 min. The extract was filtered and the pentane was removed in vacuo. Recrystallization of the residue from ether at −25°C produced orange crystals; yield 1.283 g (55%): ^{1}H-NMR δ 6.91 (m, 4), 6.80 (d, 2), 6.58 (t, 2), 3.13 (s, 12, N*Me*$_2$), 0.21 (s, 18, Si*Me*$_3$); ^{13}C-NMR δ 149.74, 148.23, 125.26, 122.26, 119.75, 117.97, 47.38 (N*Me*$_2$), 3.03 (Si*Me*$_3$). Anal. Calc. for $C_{22}H_{38}N_4OSi_2Ti$: C, 55.21; H, 8.00; N, 11.71. Found: C, 55.08; H, 8.11; N, 11.63%.

4.4. [**1**]$TiCl_2$

A mixture of [**1**]$Ti(NMe_2)_2$ (1.00 g, 2.09 mmol) and Me_3SiCl (1.00 g, 9.22 mmol) in toluene (10 ml) was heated in a sealed Schlenk tube to 100°C. After 7 days the reaction mixture was filtered and all volatile components were removed from the filtrate in vacuo. The black residue was redissolved in methylene chloride (~10 ml) and the solution was filtered and then concentrated in vacuo to ~2 ml. The solution was layered with pentane (~2 ml) and stored at −25°C to yield 595 mg of large deep purple–black crystals. Concentration of the mother liquor afforded a second crop of 117 mg; total yield 712 mg (74%): ^{1}H-NMR δ 6.87 (d, 2), 6.79 (t, 2), 6.57 (t, 2), 6.36 (d, 2), 0.27 (s, 18, Si*Me*$_3$); ^{13}C-NMR δ 148.5, 145.1, 126.9, 123.8, 119.7, 119.0, 1.47 (Si*Me*$_3$). Anal. Calc. for $C_{18}H_{26}Cl_2N_2OSi_2Ti$: C, 46.86; H, 5.68; N, 6.07. Found: C, 46.75; H, 5.75; N, 6.03%.

4.5. [**1**]$TiMe_2$

[**1**]$TiCl_2$ (261 mg, 566 μmol) was treated with MeMgI (380 μl, 3.0 M in ether) at −25°C. The product was isolated as described for [**1**]$Ti(NMe_2)_2$: yield 174 mg (73%): ^{1}H-NMR δ 6.89–6.81 (m, 4), 6.76 (d, 2), 6.57 (t, 2), 1.63 (s, 6, Ti*Me*$_2$), 0.28 (s, 18, Si*Me*$_3$); ^{13}C-NMR δ 149.0, 145.4, 126.4, 122.1, 121.7, 119.5, 66.6 (Ti*Me*$_2$), 1.8 (Si*Me*$_3$). Anal. Calc. for $C_{20}H_{32}N_2Si_2OTi$: C, 57.12; H, 7.67; N, 6.66. Found: C, 57.04; H, 7.65; N, 6.73%.

4.6. [**1**]$ZrCl_2$ via [**1**]$Zr(NMe_2)_2$

H_2[**1**] (1.29 g, 3.75 mmol) and $Zr(NMe_2)_4$ (1.00 g, 3.75 mmol) were dissolved in pentane (10 ml) at 25°C. After 18 h all volatile components were removed in vacuo. The off-white residue was identified as [**1**]$Zr(NMe_2)_2$ on the basis of H- and C-NMR spectra: ^{1}H-NMR δ 6.91 (m, 6), 6.55 (m, 2), 2.93 (s, 12, N*Me*$_2$), 0.24 (s, 18, Si*Me*$_3$); ^{13}C-NMR δ 148.3, 146.4, 126.1, 123.3, 119.1, 117.6, 43.1, 2.4.

[**1**]$Zr(NMe_2)_2$ was dissolved in ether (20 ml) and Me_3SiCl (1.4 ml, 11.25 mmol) was added. After a few minutes a solid began to precipitate. After 90 min the volume of the mixture was reduced to ~10 ml and pentane (20 ml) was added. Copious amounts of pale yellow powder precipitated. All volatile components were removed and the yellow powder was washed with pentane (10 ml) and then dried in vacuo; yield 1.85 g (97%). An analytically pure sample was obtained by recrystallization from hot toluene: ^{1}H-NMR (CD_2Cl_2) δ 7.19 (m, 4), 6.96 (m, 2), 6.81 (dd, 2), 0.24 (s, 18, Si*Me*$_3$); ^{13}C-NMR (CD_2Cl_2) δ 147.85, 142.14, 127.98, 122.89, 122.54, 118.97, 1.07 (Si*Me*$_3$). Anal. Calc. for $C_{18}H_{26}Cl_2N_2OSi_2Zr$: C, 42.84; H, 5.19; N, 5.55. Found: C, 43.07; H, 5.15; N, 5.49%.

4.7. [**1**]HfCl$_2$ via [**1**]Hf(NMe$_2$)$_2$

A solution of Hf(NMe$_2$)$_4$ (1.60 g, 4.51 mmol) and H$_2$[**1**] (1.55 g, 4.51 mmol) in pentane (30 ml) was allowed to stand at r.t. for 3 days. All volatile components were then removed in vacuo. The colorless residue was identified as [**1**]Hf(NMe$_2$)$_2$ on the basis of H- and C-NMR spectra: ^{1}H-NMR δ 6.92 (m, 6), 6.55 (t, 2), 3.00 (s, 12, N*Me*$_2$), 0.24 (s, 18, Si*Me*$_3$); ^{13}C-NMR δ 148.3, 145.8, 126.3, 124.1, 119.3, 117.8, 42.9 (N*Me*$_2$), 2.5 (Si*Me*$_3$).

The [**1**]Hf(NMe$_2$)$_2$ was redissolved in ether (30 ml) and Me$_3$SiCl (1.5 ml, 11.8 mmol) was added to this solution. The reaction mixture was stirred at r.t. for 2 days and the solvent was then removed in vacuo. Recrystallization at −25°C of the residue from boiling methylene chloride produced colorless microcrystalline material; yield 2.09 g (78%): ^{1}H-NMR (CD$_2$Cl$_2$) δ 7.19 (m, 4), 6.93 (t, 2), 6.86 (d, 2), 0.22 (s, 18, Si*Me*$_3$); ^{13}C-NMR (CD$_2$Cl$_2$) δ 147.8, 141.7, 128.1, 123.7, 122.0, 118.9, 1.3 (Si*Me*$_3$). Anal. Calc. for $C_{18}H_{26}Cl_2HfN_2OSi_2$: C, 36.52; H, 4.43; N, 4.73. Found: C, 36.35; H, 4.39; N, 4.70%.

4.8. [**1**]ZrMe$_2$

A solution of MeMgI in ether (3.0 M, 710 µl) was added to a suspension of [**1**]ZrCl$_2$ (535 mg, 1.06 mmol) in ether (10 ml) at −25°C. The reaction mixture was allowed to warm to r.t. and was stirred for 20 min. All volatile solvents were then removed in vacuo and the residue was extracted with pentane (10 ml) for 15 min. The extract was filtered and the pentane was removed in vacuo. Recrystallization of the residue from a mixture of ether and pentane at −25°C produced colorless crystals; yield 288 mg (55%): ^{1}H-NMR δ 6.85 (m, 6), 6.54 (m, 2), 0.82 (s, 6, Zr*Me*$_2$), 0.26 (s, 18, Si*Me*$_3$); ^{13}C-NMR δ 148.73, 143.94, 126.85, 123.16, 120.66, 118.94, 47.19 (Zr*Me*$_2$), 1.53 (Si*Me*$_3$). Anal. Calc. for $C_{20}H_{32}Si_2N_2OZr$: C, 51.79; H, 6.95; N, 6.04. Found: C, 51.49; H, 7.20; N, 6.04%.

4.9. [**1**]HfMe$_2$

A solution of MeMgI in ether (3.0 M, 1.7 ml) was added to a suspension of [**1**]HfCl$_2$ (1.51 g, 2.55 mmol) in ether (30 ml) at −25°C. The reaction mixture was stirred for 15 min. All volatile components were then removed in vacuo and the residue was extracted with pentane (30 ml) for 15 min. The extract was filtered and the pentane was removed in vacuo. Recrystallization of the residue from a mixture of ether and pentane at −25°C produced colorless microcrystals; yield 1.056 g (75%): ^{1}H-NMR δ 6.86 (m, 6), 6.54 (t, 2), 0.63 (s, 6, Hf*Me*$_2$), 0.23 (s, 18, Si*Me*$_3$); ^{13}C-NMR δ 148.56, 143.31, 127.08, 124.13, 120.69, 119.12, 58.06 (Hf*Me*$_2$), 1.57 (Si*Me*$_3$). Anal. Calc. for $C_{20}H_{32}HfN_2OSi_2$: C, 43.59; H, 5.85; N, 5.08. Found: C, 43.68; H, 5.79; N, 5.02%.

4.10. H$_2$[**2**]

A 1 l three-necked round-bottom flask was equipped with a magnetic stir-bar, two 120 ml additional funnels, and a septum. The assembly was purged with nitrogen for 1 h, and anhydrous THF (500 ml) was added by syringe. Two solutions were prepared as follows and transferred to the two additional funnels, respectively.

Solution 1: A 250 ml one-necked round-bottom flask was charged with a magnetic stir-bar, O(*o*-C$_6$H$_4$NH$_2$)$_2$ (4.975 g, 0.025 mol) and THF (45 ml). The solution was chilled in an acetone/dry ice cold bath. *n*-Butyllithium (20.0 ml, 2.5 M in hexane, 0.050 mol) was added by syringe. The solution turned green after about half the *n*-butyllithium had been added, then orange eventually. The solution was slowly warmed up to r.t. and stirred at r.t. for an additional 3 h. The resulting solution was transferred via a cannula to one of the additional funnels to which extra THF was added to make up to 100 ml.

Solution 2: A THF solution (100 ml) of ClMe$_2$SiCH$_2$CH$_2$SiMe$_2$Cl (5.348 g, 0.025 mol) was placed in the other additional funnel.

These two solutions were added at the same rate (~2 drops s^{-1}) to the 1 l three-necked round-bottom flask containing 500 ml THF while the reaction solution was stirred vigorously. The reaction mixture was stirred overnight and transferred to a 1 l one-neck round bottom flask and solvent was removed on a rotary evaporator. The residue thus obtained was extracted with pentane (300 ml) and the mixture was filtered through Celite. Solvent was removed in vacuo to give a brown oily residue which solidified after several days. It was recrystallized from ether at −35°C to give colorless crystals; yield (5 crops) 5.89 g (69%): ^{1}H-NMR δ 7.15 (d, 2, Ar), 6.90 (m, 4, Ar), 6.65 (m, 2, Ar), 4.37 (br s, 2, NH), 0.70 (s, 4, CH$_2$), 0.03 (s, 12, SiMe); ^{13}C-NMR (CDCl$_3$) δ 148.11 (C$_{\text{ipso}}$), 139.47 (C$_{\text{ipso}}$), 124.84 (C$_{\text{Ar}}$), 121.31 (C$_{\text{Ar}}$), 118.83 (C$_{\text{Ar}}$), 117.78 (C$_{\text{Ar}}$), 7.75 (CH$_2$), 0.60 (SiMe). HRMS (EI, 70 eV): 342.15842. Calc. for $C_{18}H_{26}N_2OSi_2$: 342.15837.

4.11. [**2**]Zr(NMe$_2$)$_2$(HNMe$_2$)

A solution of H$_2$[**2**] (407 mg, 1.188 mmol) in pentane (10 ml) was added to a solution of Zr(NMe$_2$)$_4$ (318 mg, 1.188 mmol) in pentane (10 ml) at r.t. The clear solution was shaken thoroughly then slowly poured into another flask to initiate the formation of crystals. The reaction solution was stood at r.t. overnight. The super natant was decanted away from the colorless crystals, which were then dried in vacuo. Repeated reduction of the volume of the mother liquor afforded two more crops; total yield (3 crops) 603 mg (90%): ^{1}H-NMR δ 7.33 (d, 2, Ar), 7.00–6.96 (m, 4, Ar), 6.59 (t, 2, Ar), 2.86 (br s, 12, ZrNMe$_2$), 1.80 (d, 6, HN*Me*$_2$), 1.43 (m, 2, CH$_2$), 1.18 (hept, 1, *H*NMe$_2$), 0.98 (m, 2, CH$_2$), 0.49 (s, 6, MeSi), 0.15 (s, 6, MeSi); ^{13}C-NMR δ 153.73 (C$_{ipso}$), 149.18 (C$_{ipso}$), 126.07 (C$_{Ar}$), 123.74 (C$_{Ar}$), 120.02 (C$_{Ar}$), 117.49 (C$_{Ar}$), 44.04 (br s, ZrN*Me*$_2$), 40.11 (HN*Me*$_2$), 13.05 (CH$_2$), 5.07 (SiMe), 0.79 (SiMe). Anal. Calc. for $C_{24}H_{43}N_5OSi_2Zr$: C, 51.02; H, 7.67; N, 12.39. Found: C, 50.88; H, 7.59; N, 12.32%.

4.12. [**2**]Zr(NMe$_2$)$_2$(py)

Neat pyridine (0.300 g, 3.793 mmol) was added to a solution of [**2**]Zr(NMe$_2$)$_2$(HNMe$_2$) (1.00 g, 1.77 mmol) in ether (8 ml) at r.t. The solution turned yellow immediately. After 4 h all volatile components were removed in vacuo to give yellow crystalline solid; yield 1.050 g (99%): ^{1}H-NMR δ 8.53 (d, 2, Ar), 7.28 (d, 2, Ar), 7.06 (d, 2, Ar), 6.99 (t, 2, Ar), 6.72 (t, 1, Ar), 6.57 (t, 2, Ar), 6.45 (t, 2, Ar), 3.04 (br s, 6, NMe$_2$), 2.76 (br s, 6, NMe$_2$), 1.49 (m, 2, CH$_2$), 1.06 (m, 2, CH$_2$), 0.57 (s, 6, Me), 0.24 (s, 6, Me); ^{13}C-NMR δ 153.65 (C$_{ipso}$), 150.78 (C$_{Ar}$), 149.25 (C$_{Ar}$), 138.31 (C$_{Ar}$), 125.88 (C$_{Ar}$), 124.44 (C$_{Ar}$), 123.40 (C$_{Ar}$), 119.98 (C$_{Ar}$), 117.54 (C$_{Ar}$), 45.03 (NMe), 44.22 (NMe), 12.73 (CH$_2$), 4.90 (SiMe), 1.14 (SiMe). Anal. Calc. for $C_{27}H_{41}N_5OSi_2Zr$: C, 54.14; H, 6.90; N, 11.69. Found: C, 53.94; H, 6.78; N, 11.56%.

4.13. [**2**]Zr(NMe$_2$)$_2$(2,4-lutidine)

Neat 2,4-lutidine (12 mg, 0.112 mmol) was added to a solution of [**2**]Zr(NMe$_2$)$_2$(HNMe$_2$) (12 mg, 0.021 mmol) in ether (1 ml) at r.t. The solution was stirred for 6.5 h and all volatile materials were removed in vacuo to give yellow crystalline product; yield 13 mg (98%): ^{1}H-NMR δ 8.48 (d, 1, lut.), 7.25 (d, 2, Ar), 7.04 (d, 2, Ar), 6.95 (t, 2, Ar), 6.54 (t, 2, Ar), 6.42 (m, 2, Ar), 3.19 (br s, 6, NMe$_2$), 2.71 (br s, 6, NMe$_2$), 2.42 (s, 3, *Me*-lutidine), 1.73 (s, 3, *Me*-lutidine), 1.49 (m, 2, CH$_2$), 1.04 (m, 2, CH$_2$), 0.56 (s, 6, MeSi), 0.19 (s, 6, MeSi). Anal. Calc. for $C_{29}H_{45}N_5OSi_2Zr$: C, 55.54; H, 7.23; N, 11.17. Found: C, 55.39; H, 7.20; N, 11.12%.

4.14. [**2**]ZrCl$_2$(py)

Neat Me$_3$SiCl (1.4 ml, 10.764 mmol) was added to a solution of [**2**]Zr(NMe$_2$)$_2$(py) (496 mg, 0.828 mmol) in CH$_2$Cl$_2$ (10 ml) at r.t. The reaction solution was stirred at r.t. overnight and solvent was removed in vacuo. The resulting yellow solid was washed with pentane (3 × 5 ml) and the yellow powder was collected on a fine fritted funnel dried in vacuo; yield 443 mg (92%): ^{1}H-NMR δ 8.88 (d, 2, Ar), 7.23 (d, 2, Ar), 6.80 (m, 2, Ar), 6.68–6.50 (m, 5, Ar), 6.38 (t, 2, Ar), 1.84 (m, 2, CH$_2$), 0.99 (m, 2, CH$_2$), 0.71 (s, 6, SiMe), 0.13 (s, 6, SiMe); ^{13}C-NMR δ 153.66 (C$_{ipso}$), 150.58 (C$_{Ar}$), 145.28 (C$_{ipso}$), 139.34 (C$_{Ar}$), 126.97 (C$_{Ar}$), 124.19 (C$_{Ar}$), 122.44 (C$_{Ar}$), 119.87 (C$_{Ar}$), 119.26 (C$_{Ar}$), 13.26 (CH$_2$), 2.32 (SiMe), 0.54 (SiMe). Anal. Calc. for $C_{23}H_{29}Cl_2N_3OSi_2Zr$: C, 47.48; H, 5.02; N, 7.22. Found: C, 47.59; H, 5.10; N, 7.16%.

4.15. [**2**][**2′**]Zr$_2$(CH$_2$SiMe$_3$)$_2$

4.15.1. Method (a)

An ether solution of Me$_3$SiCH$_2$MgCl (0.344 ml, 1 M in diethyl ether, two equivalents) was added to a prechilled solution (−30°C) of [**2**]ZrCl$_2$(py) (100 mg, 0.172 mmol) in diethyl ether (4 ml). The reaction mixture was stirred at r.t. for 20 min and the solvent was removed in vacuo. The resulting solid residue was extracted with pentane (8 ml) and the extract was filtered through a bed of Celite. The filtrate was concentrated in vacuo to ~1 ml and chilled to −30°C to give pale yellow crystals of the product, which were isolated by decanting the solution and removing all residual solvent from the product in vacuo; yield 46 mg (52%).

4.15.2. Method (b)

Under reduced lighting, a cold solution (−30°C) of LiCH$_2$SiMe$_3$ (90 mg, 0.961 mmol, two equivalents) in diethyl ether (3 ml) was added to a vigorously stirred cold solution (−30°C) of ZrCl$_4$ (112 mg, 0.481 mmol) in diethyl ether (3 ml). The reaction mixture was stirred at r.t. for 30 min. Insoluble materials were filtered off with Celite and the filtrate (containing ZrCl$_2$(CH$_2$SiMe$_3$)$_2$(Et$_2$O)$_x$) was chilled to −30°C. To this was added solid Li$_2$[**2**] (170 mg, 0.481 mmol). The reaction mixture was stirred at r.t. overnight during which time a white solid (LiCl), apparently precipitated. The solution was filtered through a bed of Celite and the filter cake was washed with diethyl ether (2 ml). The combined filtrate and washing were concentrated in vacuo to ~1 ml to form microcrystalline solid product. The concentrated solution was chilled to −30°C and yellow crystalline product was obtained by removing the solution portion with a pipet and drying in vacuo; yield 172 mg (69%).

An X-ray quality crystal was obtained by recrystallization from a concentrated diethyl ether solution at −30°C. ^{1}H-NMR δ 7.24–6.36 (m, 16, Ar), 5.42 (s, 1, Zr–C*H*Si–Zr), 1.43–0.75 (m, 8, diastereotopic Si-(C*H*$_2$)$_2$Si), 1.01 (s, 3, NSiMe), 0.53 (s, 9, ZrCH$_2$Si*Me*$_3$), 0.40 (s, 3, NSiMe), 0.39 (s, 3, NSiMe), 0.32 (s, 9, ZrCH$_2$Si*Me*$_3$), 0.24 (s, 3, NSiMe), 0.23 (s, 3, NSiMe), −0.02 (s, 3, NSiMe), −0.60 (s, 2, ZrC*H*$_2$SiMe$_3$), −0.91 (s, 2, ZrC*H*$_2$SiMe$_3$); ^{13}C-NMR δ 163.59 (ZrCHZr, $^1J_{CH} = 103$), 157.55, 155.53, 152.23, 151.31, 147.92, 147.87, 146.65, 145.21, 144.66, 135.12, 134.80, 127.68, 127.21, 126.39, 126.30, 125.40, 124.26, 122.35, 120.95, 120.17, 118.75, 118.05, 117.20, 116.96, 71.29, 60.60, 34.79, 23.08, 15.79, 14.65, 9.38, 7.65, 5.04, 4.31, 4.15, 3.76, 0.39, −3.20, −5.13. Anal. Calc. for $C_{44}H_{68}N_4O_2Si_6Zr_2$: C, 51.01; H, 6.62; N, 5.41. Found: C, 51.19; H, 6.53; N, 5.37%.

4.16. [**2**][**2**′]$Zr_2(CH_2CMe_2Ph)_2$

To a prechilled solution (−30°C) of [**2**]$ZrCl_2$(py) (106 mg, 0.182 mmol) in diethyl ether (4 ml) was added $PhMe_2CCH_2MgCl$ (0.33 ml, 1.12 M in diethyl ether, two equivalents). The reaction mixture was stirred at r.t. for 2.5 h. Solvent was removed in vacuo to dryness. The solid residue was extracted with pentane (10 ml). The extract was filtered through a bed of Celite and filtrate was concentrated in vacuo to ∼1 ml. The concentrated solution was chilled to −30°C to give the orange crystalline product, which was isolated by decanting the solution and removing all residual solvent from the sample in vacuo; yield 33 mg (47%). Anal. Calc. for $C_{56}H_{72}N_4O_2Si_4Zr_2$: C, 59.63; H, 6.43; N, 4.97. Found: C, 59.73; H, 6.56; N, 4.88%.

4.17. Zr[**2**]$_2$

4.17.1. Method (a)

In the absence of light a mixture of $Zr(CH_2SiMe_3)_4$ (56 mg, 0.127 mmol) and H_2[**2**] (87 mg, 0.255 mmol) in toluene (3 ml) was stirred at r.t. for 4 days. All volatile components were removed in vacuo to yield the product as an orange solid; yield 98 mg (99%).

4.17.2. Method (b)

In the absence of light a mixture of $Zr(CH_2Ph)_4$ (27 mg, 0.059 mmol) and H_2[**2**] (40 mg, 0.059 mmol) in toluene (3 ml) was heated to 80°C for 4 days. After removal of all volatile components the product was obtained as an orange solid; yield 43 mg (94%). ^{1}H-NMR δ 7.06 (dd, 4, Ar), 6.97 (t, 2, Ar), 6.88 (t, 4, Ar), 6.57 (t, 4, Ar), 6.45 (t, 4, Ar), 1.64 (m, 4, CH_2), 1.05 (m, 4, CH_2), 0.46 (s, 6, SiMe), 0.09 (s, 6, SiMe), −0.03 (s, 6, SiMe), −0.04 (s, 6, SiMe); ^{13}C-NMR δ 153.84 (C, Ar), 153.80 (C, Ar), 140.82 (C, Ar), 145.93 (C, Ar), 127.05 (CH, Ar), 126.44 (CH, Ar), 122.72 (CH, Ar), 121.08 (CH, Ar), 120.54 (CH, Ar), 119.69 (CH, Ar), 119.22 (CH, Ar), 118.03 (CH, Ar), 12.28 (CH_2), 10.62 (CH_2), 5.30 (SiMe), 3.61 (SiMe), 1.76 (SiMe), 0.19 (SiMe). Anal. Calc. for $C_{36}H_{48}N_4O_2Si_4Zr$: C, 55.98; H, 6.26; N, 7.25. Found: C, 56.09; H, 6.21; N, 7.20%.

4.18. X-ray studies

Crystals of {[**1**]HfMe$(THF)_2$}[$B(C_6H_5)_4$] and [**2**][**2**′]$Zr_2(CH_2SiMe_3)_2$ were examined on a Bruker Platform diffractometer equipped with a CCD area detector and driven by the SMART [24] suite of programs. A standard hemisphere of data was obtained for both compounds. Data reduction was carried out with SAINT [24], while SHELXTL [24] was used to solve and refine both structures. Patterson methods were employed to locate the heavy atoms in each instance, while subsequent difference Fourier calculations revealed the positions of the remaining non-hydrogen atoms. Those atoms were treated as anisotropic scatterers. Hydrogen atoms were placed in calculated positions and were allowed to ride upon their respective non-hydrogen atoms. In the case of {[**1**]HfMe$(THF)_2$}[$B(C_6H_5)_4$] an empirical absorption correction was applied.

5. Supplementary information

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 132502 for {[**1**]HfMe$(THF)_2$}[$B(C_6H_5)_4$] and 132501 for [**2**][**2**′]$Zr_2(CH_2SiMe_3)_2$. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ (Fax: +44-1223-336-033 or e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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