Amide-Silyl Ligand Exchanges and Equilibria among Group 4 Amide and Silyl Complexes

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Supporting Information

$KNMe_2$ is expected to be a product in the reaction in Eq. 7. It was prepared in order to obtain its NMR spectra.[S1] In its preparation, toluene was first treated with a superbasic, 1:1 molar mixture of n-BuLi and $KOBu^t$ to yield KCH_2Ph (Eq. S1).[S2] This was followed by the addition of 1 equiv of $HNMe_2$ to give $KNMe_2$ (Eq. S2). The transmetallation in Eq. S1 is an exothermal reaction due to the formation of the strong Li-O bond. $KNMe_2$ was found to be pyrophoric and unstable in benzene-d_6 and THF-d_8, decomposing to unknown species.

$$PhCH_3 + \text{n-BuLi} + KOBu^t \longrightarrow PhCH_2K + \text{n-BuH} + LiOBu^t \qquad \text{(Eq. S1)}$$

$$PhCH_2K + HNMe_2 \longrightarrow KNMe_2 + PhCH_3 \qquad \text{(Eq. S2)}$$

Experimental

Preparation of $KNMe_2$. n-BuLi (5.5 mL, 1.6 M in hexane; 8.8 mmol) was added dropwise to a suspension of $KOBu^t$ (1.0 g, 8.9 mmol) in toluene (30 mL) at –30 °C. A red solid was observed as a precipitate. After 2 h, the precipitate was filtered. Then the red solid was washed with pentane (20 mL) twice. At –30 °C, $HNMe_2$ (5.5 mL, 1.6 M in THF, 8.8 mmol) was added to a suspension of the red solid in toluene (30 mL). The solution was stirred for another 2 h. The red solid disappeared, and a white solid gradually formed during this time. The solid was washed with pentane to give a white solid of $KNMe_2$ (655 mg, 7.87 mmol, 90% yield). In ^1H NMR in THF-d_8 at 23 °C, a peak at 2.40 ppm was observed. In $^{13}C\{^1H\}$ NMR at 23 °C, a weak, broad peak at 41.0 ppm was observed. During the ^{13}C data acquisition, $KNMe_2$ in THF-d_8 decomposed to unknown species.

NMR assignments for $Zr(NMe_2)_5^-$ (4a) in THF-d_8. In a solution of crystals of **5** in THF-d_8 giving the equilibrium in Eq. 1, assignments of ^1H and ^{13}C NMR spectra of $Zr(NMe_2)_5^-$ (**4a**) in Eq. 1 were made, as discussed earlier. These assignments were supported by the following

additional studies.

In the ^{13}C and ^{1}H spectra of a mixture (**A**) of $Zr(NMe_2)_4$ (**1a**, 31 mg, 0.12 mmol) and $LiNMe_2$ (2.9 mg, 0.057 mmol) in THF-d_8, two peaks of ca. equal intensity (^{1}H: 2.89 ppm, ^{13}C: 44.74 ppm and ^{1}H: 2.81 ppm, 43.11 ppm, respectively) were observed. The peaks at 2.89 ppm in ^{1}H and 44.74 ppm in ^{13}C NMR were assigned to those of **1a**. When 3.2 mg of $LiNMe_2$ (0.063 mmol; Total of the two portions: 0.120 mmol) was added to the mixture (**B**), only the peaks at 2.81 ppm and 43.11 ppm in ^{1}H and ^{13}C NMR, respectively, were observed. These were assigned to be those of $Zr(NMe_2)_5^-$ (**4a**).

When another portion of $LiNMe_2$ (3.7 mg, 0.073 mmol) was added to this mixture (**C**), a new peak (^{1}H: 2.74 ppm, ^{13}C: 46.39 ppm) identified to be that of $Zr(NMe_2)_6^{2-}$ (**10**) was observed along with that of $Zr(NMe_2)_5^-$ (**4a**) The results suggest that **A** is a mixture of **1a** and $Zr(NMe_2)_5^-$ (**4a**), and that **B** (molar ratio of **1a**/$LiNMe_2$ = 1) is predominantly **4a**. With the addition of a total of 1.6 equiv of $LiNMe_2$ to $Zr(NMe_2)_4$ (**1a**) in **C**, it is a mixture of $Zr(NMe_2)_5^-$ (**4a**) and $Zr(NMe_2)_6^{2-}$ (**11**).

Formation of $Zr(NMe_2)_4(THF)_2$ in toluene-d_8. Bradley, Chisholm and co-workers have reported that, in benzene and toluene, $Zr(NMe_2)_4$ (**1a**) shows a degree of oligomerization.[7,8a,21] For a mixture of **1a** (48.2 mg, 0.180 mmol) and THF (8.9 mg, 0.12 mmol) in toluene-d_8 at 223 K, the resonances of $Zr(NMe_2)_4(THF)_2$ was observed at 3.29 (THF), 2.98 (N*Me*$_2$) and 1.11 (THF) ppm in ^{1}H NMR spectrum, and 68.86 (THF), 43.36 (N*Me*$_2$), and 25.64 (THF) ppm in ^{13}C NMR spectrum, respectively. In addition, the NMR resonances of the dimer of **1a**[8a] [^{1}H NMR δ 2.88 (terminal –N*Me*$_2$), 2.34 (bridging –N*Me*$_2$); ^{13}C δ 43.76 (terminal and bridging –N*Me*$_2$)] were observed as well. At 263 K, the amide peaks in the ^{1}H NMR spectrum of the mixture of $Zr(NMe_2)_4(THF)_2$ and the dimer of **1a** started to coalescence. At 296 K, only one amide

resonance was observed in the ^{1}H NMR spectrum.

Additional References

S1. $KNMe_2$ has been prepared from the reaction of KNH_2 with $HNMe_2$. Lambert, I.; Ravoire, J. Ger. Offen. 1971, German Patent Application: DE 71-2117970 19710414. *Chemical Abstracts* No. 76:16262.

S2. Schlosser, M.; Hartmann, J. *Angew. Chem.* **1973**, *85*, 544.

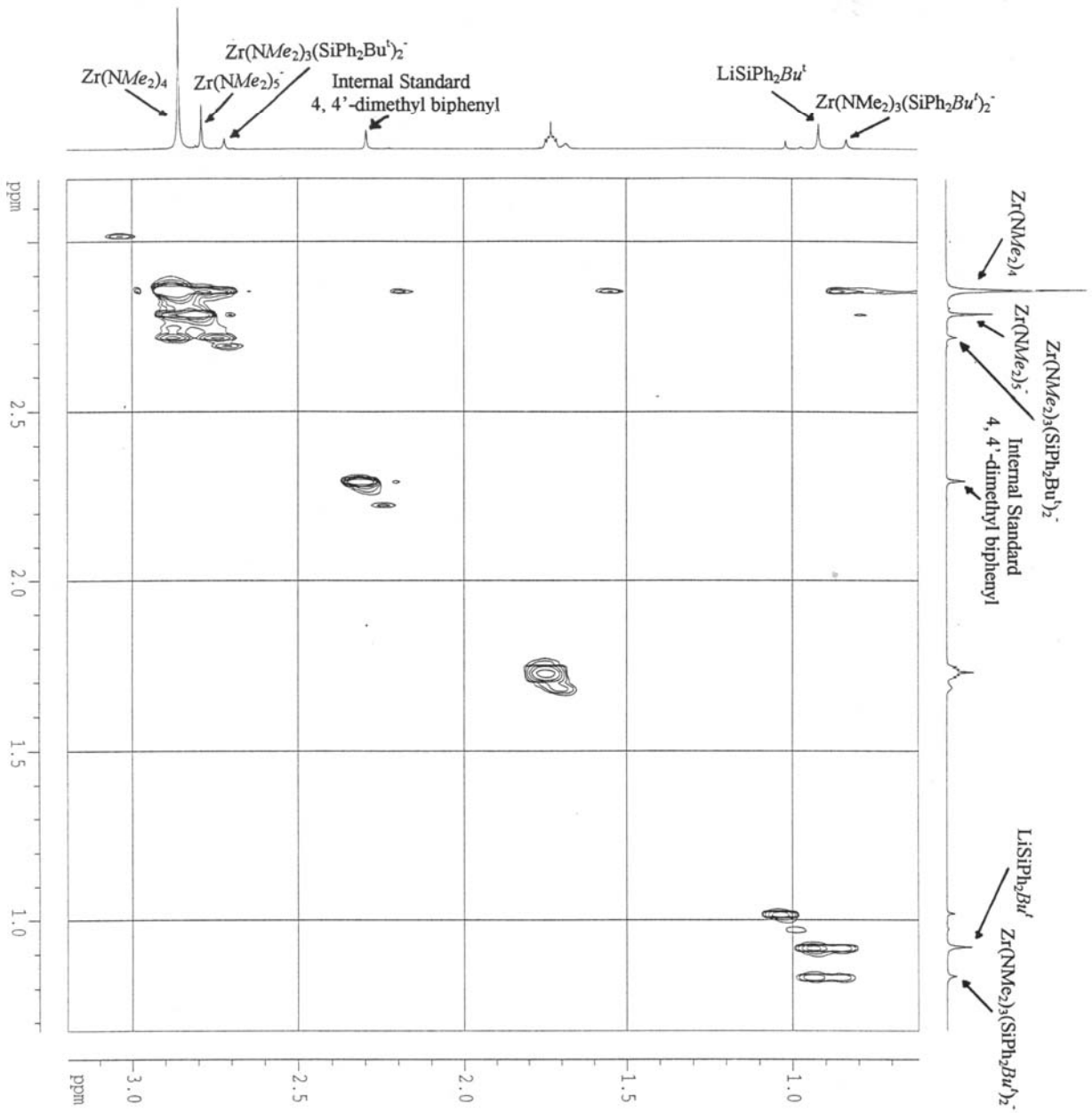

Figure S1. EXSY spectrum (THF-d_8, 400.0 MHz, 32 °C, t_{mix} = 2 s) of a mixture of **1a** and **2**.

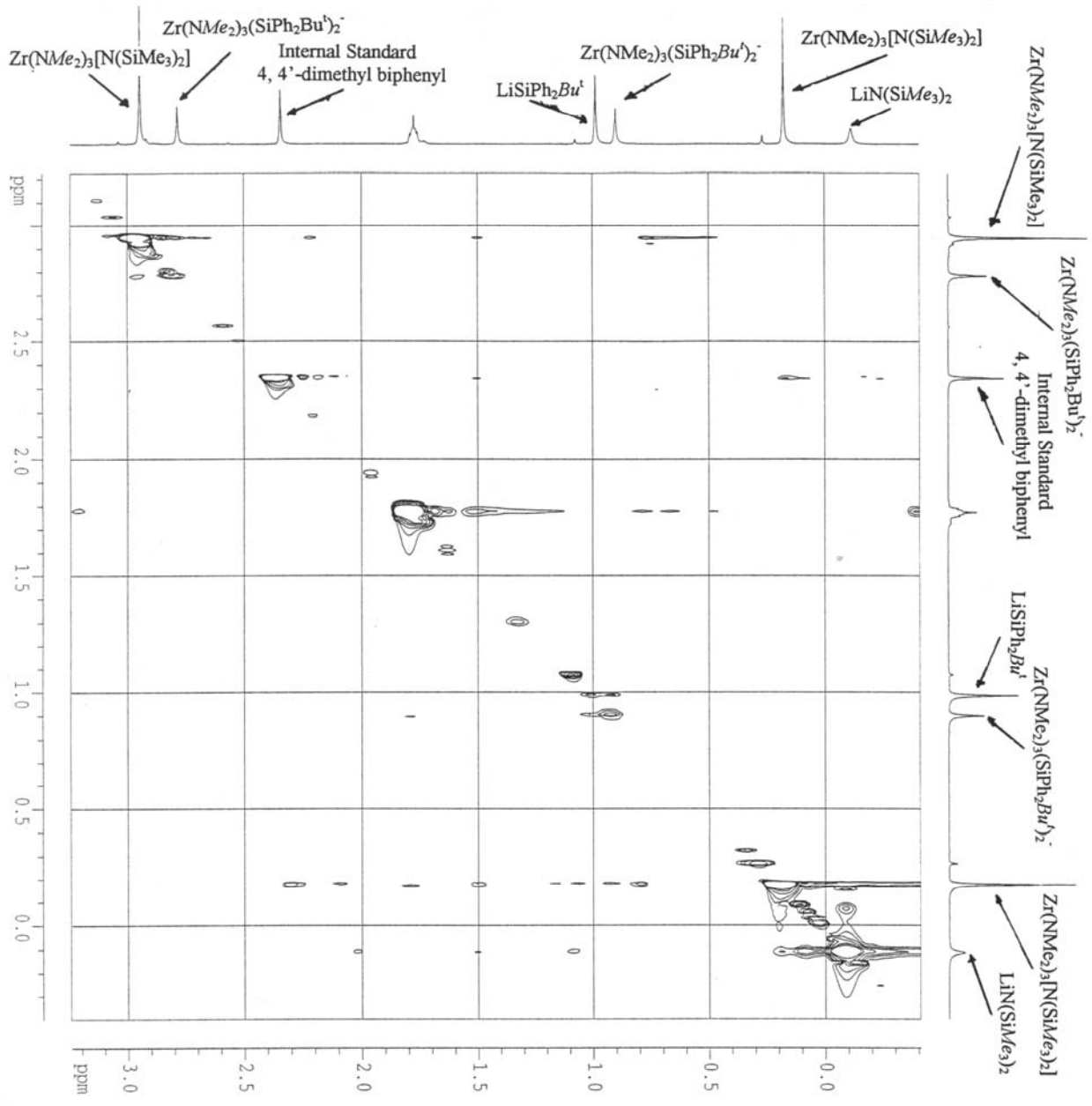

Figure S2. EXSY spectrum (THF-d_8, 400.0 MHz, 32 °C, t_{mix} = 4 s) of a mixture of **6a** and **2**. EXSY spectrum (THF-d_8, 32 °C) with t_{mix} = 2 s did not show crosspeaks. Decomposition of the mixture was observed during the acquisition of the EXSY data at 32 °C, making it difficult to conduct EXSY NMR studies at a higher temperature.

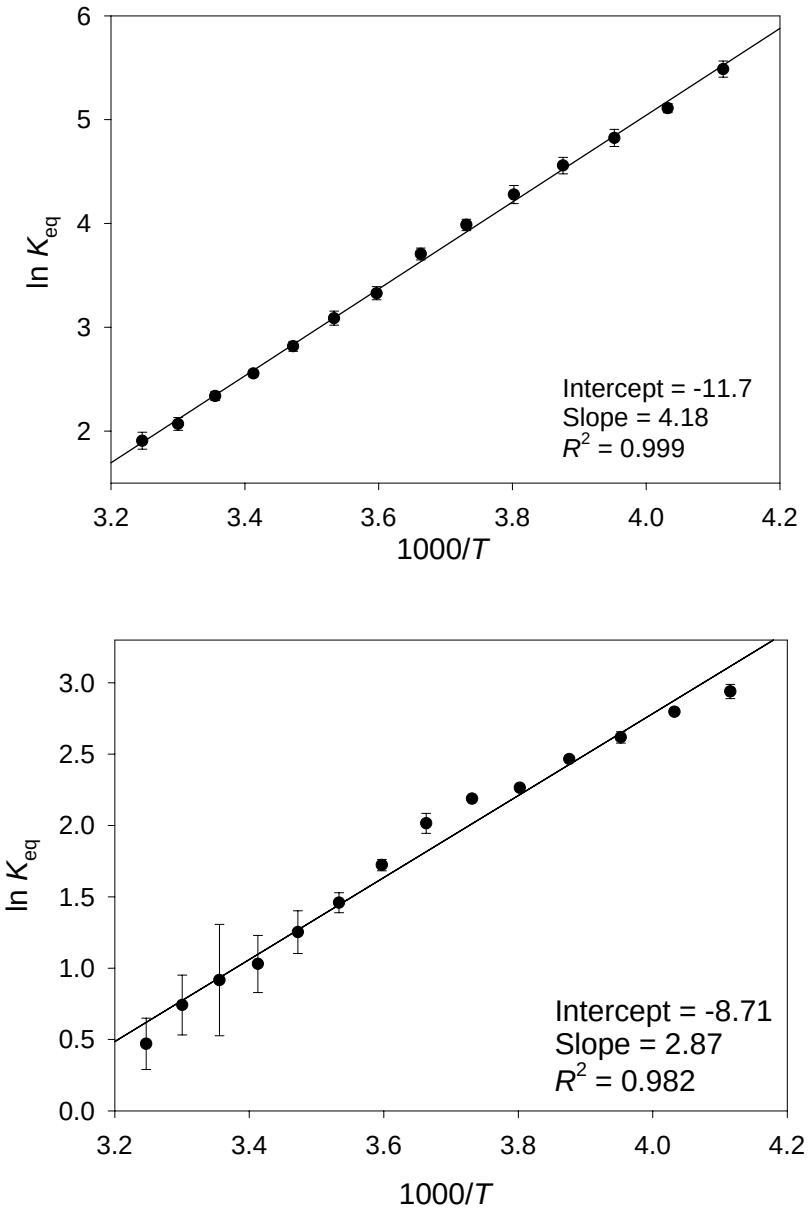

Figure S3. The ln K_{eq} *vs* 1000/T plots of the equilibria in Eq. 2: (top) Zr complexes; (bottom) Hf complexes.

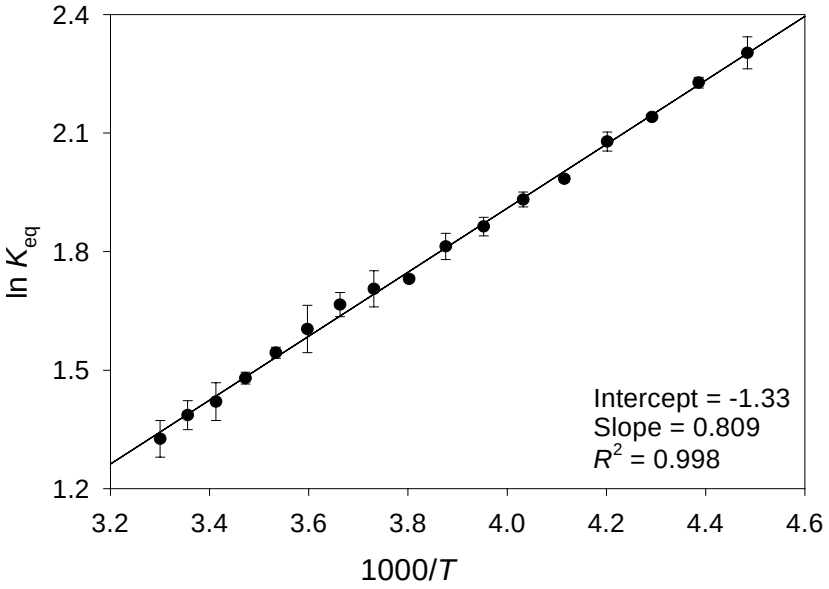

Figure S4. The ln K_{eq} *vs* 1000/T plot of the equilibrium in Eq. 4.

Table S1. Crystal data and structure refinement for **5**

Empirical formula	$C_{64}\ H_{118}\ Li_2\ N_8\ O_2\ Si_2\ Zr_2$	
Formula weight	1316.18	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*C*2/c	
Unit cell dimensions	a = 25.145(3) Å	α = 90°
	b = 17.770(3) Å	β = 97.789(3)°
	c = 16.346(3) Å	γ = 90°
Volume	7236(2) Å^3	
Z	4	
Density (calculated)	1.208 g/cm^3	
Absorption coefficient	0.368 mm^{-1}	
F(000)	2816	
Crystal size	0.40 × 0.25 × 0.25 mm^3	
Theta range for data collection	1.41 to 28.28°	
Index ranges	$-32 \le h \le 33$, $-23 \le k \le 23$, $-21 \le l \le 21$	
Reflections collected	36482	
Independent reflections	8684 [R(int) = 0.0543]	
Completeness to theta = 28.28°	96.5%	
Absorption correction	Multi-scan with SADABS	
Max. and min. transmission	0.9136 and 0.8667	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8684 / 0 / 383	
Goodness-of-fit on F^2	1.041	
Final R indices [I > 2sigma(I)]	R1 = 0.0396, wR2 = 0.1030	
R indices (all data)	R1 = 0.0567, wR2 = 0.1169	
Largest diff. peak and hole	0.875 and -0.464 e.Å^{-3}	

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **5**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Zr(1)	0	1532(1)	2500	21(1)
Zr(2)	5000	1512(1)	2500	24(1)
Si(1)	1171(1)	1670(1)	2965(1)	26(1)
O(1)	3564(1)	2192(1)	1107(1)	49(1)
O(2)	3540(1)	516(1)	663(1)	49(1)
N(1)	0	2702(1)	2500	29(1)
N(2)	50(1)	945(1)	1434(1)	32(1)
N(3)	5000	2658(2)	2500	34(1)
N(4)	4821(1)	1430(1)	1121(1)	35(1)
N(5)	4251(1)	951(1)	2513(1)	34(1)
Li(1)	4012(2)	1276(2)	1271(3)	37(1)
C(1)	232(1)	3162(1)	3187(2)	38(1)
C(2)	98(1)	1342(2)	678(2)	42(1)
C(3)	5(1)	139(2)	1298(2)	51(1)
C(4)	1353(1)	1680(1)	4145(1)	32(1)
C(5)	1322(1)	1013(2)	4602(2)	43(1)
C(6)	1402(1)	1004(2)	5461(2)	52(1)
C(7)	1517(1)	1655(2)	5901(2)	56(1)
C(8)	1545(1)	2321(2)	5473(2)	59(1)
C(9)	1458(1)	2332(2)	4616(2)	46(1)
C(10)	1479(1)	2582(1)	2599(1)	29(1)
C(11)	1947(1)	2938(2)	2975(2)	38(1)
C(12)	2135(1)	3607(2)	2666(2)	48(1)
C(13)	1867(1)	3930(2)	1961(2)	47(1)
C(14)	1413(1)	3587(1)	1564(2)	40(1)
C(15)	1223(1)	2931(1)	1883(1)	32(1)
C(16)	1640(1)	910(1)	2561(2)	35(1)
C(17)	2223(1)	967(2)	2975(2)	55(1)
C(18)	1629(1)	1039(2)	1634(2)	43(1)
C(19)	1429(1)	113(2)	2672(2)	58(1)
C(20)	4554(1)	3120(2)	2656(3)	68(1)

C(21)	4906(1)	743(2)	672(2)	54(1)
C(22)	4924(1)	2059(2)	591(2)	53(1)
C(23)	4248(1)	127(2)	2474(2)	57(1)
C(24)	3880(1)	1204(2)	3069(2)	50(1)
C(25)	2982(1)	593(2)	677(3)	86(1)
C(26)	2700(1)	-5(2)	166(2)	63(1)
C(27)	3124(1)	-569(2)	77(3)	70(1)
C(28)	3637(1)	-204(2)	312(3)	83(1)
C(29)	3568(2)	2640(2)	371(3)	82(1)
C(30)	3368(3)	3369(3)	514(3)	113(2)
C(31)	3063(2)	3290(3)	1206(3)	108(2)
C(32)	3160(1)	2513(2)	1548(2)	56(1)

Table S3. Bond lengths (Å) and angles (°) for **5**

Zr(1)-N(2)	2.0488(19)	N(4)-C(21)	1.454(3)
Zr(1)-N(2)#1	2.0488(19)	N(4)-C(22)	1.459(3)
Zr(1)-N(1)	2.080(2)	N(4)-Li(1)	2.099(4)
Zr(1)-Si(1)#1	2.9507(7)	N(5)-C(24)	1.459(3)
Zr(1)-Si(1)	2.9507(7)	N(5)-C(23)	1.465(3)
Zr(2)-N(3)	2.036(3)	N(5)-Li(1)	2.117(5)
Zr(2)-N(5)	2.1337(19)	C(4)-C(9)	1.397(4)
Zr(2)-N(5)#2	2.1337(19)	C(4)-C(5)	1.408(3)
Zr(2)-N(4)	2.243(2)	C(5)-C(6)	1.392(4)
Zr(2)-N(4)#2	2.243(2)	C(6)-C(7)	1.373(5)
Zr(2)-Li(1)#2	3.005(4)	C(7)-C(8)	1.380(5)
Zr(2)-Li(1)	3.005(4)	C(8)-C(9)	1.389(4)
Si(1)-C(4)	1.920(2)	C(10)-C(15)	1.400(3)
Si(1)-C(10)	1.926(2)	C(10)-C(11)	1.403(3)
Si(1)-C(16)	1.965(2)	C(11)-C(12)	1.399(4)
O(1)-C(32)	1.440(3)	C(12)-C(13)	1.379(4)
O(1)-C(29)	1.442(4)	C(13)-C(14)	1.375(4)
O(1)-Li(1)	1.979(5)	C(14)-C(15)	1.388(3)
O(2)-C(25)	1.413(3)	C(16)-C(18)	1.529(4)
O(2)-C(28)	1.437(3)	C(16)-C(17)	1.531(4)
O(2)-Li(1)	1.975(5)	C(16)-C(19)	1.531(4)
N(1)-C(1)#1	1.447(3)	C(25)-C(26)	1.471(4)
N(1)-C(1)	1.447(3)	C(26)-C(27)	1.485(5)
N(2)-C(2)	1.442(3)	C(27)-C(28)	1.450(5)
N(2)-C(3)	1.452(3)	C(29)-C(30)	1.420(5)
N(3)-C(20)#2	1.440(3)	C(30)-C(31)	1.456(6)
N(3)-C(20)	1.440(3)	C(31)-C(32)	1.497(5)

N(2)-Zr(1)-N(2)#1	118.86(11)	N(2)-Zr(1)-Si(1)	95.01(6)
N(2)-Zr(1)-N(1)	120.57(6)	N(2)#1-Zr(1)-Si(1)	89.83(6)
N(2)#1-Zr(1)-N(1)	120.57(6)	N(1)-Zr(1)-Si(1)	85.235(13)
N(2)-Zr(1)-Si(1)#1	89.83(6)	Si(1)#1-Zr(1)-Si(1)	170.47(3)
N(2)#1-Zr(1)-Si(1)#1	95.01(6)	N(3)-Zr(2)-N(5)	117.85(5)
N(1)-Zr(1)-Si(1)#1	85.235(13)	N(3)-Zr(2)-N(5)#2	117.85(5)

N(5)-Zr(2)-N(5)#2	124.30(11)	C(2)-N(2)-Zr(1)	120.17(16)
N(3)-Zr(2)-N(4)	93.73(5)	C(3)-N(2)-Zr(1)	128.32(17)
N(5)-Zr(2)-N(4)	85.54(8)	C(20)#2-N(3)-C(20)	110.4(3)
N(5)#2-Zr(2)-N(4)	90.97(8)	C(20)#2-N(3)-Zr(2)	124.79(16)
N(3)-Zr(2)-N(4)#2	93.73(5)	C(20)-N(3)-Zr(2)	124.79(16)
N(5)-Zr(2)-N(4)#2	90.97(8)	C(21)-N(4)-C(22)	107.0(2)
N(5)#2-Zr(2)-N(4)#2	85.54(8)	C(21)-N(4)-Li(1)	99.3(2)
N(4)-Zr(2)-N(4)#2	172.54(11)	C(22)-N(4)-Li(1)	115.0(2)
N(3)-Zr(2)-Li(1)#2	98.03(8)	C(21)-N(4)-Zr(2)	122.56(18)
N(5)-Zr(2)-Li(1)#2	125.38(10)	C(22)-N(4)-Zr(2)	121.29(17)
N(5)#2-Zr(2)-Li(1)#2	44.80(10)	Li(1)-N(4)-Zr(2)	87.51(14)
N(4)-Zr(2)-Li(1)#2	134.27(10)	C(24)-N(5)-C(23)	109.6(2)
N(4)#2-Zr(2)-Li(1)#2	44.26(9)	C(24)-N(5)-Li(1)	113.0(2)
N(3)-Zr(2)-Li(1)	98.03(8)	C(23)-N(5)-Li(1)	103.4(2)
N(5)-Zr(2)-Li(1)	44.80(10)	C(24)-N(5)-Zr(2)	120.11(18)
N(5)#2-Zr(2)-Li(1)	125.38(10)	C(23)-N(5)-Zr(2)	117.76(17)
N(4)-Zr(2)-Li(1)	44.26(9)	Li(1)-N(5)-Zr(2)	89.96(13)
N(4)#2-Zr(2)-Li(1)	134.27(10)	O(2)-Li(1)-O(1)	101.6(2)
Li(1)#2-Zr(2)-Li(1)	163.93(16)	O(2)-Li(1)-N(4)	123.8(2)
C(4)-Si(1)-C(10)	104.70(10)	O(1)-Li(1)-N(4)	114.8(2)
C(4)-Si(1)-C(16)	105.79(10)	O(2)-Li(1)-N(5)	111.7(2)
C(10)-Si(1)-C(16)	100.95(10)	O(1)-Li(1)-N(5)	115.9(2)
C(4)-Si(1)-Zr(1)	110.65(7)	N(4)-Li(1)-N(5)	89.68(18)
C(10)-Si(1)-Zr(1)	114.71(7)	O(2)-Li(1)-Zr(2)	144.9(2)
C(16)-Si(1)-Zr(1)	118.66(8)	O(1)-Li(1)-Zr(2)	112.35(18)
C(32)-O(1)-C(29)	106.5(2)	N(4)-Li(1)-Zr(2)	48.23(10)
C(32)-O(1)-Li(1)	133.2(2)	N(5)-Li(1)-Zr(2)	45.24(10)
C(29)-O(1)-Li(1)	119.9(2)	C(9)-C(4)-C(5)	115.1(2)
C(25)-O(2)-C(28)	108.4(2)	C(9)-C(4)-Si(1)	124.25(19)
C(25)-O(2)-Li(1)	117.2(2)	C(5)-C(4)-Si(1)	120.18(19)
C(28)-O(2)-Li(1)	133.3(2)	C(6)-C(5)-C(4)	122.4(3)
C(1)#1-N(1)-C(1)	111.2(3)	C(7)-C(6)-C(5)	120.6(3)
C(1)#1-N(1)-Zr(1)	124.40(13)	C(6)-C(7)-C(8)	118.6(3)
C(1)-N(1)-Zr(1)	124.40(13)	C(7)-C(8)-C(9)	120.8(3)
C(2)-N(2)-C(3)	111.4(2)	C(8)-C(9)-C(4)	122.5(3)

C(15)-C(10)-C(11)	115.4(2)	C(18)-C(16)-Si(1)	107.36(16)
C(15)-C(10)-Si(1)	118.34(17)	C(17)-C(16)-Si(1)	112.81(18)
C(11)-C(10)-Si(1)	126.25(18)	C(19)-C(16)-Si(1)	111.21(18)
C(12)-C(11)-C(10)	122.0(3)	O(2)-C(25)-C(26)	108.9(3)
C(13)-C(12)-C(11)	120.2(3)	C(25)-C(26)-C(27)	104.2(3)
C(14)-C(13)-C(12)	119.4(2)	C(28)-C(27)-C(26)	107.3(3)
C(13)-C(14)-C(15)	120.1(3)	O(2)-C(28)-C(27)	108.0(3)
C(14)-C(15)-C(10)	122.9(2)	C(30)-C(29)-O(1)	108.9(3)
C(18)-C(16)-C(17)	108.4(2)	C(29)-C(30)-C(31)	105.9(4)
C(18)-C(16)-C(19)	107.2(2)	C(30)-C(31)-C(32)	107.7(3)
C(17)-C(16)-C(19)	109.6(2)	O(1)-C(32)-C(31)	105.5(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x,y,-z+1/2 #2 -x+1,y,-z+1/2

Table S4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **5**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Zr(1)	26(1)	17(1)	21(1)	0	5(1)	0
Zr(2)	27(1)	19(1)	27(1)	0	8(1)	0
Si(1)	26(1)	26(1)	25(1)	1(1)	4(1)	3(1)
O(1)	56(1)	40(1)	55(1)	-2(1)	16(1)	15(1)
O(2)	35(1)	47(1)	64(1)	-23(1)	1(1)	1(1)
N(1)	32(1)	17(1)	39(2)	0	6(1)	0
N(2)	37(1)	32(1)	28(1)	-6(1)	5(1)	2(1)
N(3)	41(2)	22(1)	41(2)	0	8(1)	0
N(4)	36(1)	40(1)	30(1)	-2(1)	10(1)	1(1)
N(5)	34(1)	31(1)	39(1)	0(1)	11(1)	-6(1)
Li(1)	32(2)	34(2)	44(2)	-6(2)	6(2)	0(2)
C(1)	38(1)	29(1)	47(2)	-7(1)	8(1)	0(1)
C(2)	45(2)	48(2)	34(1)	0(1)	8(1)	-5(1)
C(3)	72(2)	32(1)	50(2)	-8(1)	12(1)	3(1)
C(4)	27(1)	40(1)	27(1)	2(1)	4(1)	6(1)
C(5)	50(2)	46(2)	34(1)	6(1)	6(1)	7(1)
C(6)	56(2)	67(2)	35(2)	18(1)	11(1)	22(1)
C(7)	51(2)	92(2)	26(1)	1(2)	6(1)	23(2)
C(8)	72(2)	70(2)	36(2)	-15(1)	11(1)	-1(2)
C(9)	59(2)	47(2)	34(1)	-4(1)	14(1)	1(1)
C(10)	28(1)	31(1)	28(1)	-3(1)	9(1)	2(1)
C(11)	30(1)	45(1)	37(1)	-3(1)	5(1)	-2(1)
C(12)	38(1)	50(2)	57(2)	-11(1)	14(1)	-16(1)
C(13)	51(2)	34(1)	59(2)	2(1)	23(1)	-6(1)
C(14)	44(1)	36(1)	42(1)	8(1)	15(1)	5(1)
C(15)	32(1)	33(1)	32(1)	2(1)	6(1)	0(1)
C(16)	36(1)	35(1)	34(1)	-1(1)	5(1)	10(1)
C(17)	39(2)	73(2)	52(2)	-5(2)	0(1)	27(1)
C(18)	49(2)	45(2)	35(1)	-6(1)	10(1)	12(1)
C(19)	82(2)	33(1)	64(2)	2(1)	28(2)	15(1)

C(20)	54(2)	38(2)	114(3)	-10(2)	25(2)	5(1)
C(21)	52(2)	66(2)	44(2)	-21(2)	7(1)	9(2)
C(22)	57(2)	70(2)	33(1)	12(1)	10(1)	-11(2)
C(23)	58(2)	34(2)	76(2)	6(1)	3(2)	-13(1)
C(24)	37(1)	69(2)	48(2)	12(1)	17(1)	4(1)
C(25)	35(2)	86(3)	136(4)	-63(3)	9(2)	-4(2)
C(26)	45(2)	63(2)	79(2)	-23(2)	4(2)	-8(1)
C(27)	58(2)	43(2)	106(3)	-17(2)	-4(2)	-3(2)
C(28)	56(2)	68(2)	120(3)	-58(2)	-11(2)	12(2)
C(29)	108(3)	76(3)	72(2)	17(2)	47(2)	37(2)
C(30)	188(6)	87(3)	76(3)	32(2)	61(3)	70(3)
C(31)	148(5)	89(3)	102(3)	29(3)	72(3)	66(3)
C(32)	59(2)	55(2)	58(2)	-3(1)	23(2)	13(2)

Table S5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **5**

	x	y	z	U(eq)
H(1A)	524	3467	3019	57
H(1B)	375	2837	3650	57
H(1C)	-44	3494	3358	57
H(2A)	415	1161	449	63
H(2B)	134	1882	791	63
H(2C)	-224	1252	279	63
H(3A)	-294	35	863	76
H(3B)	-59	-110	1810	76
H(3C)	339	-52	1128	76
H(5)	1244	554	4314	52
H(6)	1377	542	5746	63
H(7)	1576	1648	6487	67
H(8)	1624	2776	5768	71
H(9)	1471	2800	4339	55
H(11)	2142	2718	3454	45
H(12)	2450	3839	2942	57
H(13)	1993	4385	1752	56
H(14)	1230	3799	1072	48
H(15)	906	2708	1603	39
H(17A)	2441	590	2737	83
H(17B)	2238	877	3569	83
H(17C)	2362	1471	2883	83
H(18A)	1844	651	1407	64
H(18B)	1778	1537	1542	64
H(18C)	1258	1013	1361	64
H(19A)	1054	81	2416	87
H(19B)	1452	-1	3262	87
H(19C)	1645	-249	2409	87
H(20A)	4663	3439	3139	101
H(20B)	4255	2798	2762	101
H(20C)	4442	3438	2174	101

H(21A)	4655	728	158	81
H(21B)	4846	306	1013	81
H(21C)	5275	733	542	81
H(22A)	5303	2057	510	79
H(22B)	4840	2533	851	79
H(22C)	4699	2009	55	79
H(23A)	4328	-79	3034	85
H(23B)	4520	-44	2141	85
H(23C)	3893	-47	2223	85
H(24A)	3513	1061	2843	75
H(24B)	3903	1752	3127	75
H(24C)	3976	969	3612	75
H(25A)	2860	1092	458	103
H(25B)	2901	552	1251	103
H(26A)	2543	194	-379	75
H(26B)	2410	-227	442	75
H(27A)	3086	-1008	439	84
H(27B)	3093	-747	-501	84
H(28A)	3866	-516	721	100
H(28B)	3825	-139	-178	100
H(29A)	3938	2677	233	99
H(29B)	3340	2400	-99	99
H(30A)	3134	3553	18	136
H(30B)	3667	3729	650	136
H(31A)	2676	3366	1019	130
H(31B)	3183	3669	1636	130
H(32A)	3289	2533	2148	67
H(32B)	2826	2212	1459	67

Table S6. Crystal data and structure refinement for $(Me_2N)_3Hf\text{-}Si(SiMe_3)_3$ (**9b**)

Empirical formula	$C_{15}\ H_{45}\ Hf\ N_3\ Si_4$	
Formula weight	558.38	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Rhombohedral	
Space group	*R*3c	
Unit cell dimensions	a = 15.483(5) Å	α = 90°
	b = 15.483(5) Å	β = 90°
	c = 19.378(8) Å	γ = 120°
Volume	4023(2) $Å^3$	
Z	6	
Density (calculated)	1.383 g/cm^3	
Absorption coefficient	4.072 mm^{-1}	
F(000)	1704	
Crystal size	0.45 × 0.40 × 0.15 mm^3	
Theta range for data collection	2.59 to 28.35°	
Index ranges	$-20 \le h \le 19$, $-19 \le k \le 20$, $-25 \le l \le 25$	
Reflections collected	11001	
Independent reflections	2027 [*R*(int) = 0.0348]	
Completeness to theta = 28.35°	94.5%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5803 and 0.2616	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2027 / 1 / 75	
Goodness-of-fit on F^2	1.178	
Final R indices [I > 2sigma(I)]	*R*1 = 0.0490, w*R*2 = 0.1350	
R indices (all data)	*R*1 = 0.0567, w*R*2 = 0.1655	
Absolute structure parameter	0.89(4)	
Largest diff. peak and hole	2.792 and -1.690 e.$Å^{-3}$	

Table S7. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **9b**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	2183(9)	2277(8)	3890(6)	55(3)
C(2)	1567(9)	1341(9)	5257(5)	47(3)
C(3)	2301(11)	453(9)	4241(8)	68(4)
C(4)	1884(8)	1964(8)	1822(7)	52(3)
C(5)	494(10)	2020(9)	2292(7)	48(3)
Hf(1)	0	0	2454(1)	20(1)
N(1)	926(7)	1415(6)	2147(4)	28(1)
Si(1)	0	0	3870(3)	18(1)
Si(2)	1582(2)	1034(2)	4331(2)	33(1)

Table S8. Bond lengths (Å) and angles (°) for **9b**.

C(1)-Si(2)	1.874(12)	Hf(1)-N(1)#1	2.017(8)
C(2)-Si(2)	1.859(11)	Hf(1)-N(1)#2	2.017(8)
C(3)-Si(2)	1.754(15)	Hf(1)-Si(1)	2.743(6)
C(4)-N(1)	1.435(14)	Si(1)-Si(2)	2.332(4)
C(5)-N(1)	1.425(14)	Si(1)-Si(2)#2	2.332(4)
Hf(1)-N(1)	2.017(8)	Si(1)-Si(2)#1	2.332(4)

N(1)-Hf(1)-N(1)#1	111.7(2)	Si(2)#2-Si(1)-Si(2)#1	106.22(18)
N(1)-Hf(1)-N(1)#2	111.7(2)	Si(2)-Si(1)-Hf(1)	112.55(16)
N(1)#1-Hf(1)-N(1)#2	111.7(2)	Si(2)#2-Si(1)-Hf(1)	112.55(16)
N(1)-Hf(1)-Si(1)	107.1(3)	Si(2)#1-Si(1)-Hf(1)	112.55(16)
N(1)#1-Hf(1)-Si(1)	107.1(3)	C(3)-Si(2)-C(2)	108.6(7)
N(1)#2-Hf(1)-Si(1)	107.1(3)	C(3)-Si(2)-C(1)	111.4(8)
C(5)-N(1)-C(4)	112.5(9)	C(2)-Si(2)-C(1)	103.9(6)
C(5)-N(1)-Hf(1)	110.1(7)	C(3)-Si(2)-Si(1)	109.1(4)
C(4)-N(1)-Hf(1)	137.4(8)	C(2)-Si(2)-Si(1)	113.8(4)
Si(2)-Si(1)-Si(2)#2	106.22(18)	C(1)-Si(2)-Si(1)	110.0(4)
Si(2)-Si(1)-Si(2)#1	106.22(18)		

Table S9. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **9b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	49(7)	33(5)	56(7)	5(5)	-8(5)	1(5)
C(2)	46(6)	51(6)	28(5)	-7(4)	-8(4)	11(5)
C(3)	74(10)	36(6)	82(10)	-30(6)	-44(8)	19(6)
C(4)	33(5)	32(5)	73(8)	4(5)	1(5)	3(4)
C(5)	60(7)	35(5)	59(7)	7(5)	19(6)	30(5)
Hf(1)	20(1)	20(1)	21(1)	0	0	10(1)
N(1)	33(4)	21(4)	27(4)	4(3)	1(3)	11(3)
Si(1)	18(1)	18(1)	20(2)	0	0	9(1)
Si(2)	22(1)	38(1)	28(1)	-1(1)	-5(1)	8(1)

Table S10. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **9b**.

	x	y	z	U(eq)
H(1A)	2806	2718	4111	82
H(1B)	1751	2554	3919	82
H(1C)	2299	2197	3414	82
H(2A)	1236	736	5521	71
H(2B)	1219	1704	5309	71
H(2C)	2240	1741	5419	71
H(3A)	2973	904	4384	101
H(3B)	2299	274	3766	101
H(3C)	2023	-136	4522	101
H(4A)	1800	2109	1353	78
H(4B)	2209	1574	1827	78
H(4C)	2285	2577	2067	78
H(5A)	878	2498	2642	72
H(5B)	-178	1606	2451	72
H(5C)	491	2363	1880	72

Table S11. Crystal data and structure refinement for $[Hf(NMe_2)_4]_2$

Empirical formula	$C_{16}\ H_{48}\ Hf_2\ N_8$	
Formula weight	709.60	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*C*2/c	
Unit cell dimensions	a = 20.429(13) Å	α = 90°
	b = 8.454(5) Å	β = 112.425(10)°
	c = 15.971(10) Å	γ = 90°
Volume	2550(3) $Å^3$	
Z	4	
Density (calculated)	1.849 g/cm^3	
Absorption coefficient	8.153 mm^{-1}	
F(000)	1376	
Crystal size	0.55 × 0.45 × 0.07 mm^3	
Theta range for data collection	2.16 to 22.50°	
Index ranges	$-21 \le h \le 21$, $-9 \le k \le 9$, $-17 \le l \le 17$	
Reflections collected	6107	
Independent reflections	1628 [R(int) = 0.0352]	
Completeness to theta = 22.50°	97.7%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5991 and 0.0940	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1628 / 0 / 126	
Goodness-of-fit on F^2	1.014	
Final R indices [I > 2sigma(I)]	R1 = 0.0358, wR2 = 0.0967	
R indices (all data)	R1 = 0.0369, wR2 = 0.1000	
Largest diff. peak and hole	2.154 and -2.286 e.$Å^{-3}$	

Table S12. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $[Hf(NMe_2)_4]_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	1440(4)	5810(12)	1231(6)	39(2)
C(2)	1062(5)	8282(14)	584(6)	43(2)
C(3)	2400(5)	7385(10)	3291(7)	31(2)
C(4)	1960(4)	5527(10)	4048(6)	36(2)
C(5)	569(4)	11207(10)	1869(6)	35(2)
C(6)	1458(4)	10959(10)	3356(5)	33(2)
C(7)	-645(5)	7788(9)	704(6)	23(2)
C(8)	-122(4)	5362(9)	1461(5)	26(2)
Hf(1)	842(1)	7734(1)	2431(1)	14(1)
N(1)	938(3)	10114(9)	2592(4)	22(1)
N(2)	1121(4)	7266(7)	1336(5)	24(2)
N(3)	1760(3)	6787(9)	3369(4)	22(1)
N(4)	-286(4)	7015(8)	1599(5)	18(2)

Table S13. Bond lengths (Å) and angles (°) for $[Hf(NMe_2)_4]_2$.

C(1)-N(2)	1.432(11)	Hf(1)-N(1)	2.028(7)
C(2)-N(2)	1.443(12)	Hf(1)-N(3)	2.064(6)
C(3)-N(3)	1.450(11)	Hf(1)-N(2)	2.074(8)
C(4)-N(3)	1.462(10)	Hf(1)-N(4)	2.262(7)
C(5)-N(1)	1.447(11)	Hf(1)-N(4)#1	2.324(7)
C(6)-N(1)	1.463(10)	Hf(1)-Hf(1)#1	3.532(2)
C(7)-N(4)	1.486(11)	N(4)-Hf(1)#1	2.324(7)
C(8)-N(4)	1.474(10)		

N(1)-Hf(1)-N(3)	106.1(3)	C(5)-N(1)-C(6)	110.2(7)
N(1)-Hf(1)-N(2)	104.6(2)	C(5)-N(1)-Hf(1)	122.5(5)
N(3)-Hf(1)-N(2)	94.1(3)	C(6)-N(1)-Hf(1)	126.5(5)
N(1)-Hf(1)-N(4)	111.6(2)	C(1)-N(2)-C(2)	108.1(8)
N(3)-Hf(1)-N(4)	139.7(3)	C(1)-N(2)-Hf(1)	123.1(6)
N(2)-Hf(1)-N(4)	90.0(3)	C(2)-N(2)-Hf(1)	128.7(6)
N(1)-Hf(1)-N(4)#1	102.9(2)	C(4)-N(3)-C(3)	108.2(6)
N(3)-Hf(1)-N(4)#1	87.4(3)	C(4)-N(3)-Hf(1)	137.8(5)
N(2)-Hf(1)-N(4)#1	150.9(3)	C(3)-N(3)-Hf(1)	113.7(5)
N(4)-Hf(1)-N(4)#1	71.0(3)	C(7)-N(4)-C(8)	109.3(6)
N(1)-Hf(1)-Hf(1)#1	92.36(14)	C(7)-N(4)-Hf(1)	117.7(5)
N(3)-Hf(1)-Hf(1)#1	126.32(18)	C(8)-N(4)-Hf(1)	95.9(4)
N(2)-Hf(1)-Hf(1)#1	129.8(2)	C(7)-N(4)-Hf(1)#1	109.8(5)
N(4)-Hf(1)-Hf(1)#1	40.29(18)	C(8)-N(4)-Hf(1)#1	123.0(5)
N(4)#1-Hf(1)-Hf(1)#1	39.00(17)	Hf(1)-N(4)-Hf(1)#1	100.7(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x,y,-z+1/2

Table S14. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $[Hf(NMe_2)_4]_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	43(4)	43(6)	32(5)	-11(4)	16(4)	13(4)
C(2)	46(5)	55(6)	36(5)	8(5)	23(4)	-1(5)
C(3)	21(5)	43(5)	24(5)	9(4)	2(4)	-1(3)
C(4)	28(4)	32(5)	42(5)	18(4)	5(3)	10(4)
C(5)	43(4)	19(4)	42(5)	10(4)	16(4)	6(4)
C(6)	46(5)	24(5)	31(4)	-9(4)	17(4)	-6(4)
C(7)	34(5)	30(5)	8(4)	1(3)	9(4)	2(3)
C(8)	29(4)	17(4)	30(4)	-9(4)	8(3)	-4(3)
Hf(1)	21(1)	9(1)	12(1)	0(1)	6(1)	0(1)
N(1)	26(3)	18(4)	23(3)	-4(3)	10(2)	-3(3)
N(2)	28(4)	29(4)	14(4)	3(3)	8(3)	-2(3)
N(3)	19(3)	25(3)	18(3)	1(3)	5(2)	1(3)
N(4)	26(4)	9(3)	17(4)	-2(3)	8(3)	5(3)

Table S15. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for $[Hf(NMe_2)_4]_2$.

	x	y	z	U(eq)
H(1A)	1141	5305	661	59
H(1B)	1489	5105	1739	59
H(1C)	1908	6025	1222	59
H(2A)	1523	8354	530	65
H(2B)	912	9339	689	65
H(2C)	712	7843	25	65
H(3A)	2725	7769	3883	47
H(3B)	2279	8256	2853	47
H(3C)	2628	6535	3085	47
H(4A)	2173	4650	3838	54
H(4B)	1539	5151	4138	54
H(4C)	2304	5936	4621	54
H(5A)	345	12035	2098	52
H(5B)	204	10637	1375	52
H(5C)	906	11689	1643	52
H(6A)	1819	11430	3167	50
H(6B)	1685	10218	3855	50
H(6C)	1220	11796	3558	50
H(7A)	-333	7756	365	35
H(7B)	-751	8891	793	35
H(7C)	-1086	7227	363	35
H(8A)	-527	4687	1403	40
H(8B)	295	5012	1980	40
H(8C)	-24	5286	907	40