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Synthesis and Characterization of Lithium, Zirconium, and Hafnium Derivatives of *N*-Isopropyl-2-(isopropylamino)troponiminate

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The reaction of *N*-isopropyl-2-(isopropylamino)troponimine, [(*i*-Pr)$_2$ATI]H, with *n*-BuLi in Et$_2$O−THF gave [(*i*-Pr)$_2$ATI]Li(THF)$_2$ in excellent yield. The [(*i*-Pr)$_2$ATI]$_2$ZrCl$_2$ and [(*i*-Pr)$_2$ATI]$_2$HfCl$_2$ complexes were prepared by treating the respective metal tetrachlorides with 2 equiv of the lithium adduct. These metal complexes were characterized by NMR spectroscopy and X-ray crystallography. X-ray crystallographic data of the lithium, zirconium, and hafnium complexes show monomeric structures in the solid state. The lithium complex has a tetrahedral lithium ion and a slightly twisted C$_7$N$_2$Li framework. The zirconium and hafnium metal centers in [(*i*-Pr)$_2$ATI]$_2$ZrCl$_2$ and [(*i*-Pr)$_2$ATI]$_2$HfCl$_2$ show pseudooctahedral geometry with chlorides occupying the *cis* positions. The dialkyl derivative [(*i*-Pr)$_2$ATI]$_2$Zr(CH$_2$SiMe$_3$)$_2$ was prepared by treating Zr(CH$_2$SiMe$_3$)$_4$ with 2 equiv of the free ligand [(*i*-Pr)$_2$ATI]H. Crystal data with Mo Kα ($\lambda = 0.710\,73$ Å) at 193 K: [(*i*-Pr)$_2$ATI]Li(THF)$_2$, C$_{21}$H$_{35}$LiN$_2$O$_2$, $a = 9.2318(8)$ Å, $b = 14.624(2)$ Å, $c = 16.071(2)$ Å, $\beta = 94.954(5)°$, $V = 2661.3(5)$ Å^3, monoclinic, space group $P2_1/n$, Z = 4, $R = 0.0607$; [(*i*-Pr)$_2$ATI]$_2$ZrCl$_2$, C$_{26}$H$_{38}$Cl$_2$N$_4$Zr, $a = 9.569(3)$ Å, $b = 15.877(4)$ Å, $c = 18.241(6)$ Å, $\beta = 94.480(10)°$, $V = 2763.0(14)$ Å^3, monoclinic, space group $P2_1/n$, $Z = 4$, $R = 0.0401$; [(*i*-Pr)$_2$ATI]$_2$HfCl$_2$, C$_{26}$H$_{38}$Cl$_2$HfN$_4$, $a = 9.540(1)$ Å, $b = 15.813(2)$ Å, $c = 18.118(3)$ Å, $\beta = 94.546(11)°$, $V = 2724.8(7)$ Å^3, monoclinic, space group $P2_1/n$, $Z = 4$, $R = 0.0313$.

Introduction

Homogeneous olefin polymerization is one of the most important processes catalyzed by early transition metal complexes.[1−5] The vast majority of metal adducts used in this application are derived from cyclopentadienyl ligands or their ring-anellated systems (e.g., indenyl or fluorenyl ligands).[6−9] Various substituents have been used on these ligands to modulate the steric and electronic properties of the metal center.[10] More drastic modifications to the metal coordination environment involve the use of ligands other than cyclopentadienyl (or related ligand) systems. Recently, there has been significant activity in the latter direction. For example, a number of metal complexes of titanium, zirconium, or hafnium have been synthesized in which one or more cyclopentadienyls have been replaced by anionic, nitrogen-based ancillary ligands such as amides,[11−24] amidinate,[25−30] tris(pyrazolyl)borate,[31,32] diazabutadiene,[33,34] porphyrin,[35−37] and tetraazaannulene.[38−44] Their use as cocatalysts in the polymerization of olefins has also been investigated. Furthermore, it has been noted that the amidinates such as [PhC(NSiMe$_3$)$_2$]$^-$ have steric properties similar to those of cyclopentadienyl ligands.[25−27]

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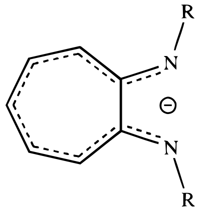
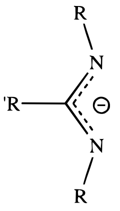


Aminotroponiminate
10π electron system



Amidinate
4π electron system

We are interested in investigating the use of aminotroponiminates [ATI]$^-$ as ancillary ligands (particularly as an alternative to the ubiquitous cyclopentadienyl ligand) in group 4 metal chemistry. The aminotroponiminate can be compared to the amidinate ligand. They are both bidentate, monoanionic, formally 4-electron-donor ligand systems. However, upon coordination, aminotroponiminate forms a five-membered chelate ring whereas amidinate forms a four-membered metallacycle. Furthermore, unlike amidinate, [ATI]$^-$ features a delocalized 10-π-electron ligand backbone. In addition, the studies involving the [ATI]$^-$ ligand (including those of the related tropocoronand) have mostly been limited to the first-row middle and late transition metal ions such as manganese, iron, cobalt, nickel, copper, and zinc[45-58] whereas the amidinates have been used fairly widely as ligands for a broad spectrum metal ions.[27]

Experimental Section

All operations were carried under an atmosphere of purified nitrogen using standard Schlenk techniques or in a Vacuum Atmospheres single-station drybox equipped with a −25 °C refrigerator. Solvents were distilled from conventional drying agents and degassed twice prior to use. Glassware was oven-dried at 150 °C overnight. [(*i*-Pr)$_2$ATI]H and $Zr(CH_2SiMe_3)_4$ were prepared according to the previously reported method.[59,60] *n*-BuLi (1.6 M solution in hexane), $ZrCl_4$, and $HfCl_4$ were obtained from the Aldrich and used as received. The ^1H and ^{13}C NMR spectra were recorded in C_6D_6 at room temperature on a Bruker MSL-300 spectrometer (^1H, 300.15 MHz; ^{13}C, 75.47 MHz) or a Nicolet NT-200 spectrometer (^1H, 200.06 MHz; ^{13}C, 50.31 MHz), unless otherwise noted. Chemical shifts for ^1H NMR spectra are relative to internal Me_4Si. The ^{13}C NMR spectra were run with ^1H decoupling, and the chemical shifts are reported in ppm vs Me_4Si (C_6D_6 at 128.0 ppm). Melting points were obtained on a Mel-Temp II apparatus and were not corrected. Elemental analyses were performed by the Texas Analytical Laboratories, Inc., Houston, TX.

Preparation of [(*i*-Pr)$_2$ATI]Li(THF)$_2$. A diethyl ether (30 mL) solution of [(*i*-Pr)$_2$ATI]H (315 mg, 1.6 mmol) was treated with *n*-BuLi (1.0 mL of 1.6 M solution) at 0 °C. After 30 min, the mixture was slowly brought to the room temperature. The volatile materials were removed under vacuum to yield a yellow solid (85%). After treatment with THF, X-ray-quality crystals were grown from a toluene−hexanes mixture at −20 °C. Mp: dec at 70 °C. NMR (C_6D_6): ^1H δ 1.22 (d, 12H, CH_3, $J = 6.3$ Hz), 1.29 (m, 8H, CH_2), 3.39 (m, 8H, CH_2), 4.03 (septet, 2H, $C\mathit{H}(CH_3)_2$, $J = 6.3$ Hz), 6.17 (t, 1H, H_5, $J = 8.8$ Hz), 6.53 (d, 2H, $H_{3,7}$, $J = 11.3$ Hz), 7.05 (dd, 2H, $H_{4,6}$, $J = 11.3, 8.8$ Hz); $^{13}C\{^1H\}$ δ 24.3 (CH_3), 25.4 (CH_2), 48.2 ($\mathit{C}H(CH_3)_2$), 68.2 (CH_2), 107.8 (C_5), 109.7 ($C_{3,7}$), 132.9 ($C_{4,6}$), 164.0 ($C_{2,8}$). Anal Calcd for $C_{21}H_{35}N_2O_2Li$: C, 71.16; H, 9.95; N, 7.9. Found: C, 72.42; H, 10.08; N, 8.02.

Preparation of [(*i*-Pr)$_2$ATI]$_2$ZrCl$_2$. A solution of [(*i*-Pr)$_2$ATI]H (0.55 g, 2.69 mmol) in diethyl ether (15 mL) was cooled to 0 °C and treated with *n*-BuLi (1.68 mL of 1.6 M solution, 2.69 mmol) in hexane. The mixture was allowed to warm to room temperature and kept stirring for an additional 30 min. This lithiated solution was added dropwise to $ZrCl_4$ (0.31 g, 1.35 mmol) in diethyl ether (15 mL) at 0 °C. After the addition, the mixture was allowed to warm to room temperature and stirred overnight. The color of the solution became orange-red. The volatile materials were removed under reduced pressure, and the residue was extracted into toluene. The mixture was filtered, and the filtrate was concentrated. An X-ray-quality orange-red crystal was obtained from toluene at −25 °C (81% yield). Mp: 222−225 °C. NMR (C_6D_6): ^1H δ 1.40 (d, $J = 6.6$ Hz, 24H, CH_3), 4.74 (br s, 4H, CH), 6.25 (m, 2H, H_5), 6.70 (m, 8H, $H_{3,4,6,7}$); $^{13}C\{^1H\}$ δ 20.3 (CH_3), 52.1 ($\mathit{C}H(CH_3)_2$), 117.5 (C_5), 122.6 ($C_{3,7}$), 134.4 ($C_{4,6}$), 164.8 ($C_{2,8}$). Anal. Calcd for $C_{26}H_{38}N_4ZrCl_2$: C, 54.91; H, 6.73; N, 9.85. Found: C, 54.80; H, 6.78; N, 9.74.

Preparation of [(*i*-Pr)$_2$ATI]$_2$Zr(CH$_2$SiMe$_3$)$_2$. [(*i*-Pr)$_2$ATI]H (0.5 g, 2.45 mmol) and $Zr(CH_2SiMe_3)_4$ (0.54 g, 1.22 mmol) were mixed in toluene−hexane (20 mL at 1:1), and the mixture was stirred overnight. The resulting mixture was warmed to obtain a clear solution and concentrated to ca. 10 mL. The concentrate was cooled to −25 °C, and crystalline solid was obtained in 61% yield. Mp: dec around 70 °C. NMR (C_6D_6) ^1H δ −1.54 (s, 4H, $ZrCH_2$), −0.02 (s, 18H, $Si(CH_3)_3$, 1.36 (br d, 24H, $(CH_3)_2CH$, $J = 5.0$ Hz), 3.61 (br s, 4H, CH), 6.12 (t, 2H, H_5, $J = 9.0$ Hz), 6.36 (d, 4H, $H_{3,7}$, $J = 11.0$ Hz), 6.80 (dd, 4H, $H_{4,6}$, $J = 9.0, 11.0$ Hz); $^{13}C\{H\}$ δ 4.3 ($Zr\mathit{C}H_2$), 24.6, 29.8, 48.1 ($\mathit{C}H(CH_3)_2$), 112.8 (C_5), 116.4 ($C_{3,7}$), 135.7 ($C_{4,6}$), 165.0 ($C_{2,8}$). Anal. Calcd for $C_{34}H_{60}N_4Si_2Zr$: C, 60.75; H, 9.00; N, 8.33. Found: C, 60.18; H, 8.86; N, 8.45.

Preparation of [(*i*-Pr)$_2$ATI]$_2$HfCl$_2$. This compound was prepared in a manner similar to that for [(*i*-Pr)$_2$ATI]$_2$ZrCl$_2$, using [(*i*-Pr)$_2$ATI]H (1.0 g, 4.89 mmol), *n*-BuLi in hexane (3.06 mL of a 1.6 M solution, 4.89 mmol), and $HfCl_4$ (0.79 g, 2.45 mmol). The yellow product was isolated in 74% yield. Mp: 210−214 °C. NMR (C_6D_6): ^1H δ 1.40 (br s, 24H, CH_3), 4.79 (br s, 4H, CH), 6.21 (t, $J = 8.73$, 2H, H_5), 6.72 (m, 8H, $H_{3,4,6,7}$); $^{13}C\{^1H\}$ δ 20.3 (CH_3), 52.3 ($\mathit{C}H(CH_3)_2$), 118.5 (C_5), 122.7 ($C_{3,7}$), 134.3 ($C_{4,6}$), 165.3 ($C_{2,8}$). Anal. Calcd for $C_{26}H_{38}N_4ZrCl_2$: C, 47.6; H, 5.84; N,8.54. Found: C, 47.41; H, 5.76; N, 8.43.

X-ray Structure Determination. A suitable crystal covered with a layer of hydrocarbon oil was selected and attached to a glass fiber and immediately placed in the low-temperature nitrogen stream.[61] Data collections were carried out at −80 °C on a Siemens P4 diffractometer equipped with a LT-2A device for low-temperature work and graphite-

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Table 1. Crystal Data and Summary of Data Collection and Refinement

	$[(i\text{-Pr})_2\text{ATI}]\text{Li(thf)}_2$	$[(i\text{-Pr})_2\text{ATI}]_2\text{ZrCl}_2$	$[(i\text{-Pr})_2\text{ATI}]_2\text{HfCl}_2$
empirical formula	$C_{21}H_{35}LiN_2O_2$	$C_{26}H_{38}Cl_2N_4Zr$	$C_{26}H_{38}Cl_2HfN_4$
fw	354.5	568.7	656.0
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a, Å	9.2318(8)	9.569(3)	9.5403(13)
b, Å	14.624(2)	15.877(4)	15.813(2)
c, Å	16.071(2)	18.241(6)	18.118(3)
α, deg	90	90	90
β, deg	95.954(5)	94.480(10)	94.546(11)
γ, deg	90	90	90
V, Å^3	2161.3(5)	2763.0(14)	2724.8(7)
Z	4	4	4
T, K	193	193	193
λ(Mo Kα), Å	0.710 73	0.710 73	0.710 73
d(calc), g/cm^3	1.089	1.367	1.599
abs coeff, mm^{-1}	0.068	0.612	4.045
R, R_w,^{a} %	6.07, 6.71	4.01, 3.98	3.13, 3.46

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[(i\text{-Pr})_2\text{ATI}]\text{Li(THF)}_2$

Li−N(1)	1.995(6)	Li−N(9)	1.990(6)
Li−O(1)	1.971(6)	Li−O(2)	1.960(6)
N(1)−C(2)	1.313(4)	N(9)−C(8)	1.319(4)
C(2)−C(3)	1.439(4)	C(2)−C(8)	1.500(4)
C(3)−C(4)	1.363(5)	C(4)−C(5)	1.385(5)
C(5)−C(6)	1.381(5)	C(6)−C(7)	1.383(4)
C(7)−C(8)	1.426(5)		
N(1)−Li−N(9)	81.5(2)	N(1)−Li−O(1)	117.8(3)
N(9)−Li−O(1)	120.9(3)	N(1)−Li−O(2)	118.3(3)
N(9)−Li−O(2)	115.7(3)	O(1)−Li−O(2)	102.9(3)
Li−N(1)−C(2)	114.0(3)	Li−N(1)−C(10)	125.3(3)
Li−N(9)−C(8)	113.4(3)	N(1)−C(2)−C(8)	114.4(3)
N(9)−C(8)−C(2)	113.7(3)		

Table 3. Selected Bond Lengths (Å) and Angles (deg)

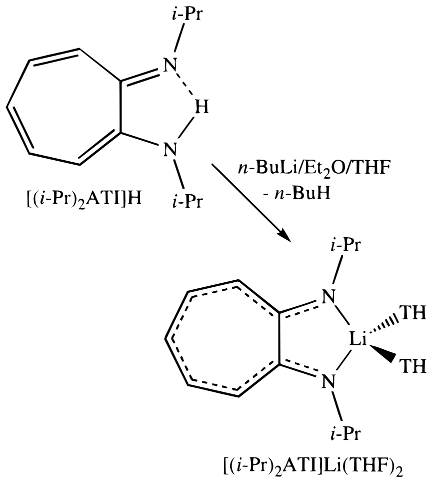
	$[(i\text{-Pr})_2\text{ATI}]_2\text{ZrCl}_2$		
Zr−Cl(1)	2.459(2)	Zr−Cl(2)	2.452(2)
Zr−N(1)	2.239(5)	Zr−N(9)	2.205(5)
Zr−N(16)	2.232(5)	Zr−N(24)	2.208(5)
N(1)−C(2)	1.363(8)	N(9)−C(8)	1.335(8)
N(16)−C(17)	1.329(8)	N(24)−C(23)	1.350(8)
C(2)−C(8)	1.477(9)	C(17)−C(23)	1.486(9)
Cl(1)−Zr−Cl(2)	98.8(1)	Cl−Zr−N(1)	94.6(1)
Cl(2)−Zr−N(1)	99.5(1)	Cl(1)−Zr−N(9)	163.0(1)
Cl(2)−Zr−N(9)	90.7(1)	N(1)−Zr−N(9)	69.8(2)
Cl(1)−Zr−N(16)	91.8(1)	Cl(2)−Zr−N(16)	158.7(1)
N(1)−Zr−N(16)	98.0(2)	N(9)−Zr−N(16)	84.0(2)
Cl(1)−Zr−N(24)	93.3(1)	Cl(2)−Zr−N(24)	91.1(1)
N(1)−Zr−N(24)	165.6(2)	N(9)−Zr−N(24)	100.7(2)
N(16)−Zr−N(24)	69.8(2)	Zr−N(1)−C(2)	117.1(4)
Zr−N(9)−C(8)	121.0(4)	Zr−N(16)−C(17)	121.0(4)
Zr−N(24)−C(23)	120.2(4)	N(1)−C(2)−C(8)	113.1(5)
N(9)−C(8)−C(2)	113.0(6)	N(16)−C(17)−C(23)	113.3(5)
N(24)−C(23)−C(17)	112.4(5)		
	$[(i\text{-Pr})_2\text{ATI}]_2\text{HfCl}_2$		
Hf−Cl(1)	2.431(2)	Hf−Cl(2)	2.430(2)
Hf−N(1)	2.178(6)	Hf−N(9)	2.217(6)
Hf−N(16)	2.189(5)	Hf−N(24)	2.203(6)
N(1)−C(2)	1.344(9)	N(9)−C(8)	1.327(9)
N(16)−C(17)	1.325(10)	N(24)−C(23)	1.375(9)
C(2)−C(8)	1.460(10)	C(17)−C(23)	1.468(10)
Cl(1)−Hf−Cl(2)	98.0(1)	Cl(1)−Hf−N(1)	93.7(2)
Cl(2)−Hf−N(1)	91.0(2)	Cl(1)−Hf−N(9)	91.9(2)
Cl(2)−Hf−N(9)	159.9(2)	N(1)−Hf−N(9)	70.9(2)
Cl(1)−Hf−N(16)	164.3(2)	Cl(2)−Hf−N(16)	90.5(2)
N(1)−Hf−N(16)	94.5(2)	Cl(2)−Hf−N(24)	99.8(2)
N(1)−Hf−N(24)	165.5(2)	N(9)−Hf−N(24)	96.9(2)
N(16)−Hf−N(24)	71.0(2)	Hf−N(1)−C(2)	119.6(5)
Hf−N(9)−C(8)	119.0(5)	Hf−N(16)−C(17)	120.0(4)
Hf−N(24)−C(23)	116.3(4)	N(1)−C(2)−C(8)	112.7(6)
N(9)−C(8)−C(2)	114.7(6)	N(16)−C(17)−C(23)	113.5(6)
N(24)−C(23)−C(17)	113.4(6)		

monochromated Mo Kα radiation (λ = 0.710 73 Å). The unit cell parameters of $[(i\text{-Pr})_2\text{ATI}]_2\text{Li(THF)}_2$, $[(i\text{-Pr})_2\text{ATI}]_2\text{ZrCl}_2$, and $[(i\text{-Pr})_2\text{ATI}]_2\text{HfCl}_2$ were determined by least-squares refinement of 15, 23, and 29 reflections, respectively. Three standard reflections were measured at every 97 data points to check for crystal deterioration and/or misalignment. No significant deterioration in intensity was observed. Data were corrected for Lorentz and polarization effects. An absorption correction was also applied for the data sets of $[(i\text{-Pr})_2\text{ATI}]_2\text{ZrCl}_2$ and $[(i\text{-Pr})_2\text{ATI}]_2\text{HfCl}_2$. All three structures were solved by direct methods, followed by successive cycles of full-matrix least-squares refinement and difference Fourier analysis. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included at calculated positions with C−H = 0.96 Å and fixed U_H. Software programs and the sources of scattering factors are contained in the SHELXTL (PC version 4.2) software package provided by Siemens Analytical X-ray Instruments, Inc.[62] Some details of the data collections and refinements are given in Table 1, and selected bond distances and angles are given in Tables 2 and 3. Further details of the structures are presented in the Supporting Information.

Results and Discussion

In view of the growing interest in using nitrogen-based chelating systems as ancillary ligands to synthesize cyclopentadienyl-free early transition metal complexes for the applications in homogeneous olefin polymerization processes, we have decided to investigate the utility of aminotroponiminates in group 4 metal ion chemistry. In contrast to the chemistry of late and middle transition metal elements, aminotroponiminates have not been used widely as ligands for the earlier members. In this paper, we describe the synthesis and structural characterization of Zr and Hf complexes containing the *N*-isopropyl-2-(isopropylamino)tropoiminate $[(i\text{-Pr})_2\text{ATI}]^-$ ligand. The solid state structure of the lithium complex $[(i\text{-Pr})_2\text{ATI}]\text{Li(THF)}_2$ is also reported.

Lithium Complex. The lithium salt of the *N*-isopropyl-2-(isopropylamino)troponimine, $[(i\text{-Pr})_2\text{ATI}]\text{Li(THF)}_2$, was prepared by treatment of $[(i\text{-Pr})_2\text{ATI}]\text{H}$ with 1 equiv of *n*-BuLi at 0° C (eq 1). This highly air- and moisture-sensitive compound was isolated as a yellow solid in excellent yield. It was characterized by ^{1}H and ^{13}C NMR spectroscopy and by



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[62] *Siemens SHELXTL (PC version 4.2)*; Siemens Industrial Automation, Inc.: Madison, WI, 1990.

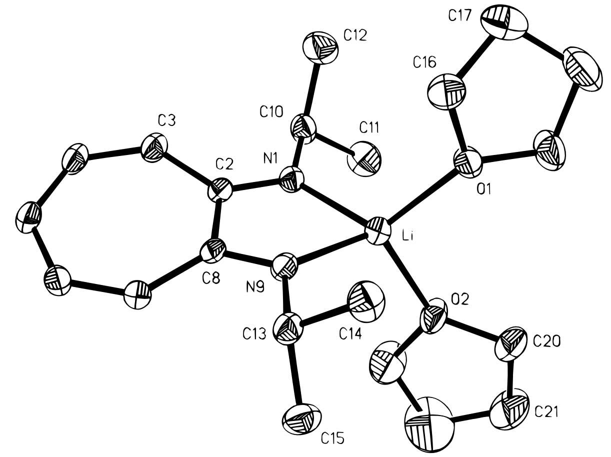


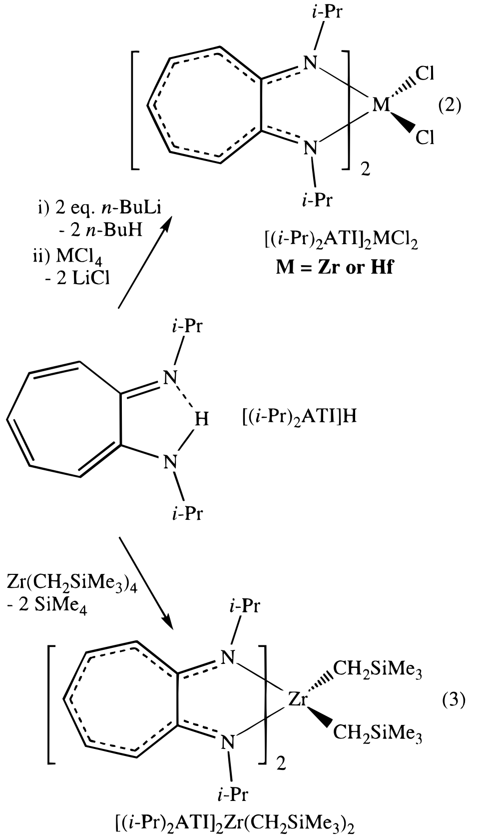
Figure 1. Structure and atom-numbering scheme for [(*i*-Pr)$_2$ATI]Li(THF)$_2$ with hydrogens omitted for clarity (thermal ellipsoids at 30% level).

elemental analysis. The room-temperature NMR spectroscopic data suggest that the molecule is very symmetric in solution. In the ^{1}H NMR spectrum, the signal of the isopropyl C*H* (δ 4.03) has shifted upfield relative to that of the parent ligand [(*i*-Pr)$_2$ATI]H (δ 3.60).[59] The two sets of multiplets at δ 1.29 and 3.39 can be assigned to the tetrahydrofuran hydrogens. It is possible to compare these with the chemical shift values of δ 1.43 and 3.57 for free THF in C_6D_6. The addition of free THF to [(*i*-Pr)$_2$ATI]Li(THF)$_2$ did not lead to an average THF signal. This suggests a fairly strong coordination of THF ligands to the lithium ion. The carbon atoms of the seven-membered ring display four well-separated singlets in the ^{13}C NMR spectrum. The ^{13}C NMR signals due to C(2,8) appear at about 12 ppm downfield from the corresponding carbons in the free ligand (δ 152.0).[59] A similar trend was observed when the amino hydrogen was replaced by the AlH_2 or $AlMe_2$ moiety.[59] For example, the C(2,8) chemical shifts for [(*i*-Pr)$_2$ATI]AlH$_2$ and [(*i*-Pr)$_2$ATI]AlMe$_2$ are 161.5 and 161.1 ppm, respectively.

The identity of [(*i*-Pr)$_2$ATI]Li(THF)$_2$ was confirmed by X-ray crystallography. The ORTEP diagram[63] of [(*i*-Pr)$_2$ATI]Li(THF)$_2$ is shown in Figure 1. To our knowledge, [(*i*-Pr)$_2$ATI]Li(THF)$_2$ represents the first structurally characterized alkali metal salt of an aminotroponiminate. The molecular structure consisted of a lithium atom chelated by the aminotroponiminate ligand (forming a five-membered LiN_2C_2 ring) and coordinated to two tetrahydrofuran molecules. The metal center adopts a distorted tetrahedral geometry with an O−Li−O angle of 102.9(3)° and an N−Li−N angle of 81.5(2)°. The Li−N and Li−O bond lengths of [(*i*-Pr)$_2$ATI]Li(THF)$_2$ are 1.995(6), 1.990(6) Å and 1.971(6), 1.960(6) Å, respectively. These and the C_{ring}−N bond distances (1.313(4) and 1.319(4) Å) show a fairly symmetric structure (closer to a C_2 axis of symmetry along Li···C(5)). The N−C_{ring} distances are shorter than the average 1.34 Å distance found in the aluminum derivatives [(*i*-Pr)$_2$ATI]AlH$_2$ and [(*i*-Pr)$_2$ATI]AlMe$_2$ or the amine N−C_{ring} distance 1.342(3) Å in the free ligand [(*i*-Pr)$_2$ATI]H.[59] They are in fact much closer to the imine N=C_{ring} distance (1.314(3) Å) in [(*i*-Pr)$_2$ATI]H. [(*i*-Pr)$_2$ATI]Li(THF)$_2$ exhibits a twisted configuration for the LiN_2C_7 moiety with a dihedral angle of 16.9° between the LiN_2C_2 ring and the seven-membered ring. Interestingly, the aluminum derivative [(*i*-Pr)$_2$ATI]AlMe$_2$ (or [(*i*-Pr)$_2$ATI]AlH$_2$) features a planar heterobicyclic AlN_2C_7 ring system.

The lithium adduct [(*i*-Pr)$_2$ATI]Li(THF)$_2$ which has a five-membered LiN_2C_2 core shows a monomeric structure in the solid state. In contrast, the amidinate [MeC$_6$H$_4$C(NSiMe$_3$)$_2$Li(THF)]$_2$, which features a 4-membered LiN_2C core, and β-diketinimate {Li[N(SiMe$_3$)C(Ph)CHC(Ph)N(SiMe$_3$)]}$_2$, which has a six-membered LiN_2C_3 chelate ring, show dimeric structures in the solid state.[64,65] The Li−N distances of [(*i*-Pr)$_2$ATI]Li(THF)$_2$ (1.995(6), 1.990(6) Å) can be compared to the corresponding values in the lithium complexes of various chelating nitrogen-based ligands with a conjugated ligand backbone. For example, Li−N bond lengths in the 3-coordinate lithium complex {Li[N(SiMe$_3$)C(Ph)CHC(Ph)N(SiMe$_3$)]}$_2$ are 1.952(10) and 1.965(9) Å,[65] those in [(4-Me-C$_6$H$_4$)NC(N(Me)Ph)C(N(Me)Ph)N(4-Me-C$_6$H$_4$)]Li$_2$(Et$_2$O)$_3$, which has both 3-coordinate and 4-coordinate Li ions, are 2.018(8), 2.161(9), 2.091(9), and 1.948(9) Å,[66] those in the 4-coordinate lithium adduct [N(4-MeC$_6$H$_4$)C(Ph)C(Ph)N(4-MeC$_6$H$_4$)]Li$_2$(THF)$_4$ are 2.18 and 1.97 Å,[67] and those in (Me$_4$taen)Li$_2$(THF)$_2$, which has a 5-coordinate lithium center, are 2.01 and 2.42 (average) Å.[42]

Zirconium and Hafnium Complexes. The zirconium and hafnium compounds [(*i*-Pr)$_2$ATI]$_2$ZrCl$_2$ and [(*i*-Pr)$_2$ATI]$_2$HfCl$_2$ were prepared in diethyl ether by the treatment of [(*i*-Pr)$_2$ATI]H with *n*-BuLi, followed by the reaction with the corresponding metal(IV) chloride, as illustrated in eq 2. Both adducts have relatively high melting points (over 210 °C). They show similar ^{1}H and ^{13}C NMR spectra, with only minor differences in the chemical shift values, suggesting closely related structures. The ^{13}C NMR spectra clearly indicate the presence of the fairly



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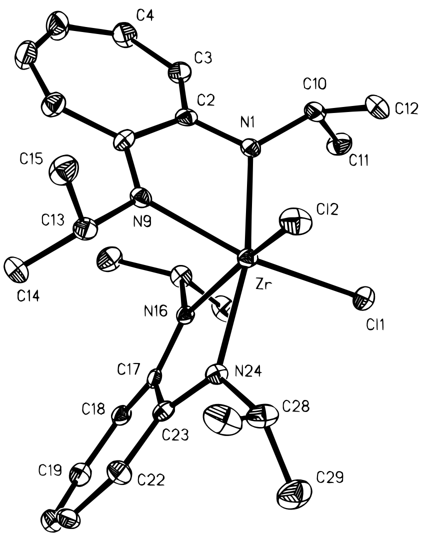

Figure 2. Structure and atom-numbering scheme for $[(i\text{-Pr})_2\text{ATI}]_2\text{ZrCl}_2$ with hydrogens omitted for clarity (thermal ellipsoids at 30% level).

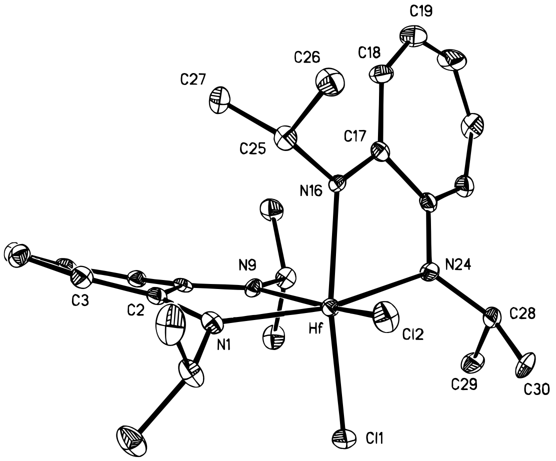

Figure 3. Structure and atom-numbering scheme for $[(i\text{-Pr})_2\text{ATI}]_2\text{HfCl}_2$ with hydrogens omitted for clarity (thermal ellipsoids at 30% level).

symmetric species in solution. The ^{1}H NMR signals of the isopropyl C*H* for $[(i\text{-Pr})_2\text{ATI}]_2\text{ZrCl}_2$ and $[(i\text{-Pr})_2\text{ATI}]_2\text{HfCl}_2$ appear as broad singlets (around δ 4.7) and show a downfield shift relative to the 3.60 ppm of $[(i\text{-Pr})_2\text{ATI}]\text{H}$. The carbon atoms of the seven-membered ring display four well-separated singlets in the ^{13}C NMR spectrum. The ^{13}C NMR resonances of C(2,8) in zirconium and hafnium adducts (δ 164.8 and 165.3) appear at a relatively downfield region compared to that of the corresponding signal for the free ligand $[(i\text{-Pr})_2\text{ATI}]\text{H}$ (δ 152.0).[59]

Synthesis of the dialkyl derivative $[(i\text{-Pr})_2\text{ATI}]_2\text{Zr}(\text{CH}_2\text{SiMe}_3)_2$ was achieved by treating $\text{Zr}(\text{CH}_2\text{SiMe}_3)_4$ with 2 equiv of the free ligand $[(i\text{-Pr})_2\text{ATI}]\text{H}$ (eq 3). This species was characterized by NMR spectroscopy and elemental analysis. Compared to that of the dichloro analog, the ^{1}H NMR resonance of the isopropyl C*H* of $[(i\text{-Pr})_2\text{ATI}]_2\text{Zr}(\text{CH}_2\text{SiMe}_3)_2$ appears at a slightly upfield position. The molecule appears to be fairly symmetric as, for example, indicated from the ^{13}C NMR spectrum. The Zr*CH*$_2$ protons and carbons appear at -1.54 and 4.3 ppm in the ^{1}H and ^{13}C NMR spectra, respectively.

We were able to obtain X-ray-quality crystals of $[(i\text{-Pr})_2\text{ATI}]_2\text{ZrCl}_2$ and $[(i\text{-Pr})_2\text{ATI}]_2\text{HfCl}_2$ from toluene at -25 °C. They were identified by single-crystal X-ray diffraction. The ORTEP diagrams[63] of $[(i\text{-Pr})_2\text{ATI}]_2\text{ZrCl}_2$ and $[(i\text{-Pr})_2\text{ATI}]_2\text{HfCl}_2$ are shown in Figures 2 and 3, respectively. The Zr and Hf complexes have very similar cell dimensions and structures. Such close similarities between the zirconium and hafnium species have been observed previously.[11,68,69] The 6-coordinate Zr and Hf centers adopt a distorted octahedral geometry. The chloride ligands occupy *cis* coordination sites. The *cis* arrangement of the halides also seems to be the preferred geometry in 6-coordinate dichlorozirconium and -hafnium complexes derived from amidinate.[25,26,70] An example of the *trans* structure was found in $\text{MCl}_2[\text{N}(\text{SiMe}_2\text{CH}_2\text{PMe}_2)_2]_2$ (M = Zr, Hf), which contains a hard−soft mixed-ligand system. [24] The heterobicyclic MN_2C_7 ring system in $[(i\text{-Pr})_2\text{ATI}]_2\text{MCl}_2$ (M = Zr, Hf) shows a notable deviation from planar structure with dihedral angles between the five-membered MN_2C_2 ring and the seven-membered ring of 9.2 and 12.8° for Zr and 9.4 and 13.0° for Hf.

In $[(i\text{-Pr})_2\text{ATI}]_2\text{ZrCl}_2$, one of the four isopropyl groups shows an orientation in which methyl groups point toward the metal center and the methyl groups of remaining three isopropyl groups point away from metal center. The ring N−Zr−N angles are 69.8(2) and 69.9(2)°. They are more acute than the angles found in $[(i\text{-Pr})_2\text{ATI}]\text{Li}(\text{THF})_2$ (81.5(2)°) and $[(i\text{-Pr})_2\text{ATI}]\text{AlH}_2$ (83.3(1)°),[59] perhaps as a consequence of the increased atomic radius of the metal ion. The ring N−Zr−N angles can be compared to the corresponding angles in the four-membered ZrN_2C ring of $[\text{C}_6\text{H}_5\text{C}(\text{NSiMe}_3)_2]_2\text{ZrCl}_2$ (61.4(2)°)[25] and five-membered ZrN_2C_2 ring of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}[\text{PhNC(Ph)C(Ph)NPh}]$ (79.7(2)°).[34] The Zr−N distances in $[(i\text{-Pr})_2\text{ATI}]_2\text{ZrCl}_2$ are 2.239(2), 2.232(5), 2.203(5), and 2.208(5) Å. These bond distances are similar to the corresponding bond distances observed in π-electron delocalized zirconium dichloride complexes such as $[\text{C}_6\text{H}_5\text{C}(\text{NSiMe}_3)_2]_2\text{ZrCl}_2$ (2.238(5), 2.204(5) Å)[25] and $(\text{OEP})\text{ZrCl}_2$ (average 2.221 Å)[37] but longer than those found in $[(\eta^1\text{-NCMe}_3)\text{SiMe}_2\text{CH}_2(\eta^5\text{-C}_{13}\text{H}_8)]\text{ZrCl}_2$ (2.060(3) Å)[11] or $(\text{Me}_4\text{taen})\text{ZrCl}_2$ (2.156(3), 2.171(3) Å).[42]

The Zr−Cl distances of $[(i\text{-Pr})_2\text{ATI}]_2\text{ZrCl}_2$ (2.459(2), 2.452(2) Å) are somewhat similar to the corresponding bond lengths found in zirconocene dichloride, $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$ (average 2.44 Å),[71] but longer than those of amidinates such as $[\text{C}_6\text{H}_5\text{C}(\text{NSiMe}_3)_2]_2\text{ZrCl}_2$ (2.4002(9) Å).[26] They can also be compared to the Zr−Cl distances in N_4-macrocyclic complexes $(\text{Me}_4\text{taa})\text{ZrCl}_2$ (2.490(2), 2.493(2) Å),[43] $(\text{Me}_4\text{taen})\text{ZrCl}_2$ (2.503(1) Å),[42] and $(\text{OEP})\text{ZrCl}_2$ (2.459(1), 2.473(1) Å).[37] The Cl−Zr−Cl angle of 98.8(1)° is slightly greater than that of $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$ (97.1(2)°).[71] The benzamidinate $[\text{C}_6\text{H}_5\text{C}(\text{NSiMe}_3)_2]_2\text{ZrCl}_2$ shows a much wider angle (103.38(7)°).[26] The C_{ring}−N bond lengths of $[(i\text{-Pr})_2\text{ATI}]_2\text{ZrCl}_2$ (average 1.343 Å) can be contrasted to 1.313(4) and 1.319(4) Å in $[(i\text{-Pr})_2\text{ATI}]\text{Li}(\text{THF})_2$, 1.337(2) Å in $[(i\text{-Pr})_2\text{ATI}]_2\text{AlMe}_2$, or 1.327 Å (average) in $[(i\text{-Pr})_2\text{ATI}]_2\text{SnMe}_2$.[59,72]

Structural features of $[(i\text{-Pr})_2\text{ATI}]_2\text{HfCl}_2$ are in general very similar to those of the zirconium analog $[(i\text{-Pr})_2\text{ATI}]_2\text{ZrCl}_2$. However, bond distances involving Hf are slightly shorter than the corresponding values in the zirconium complex (e.g., average Hf−N = 2.197 Å and average Zr−N = 2.220 Å). The Hf−N bond distances of $[(i\text{-Pr})_2\text{ATI}]_2\text{HfCl}_2$ are much longer than the distances found in $(\eta^5\text{-C}_5\text{Me}_5)\text{HfCl}[\text{NH}(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)]_3$ (2.041(4), 2.048(4) and 2.065(3) Å),[73] $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{HfCl}$ (2.040(10)

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Å),[74] or $[(Me_2PCH_2SiMe_2)_2N]HfCl_3$ (2.104(7) Å).[75] The Hf-Cl bond lengths (2.431(2), 2.430(2) Å) can be compared to the distances found in $(CH_2)_3(\eta^5\text{-}C_5H_4)_2HfCl_2$ (2.417(3), 2.429(2) Å),[76] $[(Me_3Si)_2N]_3HfCl$ (2.436(5) Å),[74] and $(\eta^5\text{-}C_5H_5)[C_6H_5C(NSiMe_3)_2]HfCl_2$ (2.399(2) Å).[30] The Cl−Hf−Cl angle of 98.0(1)° is only slightly larger than that of the $(CH_2)_3(\eta^5\text{-}C_5H_4)_2HfCl_2$ (95.87(8)°).[76]

The relatively simple NMR spectra of $[(i\text{-Pr})_2ATI]_2ZrCl_2$ and $[(i\text{-Pr})_2ATI]_2HfCl_2$ suggest that they have stereochemically nonrigid structures in solution. The solid state structure, if retained in solution, should lead to diastereotopic pairs of ligand signals and a more complex NMR spectrum. The main group 4 complex *cis*-$[(i\text{-Pr})_2ATI]_2SnMe_2$ shows such behavior.[72] However, fluxional behavior is very common in Zr and Hf chemistry.[77] For example, related species such as *cis*-$[C_6H_5C(NSiMe_3)_2]_2ZrCl_2$, *cis*-$[C_6H_5C(NSiMe_3)_2]_2ZrMe_2$, or *cis*-$(acac)_2ZrCl_2$ are highly fluxional in solution, leading to the equivalence of diastereotopic pairs of ligand signals.[26,78]

Summary and Conclusion

We have reported the syntheses and structural characterizations of the lithium adduct $[(i\text{-Pr})_2ATI]Li(THF)_2$ and the zirconium and hafnium complexes $[(i\text{-Pr})_2ATI]_2ZrCl_2$, $[(i\text{-Pr})_2ATI]_2Zr(CH_2SiMe_3)_2$, and $[(i\text{-Pr})_2ATI]_2HfCl_2$ containing the *N*-isopropyl-2-(isopropylamino)troponiminate ligand. The X-ray crystal structures show the slightly twisted heterobicyclic C_7N_2M ligand framework. The lithium complex adopts a monomeric structure with a pseudotetrahedral lithium center. The Zr and Hf complexes have 6-coordinate metal sites. The chloride ligands of $[(i\text{-Pr})_2ATI]_2ZrCl_2$ and $[(i\text{-Pr})_2ATI]_2HfCl_2$ occupy *cis* positions. The Zr and Hf complexes show fluxional behavior in solution at room temperature. The Zr−Cl distances and Cl−Zr−Cl angle of $[(i\text{-Pr})_2ATI]_2ZrCl_2$ are closer to those observed for $(\eta^5\text{-}C_5H_5)_2ZrCl_2$. The similarities in the above structural parameters are even closer than those found between $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ and amidinates. The amidinate ligands such as $[C_6H_5C(NSiMe_3)_2]^-$ have been noted to have steric properties similar to those of the cyclopentadienyl ligand.[25−27] Furthermore, group 4 metal adducts of amidinates have been useful catalysts for the olefin polymerization. Therefore, it would be interesting to investigate the effects of aminotroponiminate ancillary ligands in such processes and compare them to those of cyclopentadienyls and amidinates. We are currently investigating the reactivity of $[(i\text{-Pr})_2ATI]_2ZrCl_2$ and $[(i\text{-Pr})_2ATI]_2HfCl_2$. We are also exploring the synthesis and chemistry of aminotroponiminates with various other substituents on the nitrogens.

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Supporting Information Available: Tables of crystallographic data, atomic coordinates, anisotropic thermal parameters, and complete bond distances and angles for $[(i\text{-Pr})_2ATI]Li(THF)_2$, $[(i\text{-Pr})_2ATI]_2ZrCl_2$, and $[(i\text{-Pr})_2ATI]_2HfCl_2$ (12 pages). Ordering information is given on any current masthead page.

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