ferences in reaction pathways.

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Registry No. **Et_4N^+1**, 113724-94-0; **Na^+1**, 113724-95-1; **PPn^+1**, 113669-28-6; **Et_4N^+2**, 113669-30-0; **Na^+2**, 64883-59-6; **PPN^+2**, 113669-31-1; **Et_4N^+3**, 113669-33-3; **Na^+3**, 113669-41-3; **PPN^+3**, 113669-40-2; **PPN^+4**, 36464-58-1; **Et_4N^+5**, 113669-39-9; $[PPN]_2[FeW(CO)_9]$, 99604-07-6; $[Et_4N]_2[FeW(CO)_9]$, 99559-70-3; $W(CO)_5{\cdot}THF$, 36477-75-5; $[PPN][HFe(CO)_4]$, 56791-54-9; $Fe(CO)_4^{2-}$, 22321-35-3; $[Et_4N][HFe(CO)_4]$, 25879-01-0; $[K][PPN][P(OMe)_3(CO)_3FeW(CO)_5]$, 113669-35-5; $[PPN][P(OMe)_3(CO)_3Fe(Me)W(CO)_5]$, 113669-37-7; $W(CO)_6$, 14040-11-0; $W(CO)_5OC(O)CH_3^-$, 45146-15-4; $[PPN][W(CO)_5I]$, 81315-55-1; $MeFe(^*CO)_4W(^*CO)_5^-$, 113669-27-5; $Na[MeC(O)Fe(CO)_4]$, 64867-63-6.

Synthesis and Molecular Structure of $(\eta^5\text{-}C_5Me_5)_2Hf(H)(NHMe)$. Structural Evidence for Nitrogen-to-Hafnium π-Donation

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$Cp^*_2HfH_2$ (Cp^* = η^5-C_5Me_5) reacts with excess methylamine to afford the formally 16-electron complex $Cp^*_2Hf(H)(NHMe)$ (**2**), which has been crystallographically characterized. Crystals of **2** were grown from a cold petroleum ether solution and crystallized in space group $P2_12_12_1$ with $Z = 4$, $a = 8.601$ (4) Å, $b = 14.030$ (6) Å, and $c = 17.145$ (4) Å. The least-squares refinement converged to $R(F) = 0.034$ for 3610 unique data with $I > 0$. Complex **2** adopts an orientation about the amido nitrogen which is consistent with π-donation of the nitrogen's lone pair of electrons to the hafnium center: the methylamido moiety is essentially planar about nitrogen with the amido methyl group directed toward one Cp^* ring and the amido hydrogen directed toward the other ring. Variable-temperature NMR studies place an upper limit of about 10 kcal·mol^{-1} on the strength of this Hf–N π-interaction. These results support the correlation between the hydride chemical shift (^1H NMR) in complexes of the formula $Cp^*_2Hf(H)(X)$ and the degree of X-to-hafnium π-donation: increasing π-donation leads to higher field chemical shifts. Thus, the observation that the hydride ligand in $Cp^*_2Hf(H)(NMe_2)$ (**3**) resonates at δ 11.2 (compared to δ 9.2 for $Cp^*_2Hf(H)(NH_2)$ (**1**) and δ 9.1 for **2**) suggests that steric congestion between the amido methyl groups and the Cp^* rings prevents the dimethylamido moiety of **3** from adopting the orientation necessary for effective N-to-Hf π-donation.

Introduction

In the course of our studies of the chemistry of permethylhafnocene derivatives we have encountered and commented on unusual spectral characteristics of amido complexes of the type $Cp^*_2Hf(H)(NR'R'')$ (Cp^* = η^5-C_5Me_5; R′, R″ = H, alkyl, aryl, diazo).[2] Specifically, we were intrigued by the observations that most compounds of this class exhibit ^1H NMR spectra inconsistent with the molecular geometry required for effective π-overlap between the nitrogen lone pair and an appropriate empty, low-lying orbital of the $[Cp^*_2Hf(H)]$ fragment, even though it is generally assumed that hard π-donor ligands like OR^-, NR_2^-, and F^- form strong π-bonds with early transition metals when orbital interactions allow.[3,4] Moreover, in the absence of such a Hf–N π-interaction these complexes are electronically unsaturated, 16e species. It seemed clear that elucidation of the nature and extent of π-bonding in these and related systems was essential to understanding (and predicting) the structures and reactivities of such species. The two limiting geometries for a $Cp^*_2Hf(H)(NR'R'')$ molecule containing a planar amido moiety are illustrated in Figure 1. Structure A (where Hf–N π-bonding is maximized) is electronically preferred over structure B (where the N lone pair is orthogonal to the metal fragment's LUMO or proper π-symmetry),[5] but B is clearly a sterically more favorable geometry than is A (in A, R′ and R″ are oriented toward the bulky Cp^* rings; in B this steric congestion is minimized).[6,7] Herein we present the results of an X-ray structural study of one

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[2] (a) Hillhouse, G. L.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1025. (b) Hillhouse, G. L.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5472. (c) Roddick, D. M.; Fryzuk, M. D.; Seidler, P. F.; Hillhouse, G. L.; Bercaw, J. E. *Organometallics* **1985**, *4*, 97.

[3] For a good discussion of orbital constraints and symmetry requirements of the bent metallocene derivatives, see: Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

[4] (a) Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organo-Zirconium and -Hafnium Compounds*; Ellis Horwood Ltd.: West Sussex, 1986. (b) Wailes, P. C.; Coutts, R. S. P.; Weigold, H. *Organometallic Chemistry of Titanium, Zirconium, and Hafnium*; Academic: New York, 1974. (c) Marsella, J. A.; Moloy, K. G.; Caulton, K. G. *J. Organomet. Chem.* **1980**, *201*, 389.

[5] Extended Hückel calculations on the parent $(\eta^5\text{-}C_5H_5)_2Hf(H)(NH_2)$ system show structure A to be 0.51 eV more stable than B. A is 0.87 eV more stable than a third hypothetical structure having a pyramidal amido group. Hoffman, D.; Hoffmann, R., private communication.

[6] Simple close-contact calculations were carried out[6a] for idealized structures A and B on a $Cp^*_2Hf(H)(NHMe)$ model by using standard $[Cp^*_2M(H)X]$ fragment parameters (from the structure of $Cp^*_2Zr(H)(OCH{=}WCp_2)$)[6b] and the following approximated intramolecular distances: Hf–N = 2.04 Å; Hf–H = 1.90 Å; N–C = 1.47 Å; C–H = 1.09 Å; N–H = 1.02 Å. Angles were 120° about N and tetrahedral about the amido methyl. These calculations showed severe intramolecular nonbonded contacts (<0.6 Å) between the amido Me hydrogens and ring Me hydrogens for A; these close contacts were considerably relieved by rotation about the Hf–N bond and were minimized in the B conformation having the amido Me directed toward the hydride ligand (i.e., R′ = Me and R″ = H), the closest Me–Me contact being 2.1 Å; this was better than the B conformation that has R′ = H and R″ = Me (here the closest Me–Me contact was 1.2 Å). (a) Miller, G. J., private communication. (b) Wolczanski, P. T.; Threlkel, R. S.; Santarsiero, B. D. *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.* **1983**, *C39*, 1330.

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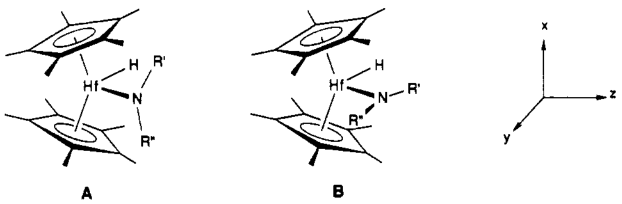

Figure 1. The two limiting geometries for a complex of the type $Cp^*_2Hf(H)(NR'R'')$ which contains a planar amido group.

Table I. Summary of Crystallographic Data for 2

compd	$(\eta^5\text{-}C_5(CH_3)_5)_2Hf(H)(NHCH_3)$
formula	$C_{21}H_{35}HfN$
gfw	480.00
color of cryst	colorless
a, Å	8.601 (4)
b, Å	14.030 (6)
c, Å	17.145 (4)
V, Å^3	2068.9 (14)
Z	4
space group	$P2_12_12_1$
radiatn	Mo Kα (λ = 0.71069 Å) monochromatized with highly oriented graphite
μ, cm^{-1}	53.2
d(calcd), g/cm^3	1.541
scan speed, deg (θ)/min	2
scan range, deg (θ)	1.0 + dispersion
2θ limits	$\pm h, \pm k, \pm l$ for $2\theta < 40°$; $\pm h, \pm k, \pm l$ for $40° < 2\theta < 50°$
total data collected	10271
unique data, < < 0	3641
parameters	215
GOF	1.80
$R(F)$	0.034
shift/error (final cycle)	<0.01

member of this family and discuss its implications with regard to the balance between steric and electronic factors that are important in these molecules.

Experimental Section

Reactions were carried out by using standard high-vacuum techniques using dry, air-free solvents. $Cp^*_2HfH_2$ was prepared by the literature method.[2c] Anhydrous methylamine (Matheson) was used from the cylinder and freeze–pump–thawed to remove traces of noncondensible gases.

Preparation of $Cp^*_2Hf(H)(NHCH_3)$ (2). Approximately 5 equiv of methylamine were condensed onto a −78 °C petroleum ether solution containing 0.60 g (1.34 mmol) of $Cp^*_2HfH_2$. The reaction was stirred for 12 h at ambient temperature, the volume of solvent was reduced to 5 mL, the solution was cooled to −78 °C, and the resulting precipitate was collected by filtration to afford 0.33 g (52%) of colorless, air-sensitive 2. ^1H NMR (500 MHz, C_6D_6 solution, internal tetramethylsilane reference): $\eta^5\text{-}C_5(CH_3)_5$, δ 2.03, s, 30 H; $N(CH_3)H$, δ 3.19, d, 3 H, $^3J_{H-H}$ = 7.5 Hz; $N(CH_3)H$, δ 4.25, v br, 1 H; Hf–H, δ 9.1, br s, 1 H. Anal. Calcd for $HfC_{21}H_{36}N$: C, 52.55; H, 7.35; N, 2.92. Found: C, 52.93, 52.90, 52.95, 52.82; H, 7.14, 7.22, 7.20, 7.36; N, 2.94, 2.89, 2.87, 2.87.

Table II. Fractional Atomic Coordinates and U_{eq}'s for Non-Hydrogen Atoms of 2 ($\times 10^4$)

atom	x	y	z	U_{eq}, Å^2
Hf	1551.2 (3)	401.4 (2)	2068.7 (1)	379 (1)
N	3270 (10)	−265 (6)	2665 (4)	639 (18)
C	3812 (13)	−551 (8)	3414 (6)	784 (28)
C(11)	1560 (11)	2092 (5)	2505 (4)	462 (16)
C(12)	1778 (10)	1551 (5)	3205 (4)	491 (16)
C(13)	414 (10)	1022 (5)	3325 (4)	502 (18)
C(14)	−666 (9)	1249 (7)	2747 (5)	559 (19)
C(15)	4 (10)	1930 (5)	2247 (4)	534 (18)
C (11M)	2599 (15)	2874 (7)	2251 (7)	880 (30)
C(12M)	3129 (12)	1659 (7)	3740 (6)	793 (27)
C(13M)	89 (15)	399 (8)	4008 (5)	899 (29)
C(14M)	−2328 (12)	924 (9)	2711 (7)	872 (31)
C(15M)	−885 (15)	2524 (8)	1677 (6)	897 (31)
C(21)	2721 (16)	−577 (9)	980 (5)	893 (33)
C(22)	1063 (14)	−598 (7)	861 (5)	746 (27)
C(23)	659 (8)	322 (7)	655 (4)	514 (18)
C(24)	1971 (11)	880 (6)	663 (5)	569 (21)
C(25)	3218 (9)	346 (10)	885 (5)	720 (25)
C(21M)	3653 (39)	−1457 (17)	1103 (8)	3317 (129)
C(22M)	78 (31)	−1441 (12)	839 (7)	2137 (79)
C(23M)	−927 (14)	569 (17)	377 (7)	1592 (60)
C(24M)	2086 (24)	1892 (7)	339 (6)	1396 (51)
C(25M)	4852 (15)	759 (19)	882 (7)	1939 (79)

Table III. Selected Hydrogen Atom Coordinates ($\times 10^4$) and B's for 2

atom	x	y	z	B, Å^2
H	−241 (98)	−445 (73)	2307 (46)	6.0
H(4)	4268 (103)	−423 (75)	2329 (51)	6.0
H(1)	3996	−1224	3440	7.0
H(2)	4815	−284	3518	7.0
H(3)	3133	−395	3814	7.0

Table IV. ^1H NMR Chemical Shifts for the Hydride Resonances of Amido Derivatives of the Formula $(C_5Me_5)_2Hf(H)(NR'R'')$[a]

compd	δ (Hf-H)	ref
$Cp^*_2Hf(H)(NH_2)$ (1)	9.3	2b
$Cp^*_2Hf(H)(NHMe)$ (2)	9.1	this work
$Cp^*_2Hf(H)(NMe_2)$ (3)	11.5	2b
$Cp^*_2Hf(H)(NHPh)$	11.6	2a
$Cp^*_2Hf(H)(NHTol)$	11.4	2a
$Cp^*_2Hf(H)(NHNNTol)$	11.2	2a
$Cp^*_2Hf(H)(NTolNNTol)$	11.2	2a

[a] C_6D_6 solution.

X-ray Structural Determination of 2. Colorless prisms were grown by slowly cooling a saturated solution of 2 to −78 °C. The air-sensitive crystals were mounted and sealed in quartz capillaries and were shown to be orthorhombic, space group $P2_12_12_1$ on the basis of photographic workup. Data collection was carried out on an Enraf-Nonius CAD4 diffractometer as described in Table I. Four check reflections were monitored during the course of the data collection (146 h) and showed no significant decrease in intensity. A sphere of data ($2\theta < 40°$) and a hemisphere ($\pm h$,$+k$,±l; $40° < 2\theta < 50°$) of data were collected, the data were reduced to F_o^2 and averaged over 222 symmetry yielding 3641 reflections. The position of the Hf was derived from the Patterson map, and the remaining structure was revealed by electron density maps. All methyl hydrogen atoms were located in difference Fourier maps and were not refined; the coordinates for the H atoms on Hf and N were taken from a Fourier map and were refined. No H-atom B values were refined. Full-matrix least-squares refinement of a scale factor, an isotropic extinction parameter, atom coordinates, and anisotropic Gaussian parameters resulted in a GOF = $\{\sum w[F_o^2 - (F_c/k)^2]^2/(n - \upsilon)\}^{1/2}$ = 1.80 (n = 3641 reflections, υ = 215 parameters), $R_F = \sum(||F_o| - |F_c||)/\sum|F_o|$ = 0.034 (3610 reflections, $l > 0$), and R'_F = 0.032 (3429 reflections, $l > 3\sigma$). The final value of the isotropic secondary extincition parameter g was 0.102 (53) × 10^{-6}. Anomalous dispersion terms were included in the Hf form factors. The final difference Fourier map indicated peaks and valleys of height ca. 2 e/Å^3 around the Hf atom, presumably residuals from absorption errors, and the remainder of the map was relatively flat with no peaks larger than 1 e/Å^3. All calculations were carried out by using the CRYM system of programs of a VAX 11/750 computer.

The final positional and thermal parameters for the refined nonhydrogen atoms appear in Table II. Table III lists the positional and thermal parameters for selected hydrogen atoms (those *not* associated with the Cp* rings; a complete listing is given

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(7) X-ray structural studies of intramolecular non-bonded contacts and associated steric factors in the related Zr–hydroxy derivatives $Cp^*_2Zr(OH)(Cl)$ and $Cp^*_2Zr(OH)_2$ have been described. Bortolin, R.; Patel, V.; Munday, I.; Taylor, N. J.; Carty, A. J. *J. Chem. Soc., Chem. Commun.* **1985**, 456.

Table V. Selected Bond Distances (Å) in 2

Hf–H	1.99 (9)	C(12)–C(12M)	1.488 (13)
Hf–N	2.027 (8)	C(13)–C(14)	1.396 (12)
Hf–C(11)	2.487 (7)	C(13)–C(13M)	1.488 (13)
Hf–C(12)	2.536 (8)	C(14)–C(15)	1.407 (11)
Hf–C(13)	2.521 (8)	C(14)–C(14M)	1.502 (14)
Hf–C(14)	2.531 (9)	C(15)–C(15M)	1.495 (14)
Hf–C(15)	2.543 (8)	C(21)–C(22)	1.441 (15)
Hf–C(21)	2.527 (11)	C(21)–C(25)	1.375 (15)
Hf–C(22)	2.536 (10)	C(21)–C(21M)	1.487 (26)
Hf–C(23)	2.545 (8)	C(22)–C(23)	1.384 (13)
Hf–C(24)	2.528 (9)	C(22)–C(22M)	1.456 (21)
Hf–C(25)	2.486 (10)	C(23)–C(24)	1.373 (12)
Hf–R(1)[a]	2.220	C(23)–C(23M)	1.486 (18)
Hf–R(2)[b]	2.231	C(24)–C(25)	1.363 (13)
N–C	1.424 (13)	C(24)–C(24M)	1.528 (16)
N–H(4)	1.06 (9)	C(25)–C(25M)	1.520 (20)
C(11)–C(12)	1.431 (11)	C–H(1)	0.96
C(11)–C(15)	1.427 (11)	C–H(2)	0.96
C(11)–C(11M)	1.481 (14)	C–H(3)	0.93
C(12)–C(13)	1.404 (11)		

[a] Ring 1 centroid: atoms C(11), C(12), C(13), C(14), and C(15).
[b] Ring 2 centroid: atoms C(21), C(22), C(23), C(24), and C(25).

in Table X3 of the supplementary material).

Results and Discussion

The chemical shifts for the hydride resonances of several members of the Cp*$_2$Hf(H)(NR′R″) family are shown in Table IV. As discussed elsewhere, these resonances are generally useful indicators of the degree of π-donation to Hf from X in Cp*$_2$Hf(H)(X) complexes, particularly when comparison are made for members of a related series of compounds (for example, intraset comparisons for {I, Br, Cl, F} or for the nitrogen series in Table IV).[2c,8] One thus concludes, on the basis of the upfield chemical shift values for the hydride resonances of Cp*$_2$Hf(H)(NH$_2$) (1)[2b] and Cp*$_2$Hf(H)(NHCH$_3$) (2) with respect to the hydride resonances of all of the other azo derivatives listed ($\Delta \approx 2$ ppm),[8] that the amido ligands in both 1 and 2 are small enough to adopt structure A and are effective π-donors.[9] By the same criterion the other, sterically bulkier azo derivatives are not good π-donating ligands in this system. Even for Cp*$_2$Hf(H)(NMe$_2$) (3), steric factors dominate and the complex appears to adopt a geometry approximated by B.[10]

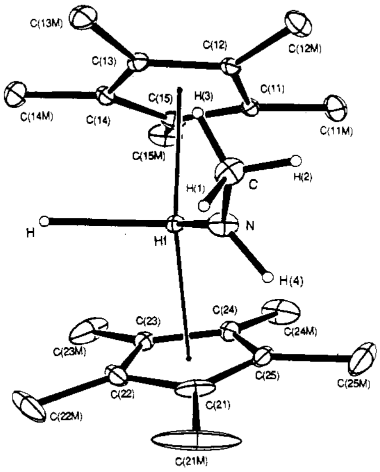

Figure 2. An ORTEP view of 2. The ring hydrogen atoms have been omitted for clarity. The thermal ellipsoids are drawn at the 50% probability level (except those of the hydrogen atoms that have been drawn artificially small).

Table VI. Selected Bond Angles (deg) in 2

R(1)–Hf–R(2)	139.1	C(21M)–C(21)–C(22)	122.5 (13)
H–Hf–N	101 (3)	C(21M)–C(21)–C(25)	129.1 (13)
Hf–N–C	145.5 (7)	C(23)–C(22)–C(21)	105.4 (9)
Hf–N–H(4)	100 (5)	C(22M)–C(22)–C(21)	126.6 (11)
C(15)–C(11)–C(12)	107.4 (6)	C(22M)–C(22)–C(23)	127.3 (11)
C(11M)–C(11)–C(12)	124.0 (7)	C(24)–C(23)–C(22)	108.8 (8)
C(11M)–C(11)–C(15)	126.3 (7)	C(23M)–C(23)–C(22)	122.0 (9)
C(13)–C(12)–C(11)	107.1 (7)	C(23M)–C(23)–C(24)	128.7 (9)
C(12M)–C(12)–C(11)	124.4 (7)	C(25)–C(24)–C(23)	109.7 (8)
C(12M)–C(12)–C(13)	128.0 (7)	C(24M)–C(24)–C(23)	125.4 (9)
C(14)–C(13)–C(12)	109.4 (7)	C(24M)–C(24)–C(25)	124.1 (9)
C(13M)–C(13)–C(12)	125.7 (8)	C(24)–C(25)–C(21)	107.8 (9)
C(13M)–C(13)–C(14)	124.6 (8)	C(25M)–C(25)–C(21)	130.4 (11)
C(15)–C(14)–C(13)	108.3 (7)	C(25M)–C(25)–C(24)	121.2 (10)
C(14M)–C(14)–C(13)	126.4 (8)	H(1)–C–N	112.0
C(14M)–C(14)–C(15)	124.9 (8)	H(2)–C–N	110.6
C(14)–C(15)–C(11)	107.7 (7)	H(3)–C–N	113.2
C(15M)–C(15)–C(11)	126.4 (8)	H(2)–C–H(1)	103.3
C(15M)–C(15)–C(14)	124.5 (8)	H(3)–C–H(1)	107.8
C(25)–C(21)–C(22)	108.1 (9)	H(3)–C–H(2)	109.6

Although our analyses of these structures seem straightforward, they are based solely on ^{1}H NMR studies and simple close-contact calculations, so we set out to determine the solid-state molecular structure of 2 by X-ray diffraction methods. We chose 2 because (1) it appeared to be on the border between sterically allowed and prevented Hf–amide π-bonding and (2) its variable-temperature ^{1}H NMR spectrum presented an interesting ambiguity: on one hand, the hydride resonance of 2 (δ 9.1, (C$_6$D$_6$)) suggested a Hf–N π-interaction and implicated structure A; on the other hand, the methyl resonance for the Cp* ligands (singlet, C$_7$D$_8$, −85 °C at 500 MHz) showed no hint of chemically inequivalent rings (not even noticeable broadening), yet when R′ ≠ R″, the rings are *necessarily* chemically inequivalent for all structures except B.

Reaction of Cp*$_2$HfH$_2$[2c] with methylamine results in evolution of dihydrogen and affords air-sensitive 2 in good yield.[10] Diffraction quality crystals of 2 were obtained by slow cooling of a saturated petroleum ether solution to −78 °C. The structure of 2 consists of discrete monomeric molecules in the unit cell. There are no significant inter- or intramolecular nonbonded contacts. A perspective view of 2 with the atom numbering scheme is shown in Figure 2. Tables V and VI contain selected intramolecular bond distances and angles. A more complete listing of these parameters is given in the supplementary material.

The most noteworthy features of the structure, as expected, are associated with the methylamido group: the amido nitrogen exhibits a planar geometry (N lies 0.054 Å out of the plane defined by Hf, H(4), and C), with the amido methyl group directed toward one Cp* ligand and the amido hydrogen (H(4)) directed toward the other ring, as in configuration A. However, as is clear from Figure 2, the amido substituents are not oriented in a plane perpendicular to the *yz* plane (defined in Figure 1); the C–N–Hf–H dihedral angle (63 (3)°) significantly deviates from the ideal 90° for the limiting structure A and results in the amido methyl group being tilted toward the central position of the permethylhafnocene "wedge" (as predicted

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[8] A more comprehensive tabulation of Cp*$_2$Hf(H)(X) hydride chemical shift data (for X = halide, amide, alkoxide, carbyl, acyl, etc.) is given in the supplementary material.

[9] There appears to be a similar trend for the hydride chemical shifts of Cp*$_2$Zr(H)(X) complexes, but it is more subtly manifested because the range in shifts is much smaller for Zr (about 5 ppm) than for Hf (about 13 ppm).

[10] Consistent with the prediction of structure B for 3 based on its low-field hydride chemical shift (δ 11.5), the low-temperature ^{1}H NMR spectrum of 3 exhibits resonances for inequivalent amido Me groups, with a substantial activation barrier to their equilibration ($\Delta G^* = 13.5 \pm 1$ kcal/mol).[2b] Similar observations have been made for related dimethylamido complexes of Th and U: Fagan, P. J.; Manriquez, J. M.; Vollmer, S. H.; Day, C. S.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 2206.

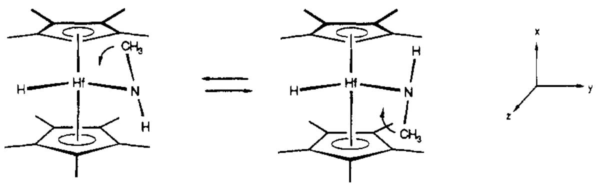

Figure 3. A depiction of the oscillation about the Hf–N bond that equilibrates the Cp* rings of $Cp^*_2Hf(H)(NHMe)$ (**2**).

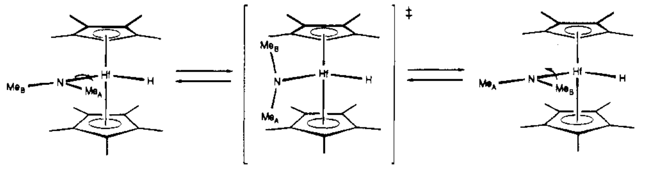

Figure 4. A depiction of the rotation about the Hf–N bond that equilibrates the amido methyl groups of $Cp^*_2Hf(H)(NMe_2)$ (**3**).

by the close-contact calculations). The amido group exhibits other distortions apparently arising from steric interplay with the Cp* ligands: the Hf–N–C angle is opened from the idealized (120°) sp^2 value to 145.5 (7)° and the C–N–H(4) angle has closed to 100 (5)°. The Hf–N bond distance of 2.027 (8) Å suggests considerable double-bond character in this linkage.[11]

The picture that emerges from consideration of the X-ray structural study, the ^{1}H NMR data, and the steric constraints seems to be a clear one. First, these structural results strongly reinforce the notion that key electronic and structural information is contained in the ^{1}H NMR chemical shift value for the Hf–*H* resonance. As an example, we can predict with a measure of confidence that the complexes $Cp^*_2Hf(H)(NHNNR)$ and $Cp^*_2Hf(H)(NRNNR)$ probably *do not* contain chelating triazenido ligands as we initially proposed;[2a] instead, the triazenido ligands in these molecules are likely bound to hafnium through only one nitrogen, since the compounds' low-field hydride resonances (Table IV) are indicative of coordinatively unsaturated species! Second, we are now in a position to address the apparent ambiguities in the dynamic ^{1}H NMR results. The processes that (a) equilibrate the Cp* rings of **2** and (b) equilibrate the amido methyl groups of **3** must be different. Reasonable descriptions of these processes are offered in Figures 3 and 4, respectively. Simple oscillation about the Hf–N bond, through the *yz* plane, equilibrates the Cp* ligands of **2**. On the basis of the variable-temperature ^{1}H NMR experiments we can place an *upper* limit on the magnitude of the activation barrier of this oscillation ($\Delta G^{\ddagger} \leq 10$ kcal/mol).[12] This, effectively, is also the upper limit on the magnitude of the Hf–N π-interaction in **2** and can be compared to the value calculated by Hoffmann for the parent system (11.8 kcal/mol).[5] This oscillation does not equilibrate the amido methyls of **3**, however. As shown in Figure 4, this requires rotation through the plane containing the Hf–N bond and perpendicular to the {N,Hf,H} plane. Since such a rotation is sterically encumbered, the barrier is much larger ($\Delta G^{\ddagger} = 13.5 \pm 1$ kcal/mol)[10] and is predominately of steric origin.

Conclusions

Steric constraints imposed on complexes of the general formula $Cp^*_2MX_2$ (M = Ti, Zr, Hf) by the two bulky pentamenthylcyclopentadienyl rings have long been recognized as playing a crucial role in the chemistries of these molecules. It is clear that in the particular case of amido complexes (M–NR′R″), steric congestion effectively prevents all but the smallest amido ligand(s) from adopting the conformation required for good ligand-to-metal π-donation. For $Cp^*_2Hf(H)(NHMe)$, an X-ray structural determination shows that the amido ligand can *approach* the necessary geometry for π-bonding, but even here the energetic magnitude of the π-interaction is quite small (less than 10 kcal/mol as estimated from ^{1}H NMR data). On the basis of thermochemical data obtained on homoleptic hafnium amides and alkoxides, Lappert has commented that the primary effect of M=N π-bonding appears to be on the molecular geometry of a complex, with little contribution to bond strengths.[13] Our results seem to support this conclusion.

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Registry No. 2, 113748-24-6; Cp^*HfH_2, 81956-87-8; methylamine, 74-89-5.

Supplementary Material Available: Data collection of the structure determination and tables of atom coordinates and U_{eg}'s, anisotropic Gaussian parameters, hydrogen atom coordinates and *B*'s, complete bond lengths and angles, selected torsion angles and least-squares planes, and ^{1}H NMR chemical shifts for the hydride resonances of compounds with the formula $Cp^*_2HfH(X)$ (10 pages); a listing of structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

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[11] There are no good literature comparisons for analogous Hf complexes, but taking into consideration that Zr has a covalent radius about 0.01 Å larger than that of Hf,[11a] this is a reasonable value for a Hf=N(sp$_2$) bond length. For comparison, D(Zr–N) = 2.072 (2) Å in $Cp_2Zr(NMe_2)(OC_6H_3\text{-}2,6\text{-}t\text{-}Bu_2)$[4a] and D(Zr–N) = 2.013(5) Å in $Cp_2Zr(N{=}CHPh)Cl$.[11b] (a) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960. (b) Erker, G.; Fromberg, W.; Atwood, J. L.; Hunter, W. E. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 68.

[12] This upper limit was calculated from the Gutowsky–Holm approximation assuming a coalescence temperature of 165 K and $\Delta\nu = 0.1$ ppm for the methyl protons of the Cp* rings at the low temperature limit.

[13] (a) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*; Ellis Horwood Ltd.: West Sussex, 1980. (b) Lappert, M. F.; Patil, D. S.; Pedley, J. B. *J. Chem. Soc., Chem. Commun.* 1975, 830.