Synthesis, Structure, and Properties of Zirconium and Hafnium Complexes Containing η^2-Pyrazolato Ligands

Elena Sebe,[a] Ilia A. Guzei,[a,c] Mary Jane Heeg,[a] Louise M. Liable-Sands,[b] Arnold L. Rheingold,[b,d] and Charles H. Winter*[a]

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Treatment of tetrakis(dimethylamido)zirconium with four equiv. of 3,5-dimethylpyrazole, 3,5-di-*tert*-butylpyrazole, or 3,5-diphenylpyrazole in refluxing toluene afforded tetrakis(η^2-3,5-dimethylpyrazolato)zirconium (86%), tetrakis(η^2-3,5-di-*tert*-butylpyrazolato)zirconium (88%), and tetrakis(η^2-3,5-diphenylpyrazolato)zirconium (85%), respectively, as colorless crystalline solids. The analogous hafnium complexes were prepared through treatment of hafnium tetrachloride with four equiv. of the potassium salts of 3,5-dimethylpyrazolate, 3,5-di-*tert*-butylpyrazolate, or 3,5-diphenylpyrazolate in tetrahydrofuran to afford tetrakis(η^2-3,5-dimethylpyrazolato)hafnium (75%), tetrakis(η^2-3,5-di-*tert*-butylpyrazolato)hafnium (58%), and tetrakis(η^2-3,5-diphenylpyrazolato)hafnium·toluene (38%), respectively, as colorless crystalline solids. X-ray crystal structures of representative members of these complexes revealed monomeric species containing four η^2-pyrazolato ligands and approximate dodecahedral geometry about the metal centers. Treatment of tetrakis(η^2-3,5-dimethylpyrazolato)hafnium with 3,5-dimethylpyrazole in a 1:1 molar ratio afforded tris(η^2-3,5-dimethylpyrazolato)(η^1-3,5-dimethylpyrazolato)(η^1-3,5-dimethylpyrazole)hafnium as colorless crystals (84%). Tris(η^2-3,5-dimethylpyrazolato)(η^1-3,5-dimethylpyrazolato)(η^1-3,5-dimethylpyrazole)hafnium contains three η^2-3,5-dimethylpyrazolato, one η^1-3,5-dimethylpyrazolato, and one η^1-3,5-dimethylpyrazole ligands. The η^1-3,5-dimethylpyrazolato and η^1-3,5-dimethylpyrazole ligands are connected through a N–H···N hydrogen bond. Tetrakis(η^2-3,5-dimethylpyrazolato) hafnium did not form an adduct with pyridine or tetrahydrofuran, suggesting that the formation of a hydrogen bond is important to the stability of adducts. Attempted sublimation of all of the new pyrazolato complexes led to some decomposition, as evidenced by the formation of the free pyrazoles in the sublimates and significant amounts of nonvolatile residues. This work greatly expands the number of zirconium and hafnium complexes that contain η^2-pyrazolato ligands.

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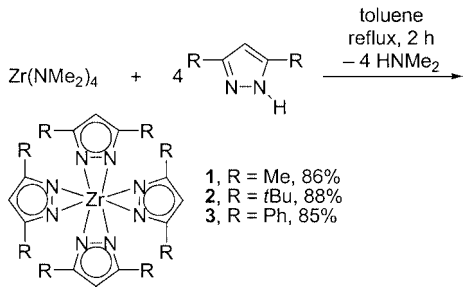
Thin films of binary zirconium and hafnium phases are of significant interest, in view of their useful properties and important applications. Hafnium oxide and hafnium silicate have much higher dielectric constants compared to silicon dioxide, and are among the best candidates to replace silicon dioxide as gate dielectric materials in future microelectronics devices.[1] Analogous zirconium phases are also of interest for similar applications.[1] Zirconium nitride (ZrN, Zr_3N_4) and hafnium nitride (HfN, Hf_3N_4) have potential uses that include hard coatings[2] and barrier layers in microelectronics devices.[3] To allow film growth by chemical vapor deposition and related techniques, it is necessary to have volatile complexes that react with additional reagents to afford the desired phases. Since zirconium and hafnium halides have low vapor pressures, there has been considerable investigation of metal–organic and inorganic hafnium complexes with useful vapor pressures. Precursors that have been investigated for the deposition of zirconium and hafnium oxide and related oxide materials contain various ligands that include alkoxide,[4] nitrate,[5] dialkylamido,[6] and others.[7] The growth of zirconium and hafnium nitride films by CVD methods has been much less explored, and has largely employed dialkylamido–based precursors.[8]

Our group and others have been exploring the coordination chemistry of pyrazolato ligands with metals across the periodic table.[9,10] In 1997, we reported the synthesis, structure, and molecular orbital calculations of titanium(IV) complexes that contain terminal η^2-pyrazolato ligands.[10d] In particular, the molecular orbital calculations predicted that filled in-plane nitrogen-based orbitals interact with empty d-orbitals on the titanium(IV) ion. Based upon this

[a] Department of Chemistry, Wayne State University, Detroit, Michigan 48202, USA
Fax: +1-313-577-8289
Tel: +1-313-577-5224
E-mail: chw@chem.wayne.edu
[b] Department of Chemistry, University of Delaware, Newark, Delaware 19716, USA
[c] Current Address: Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706, USA
[d] Current Address: Department of Chemistry, University of California, San Diego, California 93992, USA

bonding model, η^2-pyrazolato ligand coordination was predicted to be general in a wide variety of metal complexes. Subsequently, we and others have demonstrated η^2-pyrazolato ligand coordination in many transition metal, main group, and lanthanide complexes.[9,10]

As part of our goals related to further exploration of η^2-pyrazolato ligand coordination among the transition metals and the design of new volatile film growth precursors, we set out to explore zirconium and hafnium pyrazolato complexes. Herein we report the synthesis, structure, and properties of a series of monomeric zirconium(IV) and hafnium(IV) complexes that contain η^2-pyrazolato ligands. The thermal stability and volatility of these complexes are described. In addition, tetrakis(η^2-3,5-dimethylpyrazolato) hafnium forms a novel adduct with 3,5-dimethylpyrazole. There have been few reports of zirconium and hafnium pyrazolato complexes.[10c,11,12] Meyer and co-workers reported a homoleptic zirconium complex with four bulky η^2-pyrazolato ligands.[11] We have reported the synthesis and structure of several zirconium and hafnium complexes that contain pyrazolato ligands,[12] but have not published any structural studies of the homoleptic pyrazolato complexes.



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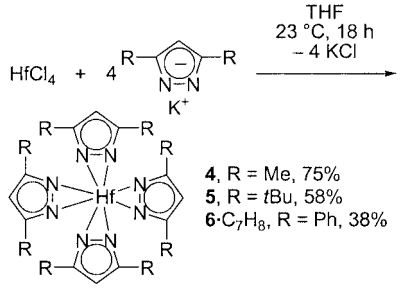

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Results and Discussion

Synthetic Chemistry

Treatment of tetrakis(dimethylamido)zirconium with four equiv. of 3,5-dimethylpyrazole, 3,5-di-*tert*-butylpyrazole, or 3,5-diphenylpyrazole in refluxing toluene afforded tetrakis(η^2-3,5-dimethylpyrazolato)zirconium (**1**, 86%), tetrakis(η^2-3,5-di-*tert*-butylpyrazolato)zirconium (**2**, 88%), and tetrakis(η^2-3,5-diphenylpyrazolato)zirconium (**3**, 85%), respectively, as colorless crystalline solids [Equation (1)]. We have previously reported that treatment of group 4 and 5 metal chlorides with potassium pyrazolato salts constitutes an excellent synthetic route to the corresponding group 4 and 5 pyrazolato complexes.[12,13] Accordingly, salt metathesis routes to hafnium pyrazolato complexes were explored. Treatment of hafnium tetrachloride with 4 equiv. of the potassium salts of 3,5-dimethylpyrazolate,[12b] 3,5-di-*tert*-butylpyrazolate,[13] or 3,5-diphenylpyrazolate[13] in tetrahydrofuran at ambient temperature for 18 h afforded tetrakis(η^2-3,5-dimethylpyrazolato)hafnium (**4**, 75%), tetrakis(η^2-3,5-di-*tert*-butylpyrazolato)hafnium (**5**, 58%), and tetrakis(η^2-3,5-diphenylpyrazolato)hafnium·toluene (**6**·C_7H_8, 38%), respectively, as colorless crystalline solids [Equation (2)]. Complexes **1**–**3** were alternatively prepared by salt metathesis routes similar to those for **4**, **5**, and **6**·C_7H_8. The isolated yields of **1**–**3** were similar to those obtained by protonolysis reactions from tetrakis(dimethylamido)zirconium.

The structural assignments for **1**–**5** and **6**·C_7H_8 were based upon spectral and analytical data. In addition, X-ray crystal structure determinations were carried out for **1**, **3**, **4**, and **6**·C_7H_8, as described below. Complexes **1**, **3**, **4**, and **6**·C_7H_8 are monomeric in the solid state, with four η^2-pyrazolato ligands and eight-coordinate metal centers. They are stable indefinitely at ambient temperature under dry argon or nitrogen. The ^1H and $^{13}C\{^1H\}$ NMR spectra of **1**–**5** and **6**·C_7H_8 are consistent with the solid-state structures, and reveal the expected resonances for one type of pyrazolato ligand. In the dodecahedral structures of **1**–**5** and **6**·C_7H_8, the 3- and 5-substituents on each pyrazolato ligand are in different chemical environments. The fact that only one type of chemical environment is observed in the NMR spectra of **1**–**5** and **6**·C_7H_8 indicates that the pyrazolato ligand substituents are undergoing rapid site exchange on the NMR timescale. Such site exchange probably occurs through a sliding motion of the η^2-pyrazolato ligands across the faces of the dodecahedral molecular structures, which interchanges the two types of sites and is presumably a very low energy process.

During several attempts to crystallize **4** from polar solvents such as tetrahydrofuran or diethyl ether, a new complex was obtained that had a much more complicated ^1H NMR spectrum than that of **4**. A crystal structure determination, as described below, established that this new complex was tris(η^2-3,5-dimethylpyrazolato)(η^1-3,5-dimethylpyrazolato)(η^1-3,5-dimethylpyrazole)hafnium (**7**). Complex **7** probably corresponds to a hydrolysis product of **4**. It is less soluble and more crystalline than **4**, and crystallizes selectively from the polar solvents. Since **7** could only be obtained in low and variable yields by this process, an independent synthesis was developed. Treatment of **4** with one equiv. of 3,5-dimethylpyrazole in hexane at ambient temperature for 18 h afforded **7** in 84% yield as a colorless powder [Equation (3)].

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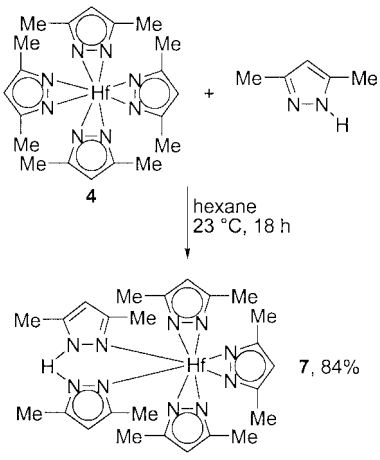

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The structural assignment for **7** was based upon spectral and analytical data, as well as an X-ray crystal structure determination, as described below. Further treatment of **7** with 3,5-dimethylpyrazole or treatment of **4** with 2 or more equiv. of 3,5-dimethylpyrazole did not lead to new complexes, and only **7** and free 3,5-dimethylpyrazole were isolated. Treatment of **1** with 3,5-dimethylpyrazole under conditions similar to the preparation of **7** afforded a species with a ^{1}H NMR spectrum that was similar to that of **7**. However, attempted crystallization of this material afforded only crystals of **1**. Treatment of **4** with pyridine in hexane, followed by crystallization, afforded only **4**. Complex **4** also did not form an isolable adduct with tetrahydrofuran. The ^{1}H NMR spectrum of **4** at ambient temperature in [D_8]toluene in the presence of pyridine (1 equiv.) showed no evidence for the formation of a pyridine adduct. Treatment of **3** or **6**·C_7H_8 with 3,5-diphenylpyrazole (1 equiv.) in [D_8] toluene showed no evidence for adduct formation, and crystallization always afforded pure **3** or **6**·C_7H_8. Similarly, there was no evidence for adduct formation between **2** or **5** and 3,5-di-*tert*-butylpyrazole.

In the solid state, complex **7** contains three η^2-3,5-dimethylpyrazolato, one η^1-3,5-dimethylpyrazolato, and one η^1-3,5-dimethylpyrazole ligands, as described below. The η^1-3,5-dimethylpyrazolato and η^1-3,5-dimethylpyrazole ligands are connected through a N–H···N hydrogen bond. At 20 °C in [D_2]dichloromethane (**7** is much more soluble in this solvent than in toluene), the ^{1}H NMR of **7** exhibited one slightly broad resonance for the methyl groups at δ = 2.17 ppm, one slightly broad resonance at δ = 5.99 ppm for the pyrazolato core C–*H* fragment, and a very broad resonance at δ = 10.3 ppm for the pyrazole N–*H* group. This spectrum indicates that proton exchange between the pyrazole and four pyrazolato ligands and site exchange among the pyrazolato ligands are fast on the NMR timescale at 20 °C. At –93 °C in [D_2]dichloromethane, the ^{1}H NMR was much more complicated. Resonances due to pyrazole N–*H* groups were observed at δ = 16.88, 16.58, 13.70, and 11.19 ppm. If the solid-state structure of **7** is maintained in solution, a single pyrazole N–*H* resonance should be observed. In the pyrazolato core C–*H* resonance region, nine singlets of various intensities were observed between δ = 5.48–6.30 ppm, compared to the five expected resonances if the molecular structure of **7** were maintained in solution. In the methyl resonance region, at least 20 singlets were observed between δ = 0.89–2.35 ppm. The ^{1}H NMR spectrum at –93 °C demonstrates that **7** exists as a mixture of at least several complexes in solution.

Volatility and Thermal Stability Study

Complexes **1**–**7** were evaluated for their volatility and thermal stability in order to assess their potential viability as film growth precursors. Sublimation was observed beginning at about the temperatures at which the free pyrazoles sublime (3,5-dimethylpyrazole, 45 °C/0.05 Torr; 3,5-diphenylpyrazole, 150 °C/0.05 Torr; 3,5-di-*tert*-butylpyrazole, 80 °C/0.05 Torr). For **1**–**5** and **6**·C_7H_8, the sublimed material consisted of the free pyrazole along with smaller amounts of **1**–**5** and **6**·C_7H_8. There were substantial amounts of nonvolatile residues at the conclusion of the sublimations. Sublimation of **7** at 50–60 °C/0.05 Torr afforded 3,5-dimethylpyrazole as the sublimate. This behavior is consistent with thermal decomposition of **1**–**7** during sublimation, and thus these complexes are unlikely to serve as useful film growth precursors under thermal source delivery conditions.

X-ray Crystal Structures

X-ray crystal structures of **1**, **3**, **4**, **6**·C_7H_8, and **7** were determined to establish the geometries about the metal centers and the bonding modes of the pyrazolato ligands. Experimental crystallographic data are summarized in Table 1. Selected bond lengths and angles are given in Table 2. Perspective views of **4** and **7** are presented in Figure 1 and Figure 2. The coordination spheres of **1**, **3**, and **6**·C_7H_8 are similar to that of **4**, so a representative perspective view is only given for **4**.

The molecular structures of **1**, **3**, **4**, and **6**·C_7H_8 consist of monomeric complexes, with four η^2-pyrazolato ligands bonded to each metal center and approximate dodecahedral geometry. The metal–nitrogen distances [**1**, 2.162(5)–2.226(5); **3**, 2.173(2)–2.212(2); **4**, 2.137(8)–2.206(7); **6**·C_7H_8, 2.156(4)–2.191(4) Å] are consistent with idealized η^2-pyrazolato ligand bonding. These bond lengths are comparable for the zirconium and hafnium complexes, due to similar sizes of the zirconium(IV) (r = 0.72 Å for six coordination[14]) and hafnium(IV) (r = 0.71 Å for six coordination[14]) ions. The metal ions in **1**, **3**, **4**, and **6**·C_7H_8 lie approximately in the C_3N_2 planes of the pyrazolato ligand cores, and thus the filled in-plane nitrogen-based orbitals are involved in bonding. The pyrazolato nitrogen–nitrogen bond lengths in **1**, **3**, **4**, and **6**·C_7H_8 vary from 1.37–1.40 Å, while the nitrogen–metal–nitrogen bite angles of the pyrazolato ligands range between 36.3–37.3°.

The molecular structure of **7** consists of monomeric molecules containing three η^2-3,5-dimethylpyrazolato, one

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Table 1. Crystal data and data collection parameters for **1**, **3**, **4**, **6**·C_7H_8, and **7**.

	1	**3**	**4**	**6**·C_7H_8	**7**
Empirical formula	$C_{20}H_{28}N_8Zr$	$C_{60}H_{44}N_8Zr$	$C_{20}H_{28}HfN_8$	$C_{67}H_{52}HfN_8$	$C_{25}H_{36}HfN_{10}$
Formula mass	471.72	968.25	558.99	1147.66	655.13
Space group	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	8.7282(3)	23.9264(7)	8.760(2)	12.428(18)	9.2148(9)
b [Å]	8.7953(3)	16.1975(4)	8.792(3)	13.73(2)	10.3816(11)
c [Å]	16.4224(6)	15.9951(2)	16.410(5)	16.68(3)	17.1557(19)
α [°]	95.269(3)		95.534(5)	74.92(2)	100.493(2)
β [°]	101.460(3)	129.815(2)	101.450(7)	79.48(3)	98.953(2)
γ [°]	90.368(2)		90.138(7)	81.23(3)	112.385(2)
V [Å^3]	1229.95(7)	4761.4(2)	1232.7(6)	2686(7)	1445.7(3)
Z	2	4	2	2	2
T [K]	218(2)	218(2)	295(2)	295(2)	295(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
$\rho_{calcd.}$ [g cm^{-3}]	1.274	1.351	1.506	1.419	1.505
μ [mm^{-1}]	0.467	0.281	4.252	1.993	3.639
$R(F)$[a] (%)	8.13	4.21	4.76	3.75	3.49
$Rw(F)$[a] (%)	17.3	7.65	10.32	7.29	6.25

[a] $R(F) = \Sigma||F_o| - |F_c||/ \Sigma|F_o|$; $R_w(F) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ for $I > 2\sigma(I)$.

Table 2. Selected bond lengths [Å] and angles [°] for **1**, **3**, **4**, **6**·C_7H_8, and **7**.

	1	**3**	**4**	**6**·C_7H_8	**7**
M–N(1)	2.183(5)	2.212(2)	2.203(7)	2.156(4)	2.373(4)
M–N(2)	2.220(5)	2.180(2)	2.155(7)	2.176(4)	
M–N(3)	2.202(5)	2.173(2)	2.206(7)	2.164(4)	2.144(3)
M–N(4)	2.164(5)	2.197(2)	2.153(7)	2.179(5)	2.172(3)
M–N(5)	2.226(5)		2.185(8)	2.166(4)	2.251(4)
M–N(6)	2.162(5)		2.137(8)	2.168(4)	2.138(4)
M–N(7)	2.176(5)		2.183(7)	2.191(4)	2.229(4)
M–N(8)	2.204(5)		2.167(7)	2.171(4)	
M–N(9)					2.175(4)
M–N(10)					2.179(4)
N(1)–N(2)	1.373(6)	1.377(3)	1.394(9)	1.367(4)	1.360(5)
N(3)–N(4)	1.385(7)	1.372(3)	1.387(10)	1.365(5)	1.385(5)
N(5)–N(6)	1.394(7)		1.372(10)	1.383(4)	1.377(5)
N(7)–N(8)	1.395(6)		1.380(10)	1.370(5)	1.390(5)
N(9)–N(10)					1.370(5)
N(1)–M–N(2)	36.3(2)	36.52(7)	37.3(2)	36.79(12)	
N(3)–M–N(4)	37.0(2)	36.59(7)	37.1(3)	36.64(12)	37.41(14)
N(5)–M–N(6)	37.0(2)		37.0(3)	37.23(12)	36.45(13)
N(7)–M–N(8)	37.1(2)		37.0(3)	36.62(13)	
N(9)–M–N(10)					36.67(14)

η^1-3,5-dimethylpyrazolato, and one η^1-3,5-dimethylpyrazole ligands bound to each hafnium center. There is an intramolecular hydrogen bond between the hydrogen atom bonded to N(2) of the η^1-3,5-dimethylpyrazole ligand and N(8) of the η^1-3,5-dimethylpyrazolato ligand. The overall geometry about the hafnium center can be considered as pentagonal bipyramidal, with the nitrogen atoms of two η^2-3,5-dimethylpyrazolato and one η^1-3,5-dimethylpyrazolato ligands corresponding to the equatorial plane. The center of the nitrogen–nitrogen bond of the η^2-3,5-dimethylpyrazolato ligand containing N(9) and N(10) and the coordinated nitrogen atom of the 3,5-dimethylpyrazole ligand correspond to the axial groups. The hafnium–nitrogen bond lengths for the η^2-3,5-dimethylpyrazolato ligands fall between 2.138(4)–2.251(3) Å, and these values are similar to those observed in **1**, **3**, and **4**. The η^2-3,5-dimethylpyrazolato ligand containing N(5) and N(6) has slightly asymmetric hafnium–nitrogen bond lengths of 2.138(4) and 2.251(4) Å, respectively. This slight asymmetry may arise from steric interactions between the methyl group containing C(14) and the η^1-3,5-dimethylpyrazole ligand. The hafnium–nitrogen bond lengths for the η^1-3,5-dimethylpyrazolato and 3,5-dimethylpyrazole ligands are 2.229(4) and 2.373(4) Å, respectively. The longer hafnium–nitrogen bond length for the 3,5-dimethylpyrazole ligand is consistent with its assignment as a neutral donor. The nitrogen–nitrogen bond lengths vary from 1.360(5)–1.390(5) Å. The nitrogen–hafnium–nitrogen bite angles of the η^2-3,5-dimethylpyrazolato ligands range between 36.45(13)–37.41(14)°, and are identical to the values for **1**, **3**, **4**, and **6**·C_7H_8.

Comments on 1–7

The results described herein extend our previous studies of homoleptic titanium(IV) pyrazolato complexes[10d,10e] to

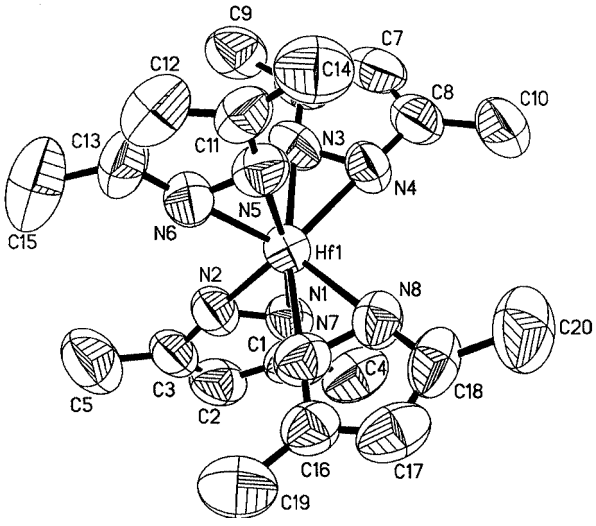

Figure 1. Perspective view of tetrakis(η^2-3,5-dimethylpyrazolato)-hafnium (**4**) with probability ellipsoids at the 50% level.

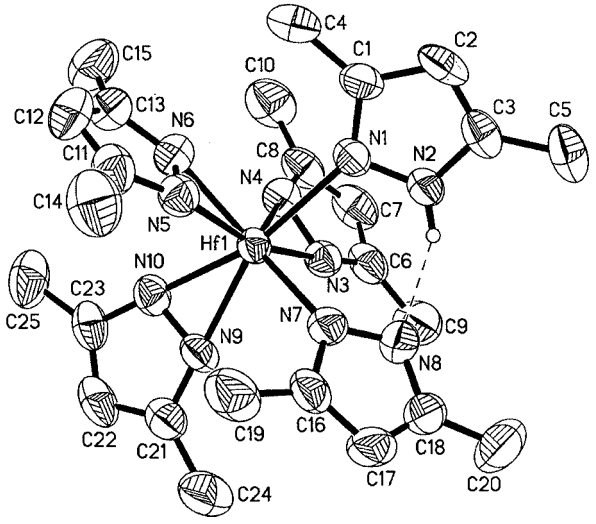

Figure 2. Perspective view of tris(η^2-3,5-dimethylpyrazolato)(η^1-3,5-dimethylpyrazolato)(η^1-3,5-dimethylpyrazole)hafnium (**7**) with probability ellipsoids at the 50% level.

the heavier group 4 elements zirconium and hafnium. $[Zr(R'_2pz)_4]$ (R′ = fluorenylmethyl) is the only other homoleptic heavier group 4 pyrazolato complex that has been structurally characterized.[11] It possesses approximate dodecahedral geometry about each zirconium ion, with zirconium–nitrogen bond lengths that range between 2.158(3)–2.210(3) Å. Thus, in spite of the bulky fluorenylmethyl substituents in the 3- and 5-positions of the pyrazolato ligands in $Zr(R'_2pz)_4$, essentially idealized η^2-pyrazolato ligands are observed. The combined results suggest that η^2-pyrazolato ligand coordination should be very common in zirconium(IV) and hafnium(IV) complexes. Excluding complexes containing tris(pyrazolyl)borate and related ligands (which possess μ–η^1:η^1-pyrazolato ligands), mixed ligand zirconium(IV) and hafnium(IV) pyrazolato complexes that have been structurally characterized to date are consistent with this prediction. For example, $[Cp_2Zr(pz)(THF)]^+BPh_4^-$ contains an η^2-pyrazolato ligand with zirconium–nitrogen bond lengths of 2.182(8) and 2.207(8) Å.[10c] $Hf(tBu_2pz)_3Cl$ contains η^2-pyrazolato ligands with hafnium–nitrogen bond lengths that range between 2.132(5)–2.162(8) Å.[12a] The metal–nitrogen bond lengths in these complexes are very similar to those observed in **1**, **3**, **4**, and **6**·C_7H_8. We have previously carried out molecular orbital calculations on the model pyrazolato complex $Ti(Me_2pz)Cl_3$,[10e] and noted that the η^2-pyrazolato ligand bonding occurs through overlap of filled symmetric and antisymmetric in-plane nitrogen-based orbitals with empty d-orbitals on the titanium center. Thus, the metal ion lies approximately in the C_3N_2 plane to maximize overlap with the in-plane nitrogen-based orbitals. The crystal structures of **1**, **3**, **4**, and **6**·C_7H_8 are consistent with this bonding model.

A surprise that emerged from this study is the formation and unusual structure of **7**. There was spectroscopic evidence in solution for a similar adduct derived from addition of 3,5-dimethylpyrazole to **1**. However, **1** crystallized selectively from these solutions, which indicates that adduct formation with 3,5-dimethylpyrazole is subtly balanced energetically with the crystallization of **1**. There was no evidence for formation of adducts between **4** and pyridine or tetrahydrofuran, either in the solution or the solid state. Accordingly, it appears that the N–H···N hydrogen bond is a key feature of the stability of **7**. Similar pyrazolato-pyrazole adducts bridged by N–H···N hydrogen bonds have been reported.[15]

Experimental Section

General: All manipulations were performed under argon using either glovebox or Schlenk line techniques. Hexane was distilled from P_2O_5, toluene was distilled from sodium, and tetrahydrofuran was distilled from purple solutions of sodium benzophenone ketyl. Tetrakis(dimethylamido)zirconium and hafnium tetrachloride were purchased from Strem Chemicals, Inc. and were used as received. 3,5-Dimethylpyrazole and 3,5-diphenylpyrazole were purchased from Aldrich Chemical Company and were sublimed prior to use. 3,5-Di-*tert*-butylpyrazole[16] and the potassium pyrazolate salts[12b,13] were prepared according to literature procedures. We previously briefly described the synthesis and characterization of **2** and **5**,[12a] but did not describe structural data or reactivity. ^1H and $^{13}C\{^1H\}$ NMR were obtained at 300, 400, 75, or 100 MHz in the indicated solvents. Infrared spectra were obtained using Nujol as the medium. Elemental analyses were performed by Midwest Microlab, Indianapolis, Indiana. Melting points were obtained with a Haake–Buchler HBI digital melting point apparatus and are uncorrected.

Preparation of Tetrakis(η^2-3,5-dimethylpyrazolato)zirconium (1): A 100 mL Schlenk flask was charged with 3,5-dimethylpyrazole (0.288 g, 3.00 mmol), toluene (35 mL), and was fitted with a reflux condenser. A solution of tetrakis(dimethylamido)zirconium (0.200 g, 0.759 mmol) in toluene (2 mL) was injected into the Schlenk flask using a syringe. The reaction mixture was then refluxed for 2 h. Upon cooling to room temperature, the volatile components were removed under reduced pressure to give an off-white solid. This solid was then extracted with hexane (20 mL), and the hexane extract was filtered through a 2-cm pad of Celite on a coarse frit to afford a clear, colorless solution. Removal of the vola-

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tile components under reduced pressure afforded **1** as a white crystalline solid (0.304 g, 86%). An analytical sample was obtained by recrystallization from a hexane solution at –20 °C, which afforded **1** as colorless crystals; m. p. 151–152 °C (dec.). IR (Nujol): $\tilde{\nu}$ = 3108 (w), 1568 (w), 1524 (s), 1440 (s), 1423 (s), 1366 (m), 1341 (w), 1320 (w), 1306 (w), 1262 (w), 1159 (w), 1116 (m), 1035 (w), 1004 (m), 959 (m), 790 (m), 729 (m), 684 (w) cm^{-1}. ^1H NMR ([D$_6$]benzene, 22 °C): δ = 2.17 (s, 24 H, C–C*H*$_3$), 5.97 (s, 4 H, pyrazolato C*H*) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]benzene, 22 °C): δ = 12.88 (s, C–*C*H$_3$), 112.18 (s, pyrazolato *C*H), 145.82 (s, *C*–CH$_3$) ppm. $C_{20}H_{28}N_8Zr$ (471.72): calcd. C 50.92, H 5.98, N 23.75; found C 50.26, H 5.87, N 23.08.

Preparation of Tetrakis(η^2-3,5-di-*tert*-butylpyrazolato)zirconium (2): In a fashion similar to the preparation of **1**, treatment of tetrakis-(dimethylamido)zirconium (0.200 g, 0.759 mmol) with 3,5-di-*tert*-butylpyrazole (0.540 g, 3.00 mmol) afforded **2** as a white crystalline solid (0.534 g, 88%). An analytical sample was obtained by recrystallization from a hexane solution at –20 °C, which afforded **2** as colorless crystals; m. p. 226 °C (dec.). IR (Nujol): $\tilde{\nu}$ = 3108 (w), 1589 (s), 1570 (s), 1248 (m), 1206 (w), 968 (w), 953 (w), 866 (m), 844 (m), 754 (w), 696 (w) cm^{-1}. ^1H NMR ([D$_6$]benzene, 22 °C): δ = 1.24 [s, 72 H, C(C*H*$_3$)$_3$], 6.34 (s, 4 H, pyrazolato C*H*) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]benzene, 22 °C): δ = 30.82 [s, C(*C*H$_3$)$_3$], 32.30 [s, *C*(CH$_3$)$_3$], 105.98 (s, pyrazolato *C*H), 159.31 [s, *C*–C(CH$_3$)$_3$] ppm. $C_{44}H_{76}N_8Zr$ (808.37): calcd. C 65.38, H 9.48, N 13.86; found C 63.42, H 9.22, N 12.77.

Preparation of Tetrakis(η^2-3,5-diphenylpyrazolato)zirconium (3): In a fashion similar to the preparation of **1**, treatment of tetrakis(dimethylamido)zirconium (0.200 g, 0.759 mmol) with 3,5-diphenylpyrazole (0.660 g, 3.00 mmol) afforded **3** as a white crystalline solid (0.616 g, 85%). An analytical sample was obtained by recrystallization from a hexane solution at –20 °C, which afforded **3** as colorless crystals; m. p. 240 °C (dec.). IR (Nujol): $\tilde{\nu}$ = 3102 (w), 1407 (w), 1366 (s), 1335 (m), 1262 (m), 1170 (w), 1156 (w), 1101 (m), 1074 (m), 1057 (w), 1023 (m), 971 (m), 918 (w), 804 (m), 761 (s), 723 (s), 691 (s) cm^{-1}. ^1H NMR ([D$_6$]benzene, 22 °C): δ = 6.92 (s, 4 H, pyrazolato C*H*), 6.98 (s, 24 H, *meta*- and *para*-C*H* of C$_6$H$_5$), 7.77 (s, 16 H, *ortho*-C*H* of C$_6$H$_5$) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$] benzene, 22 °C): δ = 109.41 (s, pyrazolato *C*H), 126.69 (s, *para*-*C*H of C$_6$H$_5$), 128.10 (s, *meta*-*C*H of C$_6$H$_5$), 128.72 (s, *ortho*-*C*H of C$_6$H$_5$), 132.18 (s, *ipso*-*C* of C$_6$H$_5$), 150.72 (s, pyrazolato *C*–C$_6$H$_5$) ppm. $C_{60}H_{44}N_8Zr$ (968.25): calcd. C 74.43, H 4.58, N 11.57; found C 74.49, H 4.62, N 11.53.

Preparation of Tetrakis(η^2-3,5-dimethylpyrazolato)hafnium (4): A 100 mL Schlenk flask was charged with hafnium tetrachloride (0.200 g, 0.624 mmol), potassium 3,5-dimethylpyrazolate (0.335 g, 2.50 mmol), and tetrahydrofuran (50 mL). The cloudy colorless reaction mixture was stirred at ambient temperature for 18 h. Then, the volatile components were removed under reduced pressure to give a white solid. This solid was extracted with hexane (80 mL), and the hexane extract was filtered through a 2-cm pad of Celite on a coarse frit to afford a colorless clear solution. Removal of the volatile components under reduced pressure afforded **4** as a white crystalline solid (0.262 g, 75%). An analytical sample was obtained by recrystallization from a hexane solution at –20 °C, which afforded **4** as colorless crystals; m. p. 149–150 °C. IR (Nujol): $\tilde{\nu}$ = 3110 (w), 1524 (m), 1366 (m), 1341 (w), 1323 (w), 1310 (w), 1262 (m), 1170 (w), 1154 (w), 1115 (m), 1037 (w), 1006 (m), 960 (m), 789 (s), 731 (s), 724 (s) cm^{-1}. ^1H NMR ([D$_6$]benzene, 22 °C): δ = 2.16 (s, 24 H, C–C*H*$_3$), 6.08 (s, 4 H, pyrazolato C*H*) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]benzene, 22 °C): δ = 13.32 (s, C–*C*H$_3$), 112.99 (s, pyrazolato *C*H), 146.15 (s, *C*–CH$_3$) ppm. $C_{20}H_{28}HfN_8$ (558.99): calcd. C 42.97, H 5.05, N 20.05; found C 42.89, H 5.01, N 20.05.

Preparation of Tetrakis(η^2-3,5-di-*tert*-butylpyrazolato)hafnium (5): In a fashion similar to the preparation of **4**, treatment of hafnium tetrachloride (0.200 g, 0.624 mmol) with potassium 3,5-di-*tert*-butylpyrazolate (0.545 g, 2.50 mmol) afforded **5** as a white crystalline solid (0.295 g, 58%). An analytical sample was obtained by recrystallization from a toluene solution at –20 °C, which afforded **5** as colorless crystals; m. p. 202 °C (dec.). IR (Nujol): $\tilde{\nu}$ = 1527 (m), 1509 (m), 1366 (s), 1304 (m), 1260 (s), 1230 (m), 1206 (w), 1094 (s), 1024 (s), 993 (m), 801 (s), 721 (m) cm^{-1}. ^1H NMR ([D$_6$] benzene, 22 °C): δ = 1.23 [s, 72 H, C(C*H*$_3$)$_3$], 6.46 (s, 4 H, pyrazolato C*H*) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]benzene, 22 °C): δ = 30.71 [s, C(*C*H$_3$)$_3$], 32.22 [s, *C*(CH$_3$)$_3$], 106.02 (s, pyrazolato *C*H), 159.14 [s, *C*–C(CH$_3$)$_3$] ppm. $C_{44}H_{76}HfN_8$ (895.63): calcd. C 59.01, H 8.55, N 12.51; found C 59.14, H 8.46, N 12.32.

Preparation of Tetrakis(η^2-3,5-diphenylpyrazolato)hafnium·Toluene (6·C$_7$H$_8$): In a fashion similar to the preparation of **4**, treatment of hafnium tetrachloride (0.200 g, 0.624 mmol) with [K(Ph$_2$pz)-(THF)]$_6$ (0.645 g, 0.325 mmol) afforded a white crystalline solid. Recrystallization of this solid from a toluene solution at –20 °C afforded **6**·C$_7$H$_8$ as colorless crystals (0.274 g, 38% based upon the potassium pyrazolato reagent); m. p. 239–240 °C (dec; toluene loss observed at 110 °C). IR (Nujol): $\tilde{\nu}$ = 1366 (s), 1303 (w), 1260 (s), 1170 (m), 1153 (m), 1097 (s), 1021 (s), 974 (w), 802 (s), 760 (m), 723 (s) cm^{-1}. ^1H NMR ([D$_6$]benzene, 22 °C): δ = 6.92 (s, 4 H, pyrazolato C*H*), 6.98 (s, 8 H, *para*-C*H* of C$_6$H$_5$), 7.00 (s, 16 H, *meta*-C*H* of C$_6$H$_5$), 7.72 (m, 16 H, *ortho*-C*H* of C$_6$H$_5$) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]benzene, 22 °C): δ = 109.15 (s, pyrazolato *C*H), 126.62 (s, *para*-*C*H of C$_6$H$_5$), 127.95 (s, *meta*-*C*H of C$_6$H$_5$), 128.34 (s, *ortho*-*C*H of C$_6$H$_5$), 132.08 (s, *ipso*-*C* of C$_6$H$_5$), 150.33 (s, pyrazolato *C*–C$_6$H$_5$) ppm. In addition, resonances due to free toluene were observed in the ^1H and $^3C\{^1H\}$ NMR spectra. $C_{67}H_{52}HfN_8$ (1147.66): calcd. C 70.12, H 4.57, N 9.76; found C 70.09, H 4.64, N 9.47.

Preparation of Tris(η^2-3,5-dimethylpyrazolato)(η^1-3,5-dimethylpyrazolato)(η^1-3,5-dimethyl-pyrazole)hafnium (7): A 100 mL Schlenk flask was charged with **4** (0.254 g, 0.454 mmol), 3,5-dimethylpyrazole (0.044 g, 0.458 mmol), and hexane (50 mL). The colorless mixture was stirred at ambient temperature for 18 h. Then, the solution was filtered through a 2-cm pad of Celite on a coarse frit to afford a clear, colorless solution. The volatile components were removed under reduced pressure to afford **7** as a white crystalline solid (0.250 g, 84%). An analytical sample was obtained by recrystallization from a hexane solution at –20 °C, which afforded **7** as colorless crystals; m. p. 71 °C (dec.). IR (Nujol): $\tilde{\nu}$ = 3248 (m, ν_{NH}), 3205 (m, ν_{NH}), 3135 (m, ν_{NH}), 3110 (m), 3040 (m), 1671 (m), 1622 (m), 1595 (m), 1568 (m), 1524 (m), 1485 (s), 1441 (s), 1418 (s), 1345 (s), 1307 (s), 1260 (s), 1155 (m), 1146 (m), 1112 (s), 1099 (s), 1029 (s), 1016 (s), 1007 (s), 958 (m), 862 (m), 833 (m), 791 (s), 730 (m), 703 (s), 659 (m) cm^{-1}. ^1H NMR ([D$_6$]benzene, 22 °C): δ = 2.12 (broad s, 30 H, C*H*$_3$), 5.89 (broad s, 5 H, pyrazolato and pyrazole C*H*), 13.0 (very broad s, 1 H, N*H*) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]benzene, 22 °C): δ = 12.56 (s, C–*C*H$_3$), 108.31 (s, pyrazolato and pyrazole *C*H), 144.95 (s, *C*–CH$_3$) ppm. $C_{25}H_{36}HfN_{10}$ (655.13): calcd. C 45.84, H 5.54, N 21.38; found C 45.67, H 5.54, N 21.06.

X-ray Crystallographic Structure Determinations for 1, 3, 4, 6·C$_7$H$_8$, and 7: Crystalline samples of all air sensitive compounds were mounted in sealed thin-walled glass capillaries under nitrogen for X-ray data collection. The single-crystal X-ray diffraction experiments for **1** and **3** were performed with a Siemens P4 diffractometer with Mo-K_α radiation and graphite monochromator. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were treated as idealized contributors. Data-

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sets for **4**, **6**·C_7H_8, and **7** were collected at room temperature with a Bruker P4/CCD diffractometer equipped with Mo radiation. For each collection, a full sphere of data was collected at 10 s/frame with 0.2° between each frame. The frame data were integrated with the manufacturer's SMART and SAINT software.[17] Absorption corrections were applied with Sheldrick's SADABS program[17] and each structure was solved and refined using the programs of SHELXL-97.[18] The crystal structures of compounds **4**, **6**·C_7H_8, and **7** consist of discrete monomeric neutral complexes. Complex **4** crystallizes as colorless flat squares. The hydrogen atoms were placed in calculated positions. Complex **6**·C_7H_8 crystallizes as colorless mounds that were grown together. A cut fragment was used for data collection and a dataset was extracted with Sparks' GEMINI software.[17] One molecule of toluene solvent per hafnium ion is present in the model. The hydrogen atoms were placed in calculated positions. Complex **7** crystallizes as colorless blocks. All atoms occupy general positions in the unit cell. The hydrogen atoms were placed in observed and calculated positions.

CCDC-269335 (for **1**), -269336 (for **3**), -269337 (for **4**), -269338 (for **6**·C_7H_8), and -269339 (for **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK; Fax: (+44)-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk.

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