Insertion reactions of phenyl isocyanate into hafnium nitrogen bonds: synthesis and reactivity of hafnium complexes bearing substituted pyrrolyl ligands

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Abstract

A bis(diethylamido)hafnium compound $[C_4H_3N(CH_2NMe_2)-2]_2Hf(NEt_2)_2$ (**1**) has been prepared in 79% yield by reacting $Hf(NEt_2)_4$ with 2 equiv. of $[C_4H_3NH(CH_2NMe_2)-2]$ in heptane via deamination. Reacting compound **1** with 2 equiv. of phenyl iso-cyanate at room temperature in diethyl ether results in the PhNCO being inserted seletively into hafnium–NEt_2 bonds to generate $[C_4H_3N(CH_2NMe_2)-2]_2Hf[PhNC(NEt_2)O]_2$ (**2**) in 56% yield. Similarly, while reacting **1** with 2 equiv. of phenyl isocyanate for a week in toluene produces a mixture of **2** and $[C_4H_3N(CH_2NMe_2)-2]Hf[PhNC(NEt_2)O]_3$ (**3**). For comparison, reacting $Hf(NEt_2)_4$ with 4 equiv. of PhNCO in a toluene solution at room temperature results in the PhNCO inserted into Hf–N bonds, and forms a tetrakis-ureato hafnium compound $Hf[PhNC(NEt_2)O]_4$ (**4**) in 88% yield. A theoretical calculation found that the unpaired electrons of the ureato fragments of **2** are resonance delocalized between the C–O, C–NPh, and C–NEt_2 bonds, which are all partially doubly bonded.
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1. Introduction

Organic isocyanates are useful compounds in organic synthesis because they are easily accessible and highly active toward unsaturated substrates [1]. In addition, isocyanate compounds are widely used in polymeriza-tion chemistry for producing polyurethane [2]. Some of the organic reactions of isocyanates are catalyzed by transition metal complexes [3–7] and the reactions of organic isocyanates with transition metals have been studied extensively. An excellent review by Braunstein

and Nobel [8] described the transition-metal-mediated reactions of organic isocyanates, which covered a broad range of metal complexes. Insertion reactions of isocya-nates into metal carbon or metal nitrogen bonds have been known [9–12]; however, the insertion reactions of isocyanates into early transition metal–nitrogen bonds still remain undeveloped [13–19]. Examples showed by Lappert and coworkers [20] were those $M(NMe_2)_4$ (M = Ti, Zr, Hf) react exothermically with excess of phenyl isocyanates to give $M[NPhC(O)NMe_2]_4$. How-ever, no crystal structures were presented.

To better understand the reactivity of isocyanates toward early transition metal nitrogen bonds, here we report the synthesis and characterization of hafnium amide complexes and their reactivity toward isocyanates.

2. Results and discussion

2.1. Synthesis and characterization

A bis(diethylamido)hafnium compound [C$_4$H$_3$N(CH$_2$NMe$_2$)-2]$_2$Hf(NEt$_2$)$_2$ (**1**) has been prepared in 79% yield by a deamination reaction between Hf(NEt$_2$)$_4$ and 2 equiv. of [C$_4$H$_3$NH(CH$_2$NMe$_2$)-2] in heptane (Scheme 1). Compound **1** is highly air- and moisture sensitive, which readily decomposes upon exposure to the atmosphere. The ^{1}H and ^{13}C NMR spectra of **1** exhibit a symmetrical geometry with only one set of signals for the substituted pyrrolyl and diethylamido ligands being observed.

Reactions of compound **1** with CO$_2$ and CS$_2$ do not result in isolable insertion products, but rather afford the regeneration of substituted pyrrolyl ligands and un-identified products. In contrast, reaction of **1** with 2 equiv. of phenyl isocyanate at room temperature in diethyl ether for 30 min results in the PhNCO being inserted selectively into Hf–NEt$_2$ bonds to generate [C$_4$H$_3$N(CH$_2$NMe$_2$)-2]$_2$Hf[PhNC(NEt$_2$)O]$_2$ (**2**) in 56% yield. The ^{13}C NMR spectrum of **2** revealed a resonance at δ 165.9, which is assignable to the quaternary carbons of ureato PhNC(NEt$_2$)O fragments. The ^{1}H NMR spectrum of **2** obtained from a 300 MHz NMR spectrometer contains sharp resonances at δ 6.59 and 6.45 attributable to the pyrrolyl fragments of the bidentate ligands. However, the dimethylamino fragments of the bidentate ligands (δ 2.18) as well as the diethylamino fragments (δ 2.78 and 0.73) exhibit broad signals. The signal-broadening can probably be attributed to the fluxionality of the ureato PhNC(NEt$_2$)O fragments of **2**, which bind to its metal center in various modes, as shown in Scheme 2. The broad signals can be resolved in higher field NMR spectrometer. When a 600 MHz NMR spectrometer was used, the ^{1}H NMR spectra of **2** exhibit two peaks for the dimethylamino groups and multiple resonances for the diethyl amino fragments. A comparison of the ^{1}H NMR spectra of **2** obtained from 300 and 600 MHz NMR spectrometers was shown in Fig. 1.

Prolong stirring of **1** with 2 equiv. of PhNCO in toluene at room temperature for 6 days, a mixture of compounds **2** and [C$_4$H$_3$N(CH$_2$NMe$_2$)-2]Hf[PhNC(NEt$_2$)O]$_3$ (**3**) can be obtained according to the ^{1}H NMR spectra. Pure compound **3** can be obtained in 14% yield after removing volatiles and repeating recrystallization of the mixture from a diethyl ether solution. The ^{13}C NMR spectrum of **3** revealed two resonances at δ 166.2 and 167.0, which are assignable to the quaternary carbons of ureato PhNC(NEt$_2$)O fragments. Again, the dimethylamino fragments of the bidentate ligands (δ 2.67) as well as the diethylamino fragments (δ 2.27–2.73 and 0.73) exhibit broad signals due to the exchanging of bonding modes as shown in Scheme 2. No reaction was observed when monitoring a C$_6$D$_6$ solution of **2** for more than 80 h. Therefore, the formation of **3** was proposed as the results of ligand redistribution, which only occurs when excess of PhNCO is present. Indeed, when small amount of PhNCO was added to the a solution of compound **2** in C$_6$D$_6$, **3** was formed together with several un-identified compounds within 12 h at 50 °C, according to the ^{1}H NMR spectra. However, the real mechanism for the ligand redistribution is still unclear. Attempts to increase the yield of compound **3** by reacting **1** with 3 equiv. of PhNCO in toluene result
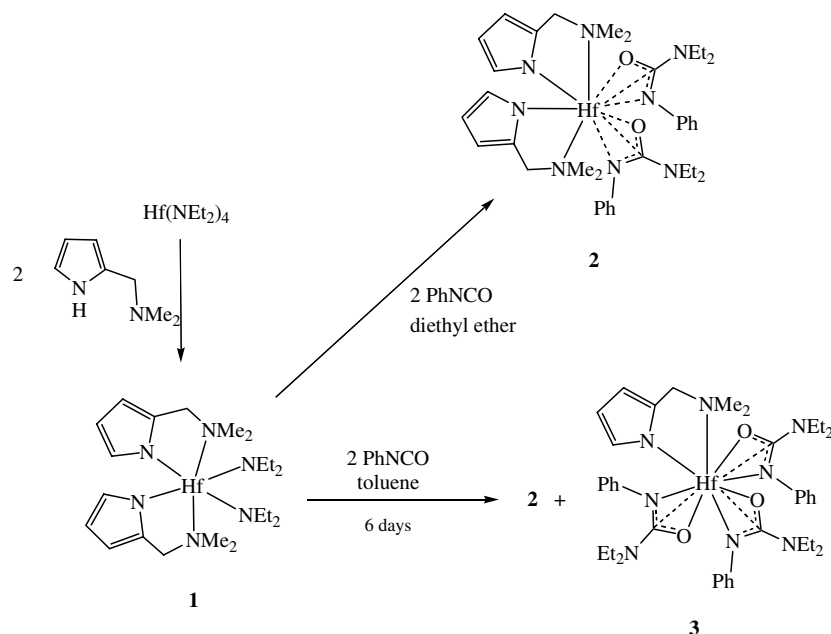
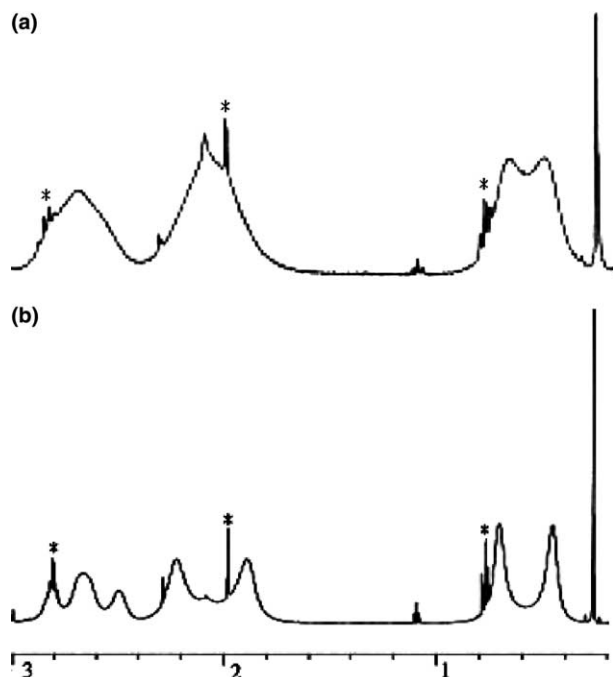Scheme 1.
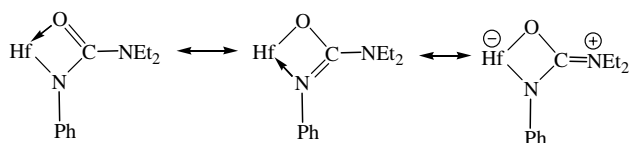
Scheme 2.
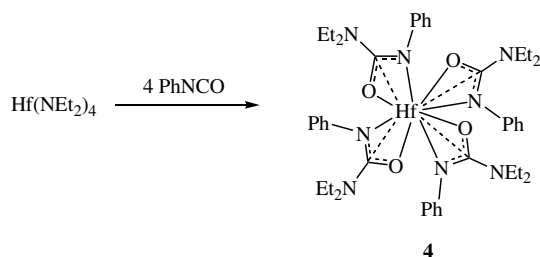
Scheme 3.

Fig. 1. The ^{1}H NMR spectra for compound **2** ranged from δ 0–3, asterisk (∗) represent un-identified products (a) 300 MHz NMR spectrometer (b) 600 MHz spectrometer.

spectrum of **4** exhibited a singlet at δ 166.6 for the quaternary carbon of ureato PhNC(NEt₂)O, which is similar to that of **2**.

2.2. Molecular structures of compounds 1, 2, 3 and 4

Crystals of **1** suitable for crystallographic studies were obtained from a toluene solution at −20 °C. Molecular structure of **1** and selected bond distances and angles are given in Fig. 2 and Table 1, respectively. The geometry of **1** is best described as a distorted octahedral with bond angles of the three axes N(1)–Hf(1)–N(6), N(4)–Hf(1)–N(5), and N(2)–Hf(1)–N(3) of 153.54(9)°, 162.45(8)°, and 165.08(8)°, respectively. The two substituted pyrrolyl ligands bond to the hafnium center with acute angles of 70.82(9)° and 71.22(8)°. The two diethylamido ligands bind to the Lewis acidic hafnium atom in an asymmetrical manner and result in a short bond distance of Hf(1)–C(19) (2.845(3) Å) with small bond angle of Hf(1)–N(6)–C(19) (106.20(19)°). However, the two diethylamido ligands

in a mixture of **2**, **3**, **4**, and several un-identified products. Therefore, we conclude that when 2 equiv. of PhNCO was added in a solution of **1**, it can only insert selectively into the Hf–amide bonds and only compounds **2** and **3** can be isolated. However, addition of PhNCO into hafnium–pyrrolyl bond may occur when excess of PhNCO was presented in the reaction solution (i.e., > 2 equiv.), according to ^{1}H NMR spectra [21]. The reaction became complicate and several un-identified products besides **2** and **3** were found. All the attempts to isolate new compounds are not successful.

For comparison, reacting Hf(NEt₂)₄ with 4 equiv. of PhNCO in a toluene solution at room temperature results in the PhNCO inserted into Hf–N bonds forming a tetrakis–ureato hafnium compound Hf[PhNC(NEt₂)O]₄ (**4**) in 88% yield (Scheme 3). A similar compound, Hf[PhNC(NMe₂)O]₄, has been synthesized by Lappert and coworkers [20]. The ^{1}H NMR spectrum of **4** exhibits only one set of quartet and triplet at δ 2.89 and 0.71 for the ethyl protons of diethylamino groups, indicating that the four ureato PhNC(NEt₂)O groups are equivalent in solution at room temperature. The ^{13}C NMR
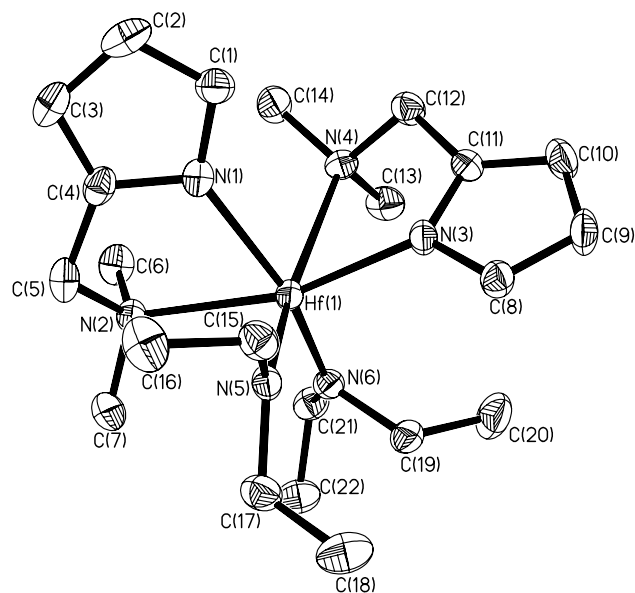

Fig. 2. The molecular structure of **1**. Thermal ellipsoids were drawn at 50% probability level.

Table 1
Selected bond distances and angles for compounds **1**, **2**, **3** and **4**

1

Hf(1)–N(1)	2.207(3)	Hf(1)–N(2)	2.495(2)	Hf(1)–N(3)	2.174(2)
Hf(1)–N(4)	2.635(2)	Hf(1)–N(5)	2.023(2)	Hf(1)–N(6)	2.046(2)
N(1)–Hf(1)–N(2)	70.82(9)	N(3)–Hf(1)–N(4)	71.22(8)		
N(1)–Hf(1)–N(6)	153.54(9)	N(2)–Hf(1)–N(3)	165.08(8)		
N(4)–Hf(1)–N(5)	162.45(8)				

2

Hf(1)–N(1)	2.202(8)	Hf(1)–N(2)	2.563(9)	Hf(1)–N(3)	2.229(8)
Hf(1)–N(5)	2.207(8)	Hf(1)–N(6)	2.552(11)	Hf(1)–N(7)	2.253(9)
Hf(1)–O(1)	2.188(7)	Hf(1)–O(2)	2.189(7)	Hf(1)–C(8)	2.648(10)
Hf(1)–C(26)	2.668(11)	N(3)–C(8)	1.334(12)	C(8)–O(1)	1.287(11)
C(8)–N(4)	1.338(12)	N(7)–C(26)	1.327(12)	C(26)–O(2)	1.312(11)
C(26)–N(8)	1.336(13)				
N(1)–Hf(1)–N(2)	67.1(3)	N(5)–Hf(1)–N(6)	66.6(3)		
O(1)–Hf(1)–N(3)	59.1(3)	O(2)–Hf(1)–N(7)	58.9(3)		
N(2)–Hf(1)–C(26)	161.7(3)	N(6)–Hf(1)–C(8)	165.1(3)		
N(3)–C(8)–O(1)	112.5(9)	N(7)–C(26)–O(2)	111.8(9)		

3

Hf(1)–O(3)	2.181(6)	Hf(1)–O(2)	2.189(5)	Hf(1)–O(1)	2.191(6)
Hf(1)–N(7)	2.206(6)	Hf(1)–N(1)	2.250(6)	Hf(1)–N(5)	2.251(6)
Hf(1)–N(3)	2.260(6)	Hf(1)–N(8)	2.468(6)	Hf(1)–C(7)	2.636(8)
Hf(1)–C(18)	2.652(8)	Hf(1)–C(29)	2.656(9)	N(1)–C(7)	1.304(10)
O(1)–C(7)	1.286(9)	O(2)–C(18)	1.295(9)	N(3)–C(18)	1.38(11)
O(3)–C(29)	1.316(12)	N(5)–C(29)	1.313(11)		
N(7)–Hf(1)–N(8)	88.1(2)	O(1)–Hf(1)–N(1)	58.5(2)		
O(2)–Hf(1)–N(3)	58.9(2)	O(3)–Hf(1)–N(5)	59.1(2)		

4

Hf(1)–N(1)	2.264(3)	Hf(1)–N(3)	2.251(3)	Hf(1)–N(5)	2.251(3)
Hf(1)–N(7)	2.252(6)	Hf(1)–O(1)	2.208(4)	Hf(1)–O(2)	2.185(3)
Hf(1)–O(3)	2.184(3)	Hf(1)–O(4)	2.189(3)	Hf(1)–C(1)	2.658(4)
Hf(1)–C(12)	2.647(4)	Hf(1)–C(23)	2.653(4)	Hf(1)–C(34)	2.655(4)
O(1)–C(1)	1.275(6)	C(1)–N(2)	1.361(5)	C(1)–N(1)	1.356(6)
O(2)–C(12)	1.289(4)	C(12)–N(4)	1.349(5)	C(12)–N(3)	1.355(5)
O(3)–C(23)	1.294(4)	C(23)–N(6)	1.347(5)	C(23)–N(5)	1.329(5)
O(4)–C(34)	1.294(4)	C(34)–N(8)	1.346(5)	C(34)–N(7)	1.340(7)
O(1)–Hf(1)–N(1)	58.96(15)	O(2)–Hf(1)–N(3)	59.55(10)		
O(3)–Hf(1)–N(5)	59.04(10)	O(4)–Hf(1)–N(7)	59.23(16)		
O(1)–C(1)–N(1)	113.6(4)	O(2)–C(12)–N(3)	112.9(3)		
O(3)–C(23)–N(5)	112.8(3)	O(4)–C(34)–N(7)	112.9(4)		

become equivalent in solution due to their low rotation energy barriers.

Crystals of **2** were obtained from a diethyl ether solution at −20 °C. The molecular structure and selected bond distances and angles of **2** are shown in Fig. 3 and Table 1, respectively. Compound **2** can be viewed as an eight coordinated hafnium compound with the two ureato ligands are bonded to hafnium through nitrogen and oxygen atoms. Compound **2** possesses two planar ureato metallacycles, which contain obtuse N–C–O angles of 112.5(9)° and 111.8(9)°, as well as acute N–Hf–O angles of 59.1(3)° and 58.9(3)°. The two substituted pyrrolyl ligands bond to the hafnium center with acute angles of 67.1(3)° and 66.6(3)°, smaller

than those of compound **1**, presumably due to the larger ureato ligands compressing the bond angles of the chelated substituted pyrrolyl ligands. The N–C (ranged from 1.327(12) to 1.338(13) Å) and C–O (1.287(11) to 1.312(11) Å) bond distances of ureato fragments are both in the range of partially double bond, indicating that the π electrons of the ureato fragments are equally delocalized in the NC(N)O core.

Crystals of **3** suitable for crystallographic studies were obtained after repeating recrystallization of a mixture of compounds **2** and **3** diethyl ether solution at −20 °C. The molecular structure and selected bond distances and angles of **3** are shown in Fig. 4 and Table 1, respectively. A disorder occurred at one of the methyl
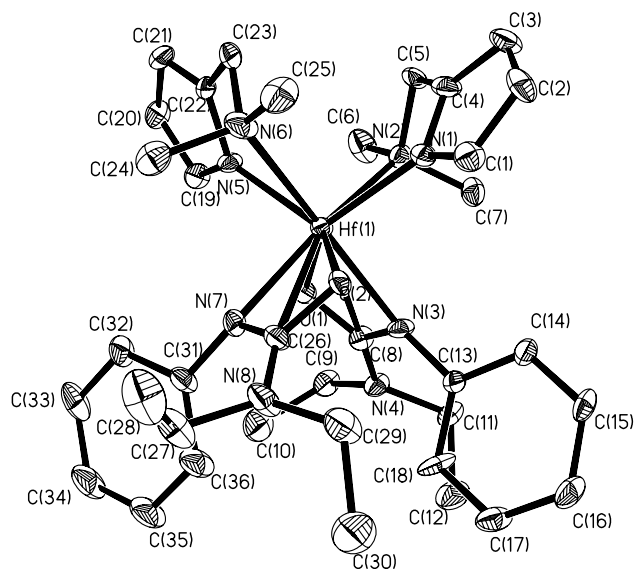
Fig. 3. The molecular structure of **2**. Thermal ellipsoids were drawn at 30% probability level.

Fig. 5. The molecular structure of **4**. Thermal ellipsoids were drawn at 30% probability level.

carbon which was separated into C(33) and C(33)′ with the occupancy ratio of 60/40. The bond distances and angles of **3** were similar to those of **2**.

Even though Hf[PhNC(NMe$_2$)O]$_4$, analogous to compound **4**, has been synthesized [20], no crystal structure of that has been obtained. Crystals of **4** suitable for crystallographic studies were obtained from a toluene solution at −20°C. The molecular structure and selected bond distances and angles of **4** are shown in Fig. 5 and Table 1, respectively. Compound **4** can also be viewed as an eight coordinate MX$_8$ geometry [22] where ureato fragments bond to the hafnium atom through nitrogen and oxygen atoms. A simplified geometry of **4** is shown in Fig. 6 where the eight coordinated atoms are located
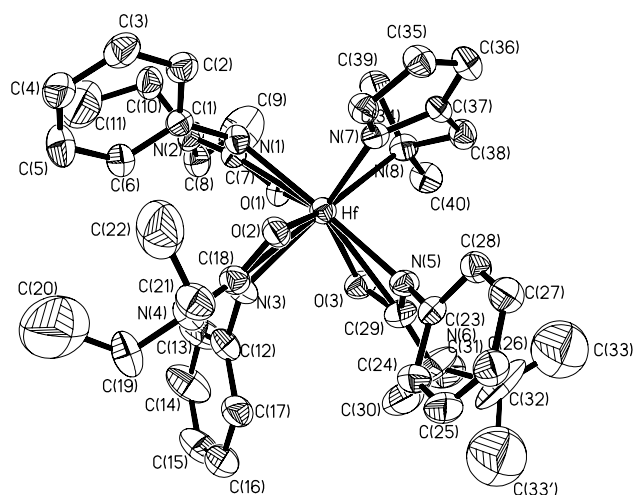

Fig. 6. Hf(η^3-NCO)$_4$ core inscribed within (a) two perpendicular rectangles and (b) an idealized cube showing the eight coordinate HfN$_4$O$_4$ unit.

on two perpendicular rectangles or in an idealized cube. The four ureato fragments coordinate to the hafnium atom forming four planar metallacycles. The bond distances and angles of **4** around the ureato metallacycles are similar to that of **2**, indicating that the π electrons of ureato fragments are evenly distributed.

2.3. Theoretical calculation

All calculations were performed using the hybrid B3LYP density functional theory [23,24]. For the basis sets we chose 6-31 G* for H, C, N, O, and LANL2DZ effective core potential plus basis functions for hafnium [25,26]. The reaction of **1** with PhNCO, which yields **2**, was calculated as an exothermic reaction with −65.7 kcal/mol for the heat of emission. The calculated bond distances and angles of **1** and **2** are close to the experimental data (see supporting information). As suggested in Scheme 2, the unpaired electrons of the ureato fragments of **2** are resonance delocalized between the C–O, C–NPh, and C–NEt$_2$ bonds, which are all partially doubly bonded.

Fig. 4. The molecular structure of **3**. Thermal ellipsoids were drawn at 30% probability level. C(33) and C(33)′ are disorder sites with occupancy ration of 60/40.
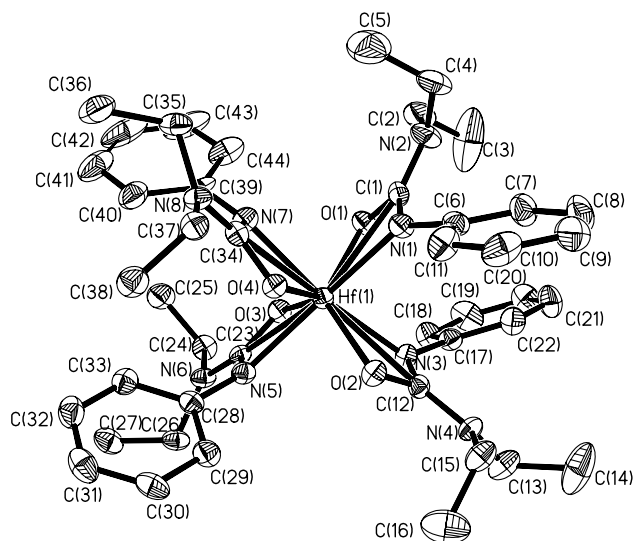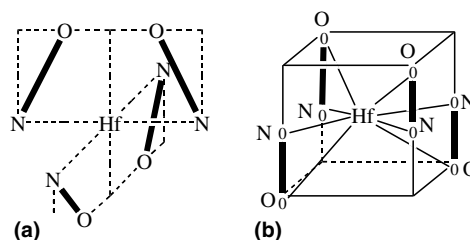
3. Experimental

3.1. General procedure

All reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques or in a glove box. Toluene, diethyl ether, and heptane were dried by refluxing over sodium benzophenone ketyl. CH_2Cl_2 was dried over P_2O_5. All solvents were distilled and stored in solvent reservoirs which contained 4 Å molecular sieves and were purged with nitrogen. $CDCl_3$ was degassed by freeze-and-thaw method and dried over 4 Å molecular sieves. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 200 or an Avance 300 NMR spectrometer at room temperature if not stated otherwise. Chemical shifts for ^{1}H and ^{13}C spectra were recorded in ppm relative to the residual protons and ^{13}C of $CDCl_3$ (δ 7.24, 77.0) and C_6D_6 (δ 7.16, 128.0). Elemental analyses were performed on a Heraeus CHN-OS Rapid Elemental Analyzer at the Instrument Center, NCHU. (2-dimethylaminomethyl)pyrrole was synthesized according to published literature [27,28]. $HfCl_4$ was purchased from Aldrich Co. and used as received.

3.2. $[C_4H_3N(CH_2NMe_2)-2]_2Hf(NEt_2)_2$ (1)

To a 100 mL Schlenk flask charged with 20 mL heptane and $Hf(NEt_2)_4$ (3.0 g, 6.42 mmol) was added dropwise with a $C_4H_4N(CH_2NMe_2)$ (1.59 g, 12.8 mmol)/heptane (20 mL) solution at room temperature with stirring for 12 h. Volatiles were removed under vacuum and the resulting solids were recrystallized from a toluene solution to generate 2.89 g of white solids in 79% yield. ^{1}H NMR (C_6D_6): 7.18 (m, 2H, pyrrolyl CH), 6.56 (m, 2H, pyrrolyl CH), 6.32 (m, 2H, pyrrolyl CH), 3.48 (m, 12H, NCH_2CH$_3$ and CH_2NMe$_2$), 2.02 (s, 12H, CH$_2$NMe_2), 0.84 (t, 12H, NCH$_2$CH_3). ^{13}C NMR (C_6D_6): 136.0 (s, pyrrolyl C_{ipso}), 128.5 (d, J_{CH} = 178 Hz, pyrrolyl CH), 109.4 (d, J_{CH} = 165 Hz, pyrrolyl CH), 104.9 (d, J_{CH} = 164 Hz, pyrrolyl CH), 63.0 (t, J_{CH} = 137 Hz, CH$_2$NMe$_2$), 48.4 (q, J_{CH} = 136 Hz, NMe_2), 40.8 (t, J_{CH} = 131 Hz, NCH_2CH$_3$), 13.0 (q, J_{CH} = 125 Hz, NCH$_2$CH_3). Anal. Calc. for $C_{22}H_{42}N_6Hf$: C, 46.43; H, 7.44; N, 14.77. Found: C, 45.60; H, 7.79; N, 15.23%.

3.3. $[C_4H_3N(CH_2NMe_2)-2]_2Hf[PhNC(NEt_2)O]_2$ (2)

To a 50 mL Schlenk flask charged with 20 mL diethyl ether and 1 (2.0 g, 3.5 mmol) was added PhNCO (0.84 g, 7.1 mmol) via syringe at room temperature. The solution color changed from pale yellow to dark red. Volatiles were removed under vacuum after 30 min stirring and the resulting solids were recrystallized from a diethyl ether solution to generate 1.59 g of white solids in 56% yield. ^{1}H NMR (C_6D_6): 7.67 (m, 2H, phenyl

CH), 7.27–6.95 (m, 10H, phenyl and pyrrolyl CH), 6.59 (m, 2H, pyrrolyl CH), 6.45 (m, 2H, pyrrolyl CH), 4.09 (d, J_{HH} = 13.2 Hz, CH_aH_bNMe$_2$), 3.14 (d, J_{HH} = 13.2 Hz, CH$_{aHb}$NMe$_2$), 2.78 (br, 8H, NCH_2CH$_3$), 2.18 (br, 12H, CH$_2$NMe_2), 0.79 (br, 6H, NCH$_2$CH_3), 0.60 (br, 6H, NCH$_2$CH_3). ^{13}C NMR (C_6D_6): 165.9 (s, NCO), 146.4 (s, phenyl C_{ipso}), 136.3 (s, pyrrolyl C_{ipso}), 129.9 (d, J_{CH} = 181 Hz, pyrrolyl CH), 128.2 (d, J_{CH} = 158 Hz, phenyl CH), 127.9, 122.9 (d, J_{CH} = 160 Hz, phenyl CH), 107.0 (d, J_{CH} = 163 Hz, pyrrolyl CH), 104.9 (d, J_{CH} = 156 Hz, pyrrolyl CH), 61.2 (t, J_{CH} = 134 Hz, CH$_2$NMe$_2$), 49.5 (q, J_{CH} = 137 Hz, NMe_2), 41.2 (t, J_{CH} = 137 Hz, NCH$_2$CH$_3$), 13.2 (q, J_{CH} = 126 Hz, NCH$_2$CH_3). Anal. Calc. for $C_{36}H_{52}N_8O_2Hf$: C, 53.56; H, 6.49; N, 13.88. Found: C, 52.73; H, 5.93; N, 13.99%.

3.4. $[C_4H_3N(CH_2NMe_2)-2]Hf[PhNC(NEt_2)O]_3$ (3)

Similar procedure as for 2 has been used here. 1 (2.0 g, 3.5 mmol) and PhNCO (0.84 g, 7.1 mmol) were used and stirred for 6 days. Repeating recrystallization of resulting mixture from a diethyl ether solution yields 0.40 g of 3 in 14% yield. Small amount of 2 was found in the final product. ^{1}H NMR (C_6D_6): 7.58 (m, 1H, phenyl CH), 6.90–7.38 (br, 15H, phenyl + pyrrolyl CH), 6.67 (m, 1H, pyrrolyl CH), 6.54 (m, 1H, pyrrolyl CH), 4.01 (m, 2H, CH_2NMe$_2$), 2.65–2.73 (br, 15H, NCH_2Me+NMe), 2.27 (br, 3H, NMe), 0.73 (br, 18H, NCH$_2$$Me$). [13]C NMR ($C_6D_6$): 167.0 (s, N$C$O), 166.2 (s, N$C$O), 146.7 (s, br, phenyl, C_{ipso}), 135.6 (s, pyrrolyl, C_{ipso}), 128.8 (d, J_{CH} = 183 Hz, pyrrolyl CH), 128.3 (d, J_{CH} = 159 Hz, phenyl CH), 124.7 (d, J_{CH} = 156 Hz, phenyl CH,), 124.3 (d, J_{CH} = 156 Hz, phenyl CH), 122.2 (d, J_{CH} = 162 Hz, phenyl CH), 106.4 (d, J_{CH} = 174 Hz, pyrrolyl CH,), 103.0 (d, J_{CH} = 163 Hz, pyrrolyl CH), 62.5 and 62.6 (two t, J_{CH} = 139 Hz, CH$_2$NMe$_2$), 48.6 (q, J_{CH} = 140 Hz, NMe), 41.4 (t, J_{CH} = 134 Hz, NCH$_2$Me), 37.2 (q, J_{CH} = 138 Hz, NMe), 13.4 (q, J_{CH} = 128 Hz, NCH$_2$$Me$). No elemental analysis was performed due to small amount of compound 2 was presented.

3.5. $Hf[PhNC(NEt_2)O]_4$ (4)

To a 50 mL Schlenk flask charged with 20 mL toluene and $Hf(NEt_2)_4$ (1.0 g, 2.14 mmol) was added PhNCO (1.02 g, 8.56 mmol) via syringe at room temperature. The color remained pale yellow after 1 h of stirring. Volatiles were removed under vacuum and the resulting solids were recrystallized from a toluene solution at −20 °C to generate 1.78 g of white solids in 88% yield. ^{1}H NMR (C_6D_6): 7.35–6.95 (m, 20H, phenyl CH), 2.89 (q, 16H, NCH_2CH$_3$), 0.71 (t, 24H, NCH$_2$CH_3). ^{13}C NMR (C_6D_6): 166.6 (s, NCO), 147.9 (s, phenyl C_{ipso}), 128.2 (d, J_{CH} = 156 Hz, phenyl CH), 124.5 (d, J_{CH} = 159 Hz, phenyl CH), 121.6 (d, J_{CH} = 159 Hz, phenyl CH),

Table 2
Crystallographic data and refinement for compounds **1**, **2**, **3** and **4**

	1	2	3	4
Formula	$C_{22}H_{42}HfN_6$	$C_{36}H_{52}HfN_8O_2$	$C_{40}H_{56}HfN_8O_3$	$C_{44}H_{60}HfN_8O_4$
F_w	569.11	807.35	875.42	943.49
Temperature (K)	293(2)	150(2)	150(1)	150(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	Cc
a (Å)	10.022(3)	15.548(4)	11.1338(1)	11.4627(15)
b (Å)	16.370(4)	10.867(3)	23.5981(3)	16.219(2)
c (Å)	15.515(4)	21.237(5)	15.1340(2)	23.993(3)
β (°)	104.020(4)	94.427(4)	105.8891(5)	100.622(2)
V (Å^3)	2469.4(11)	3577.5(14)	3824.33(8)	4384.1(10)
Z	4	4	4	4
D_{calc} (g/cm^3)	1.531	1.499	1.520	1.429
$F(000)$	1152	1648	1792	1936
θ Range (°)	1.84–27.58	1.31–27.55	1.64–25.00	1.73–27.53
No. of reflections collected	15560	24310	30498	21771
No. of independent reflections (R_{int})	5657 (0.0374)	8142 (0.1254)	6728 (0.0619)	9677 (0.0317)
No. of parameters	270	424	469	514
Goodness of fit on F^{2-}	0.848	0.898	1.127	0.921
Final R, $wR_2[I > 2\sigma(I)]$	0.0221, 0.0388	0.0606, 0.1582	0.0543, 0.1414	0.0263, 0.0544
R, wR_2 (all data)	0.0338, 0.0401	0.1205, 0.1834	0.0856, 0.1691	0.0307, 0.0544
$\Delta\rho_{max,min}$ (e Å^{-3})	0.884, −1.271	2.847, −2.502	1.984, −1.263	1.392, −0.398

41.4 (t, $J_{CH} = 137$ Hz, NCH_2CH$_3$), 13.4 (q, $J_{CH} = 126$ Hz, NCH$_2$$CH_3$). Anal. Calc. for $C_{44}H_{60}N_8O_4Hf$: C, 56.01; H, 6.41; N, 11.88. Found: C, 56.03; H, 6.07; N, 12.01.

4. X-ray structure determination of compounds 1, 2, 3 and 4

The crystals **1**, **2**, and **4** were mounted in glass fibers under nitrogen and transferred to a goniostat. Data were collected on a Bruker SMART CCD diffractometer with graphite-monochromated Mo Kα radiation with the radiation wavelength of 0.71073 Å. Data for crystal **3** were collected on a Nonius KappaCCD diffractometer. A SADABS absorption correction was made. All refinements were carried out by full-matrix least squares using anisotropic displacement parameters for all non-hydrogen atoms. All the hydrogen atoms are calculated. The crystal data are summarized in Table 2.

Acknowledgement

Appendix A. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 234583–234585 and 243419. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk). Data for theoretical calculation can be obtained from the author by request via e-mail at juihuang@cc.ncue.edu.tw. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2004.07.046.

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