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Structural studies of monocyclopentadienyl titanium and zirconium complexes containing a diisopropylamide ligand. Evidence of a β-agostic interaction in $(C_5H_5)M[N(^iC_3H_7)_2]Cl_2$ ☆

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Abstract

The stoichiometric reaction of $(C_5R_5)MCl_3$ or its THF adduct (R = H, Me; M = Ti, Zr) with one equivalent of $[Li(N(^iC_3H_7)_2)]_n$ in toluene provides a convenient method for the preparation of a series of monocyclopentadienyl Group 4 diisopropylamido complexes $(C_5R_5)M[N(^iC_3H_7)_2]Cl_2$. The molecular structures of these four mononuclear, 14-electron complexes are characterized by a pseudotetrahedral geometry with the M–N bond distance being consistent with the presence of a double bond. The stereoelectronic influence of the replacement of the C_5H_5 ring in $(C_5H_5)M[N(^iC_3H_7)_2]Cl_2$ (M = Ti(**1**), Zr(**3**)) by the stronger π-donating and bulkier C_5Me_5 ring in $(C_5Me_5)M[N(^iC_3H_7)_2]Cl_2$ (M = Ti(**2**), Zr(**4**)) is evidenced by a 10–15° increase in the Cp(c)–M–N angle and by the loss of the β-agostic interaction observed for the methine C–H bond of an isopropyl group in **1** and **3**. A comparison of the structural parameters about the electrophilic metal center of **1–4** with those of related bent metallocenes is consistent with the diisopropylamido ligand being a poorer π-donor than either the C_5H_5 or C_5Me_5 ring.

Keywords: Titanium; Zirconium; Diisopropylamide ligands

1. Introduction

Electron deficient Group 4 metallocene complexes have played a prominent role in the development of alternative catalyst systems for Ziegler–Natta olefin polymerization [1]. With the discovery of methylalumoxane [2] as an alternative co-catalyst to traditional alkyl aluminum reagents, a new class of two component, highly active metallocene-based olefin polymerization catalysts has emerged. Ewen [3] further reported that chiral catalysts derived from racemic enantiomers of ethylene-bridged bis(indenyl) Group 4 complexes, when activated with a large excess of MAO, provide stereochemical control during the polymerization of propylene. The introduction of a short interannular bridge that maintains a C_2-symmetric molecular geometry enabled Kaminsky, Brintzinger and their co-workers [4] to develop chiral *ansa*-metallocene complexes in the presence of MAO as enantioselective catalysts for α-olefin polymerization. These two component chiral metallocene/MAO-type catalysts have been more recently utilized by Coates and Waymouth [5] for the enantioselective cyclopolymerization of 1,5-hexadienes.

To investigate the influence of the ligand environment on catalyst performance, recent efforts have focused on the incorporation of alternative π-donor ligands that enhance the Lewis acidity and reduce the steric congestion at the electrophilic metal center. Bercaw and his co-workers [6] have demonstrated that the *ansa*-monocyclopentadienyl amido ligand, $[(\eta^5\text{-}C_5Me_4)SiMe_2(N\text{-}^tBu)]^{2-}$, provides a sterically-less demanding dianionic alternative to a pair of linked or unlinked cyclopentadienyl rings. Researchers at Dow Chemical [7] and Exxon [8] have independently demonstrated that the corresponding monocyclopentadienyl amido Group 4 complexes, $[(\eta^5\text{-}C_5R_4)SiR'_2(NR'')]MCl_2$ (M = Ti, Zr, Hf; R = alkyl, R′, R″ = alkyl or aryl) with excess MAO provide attractive catalyst systems for the promotion of ethylene/1-alkene copolymerizations. The high level of catalytic activity displayed by these

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☆ This paper is submitted on the occasion of the 60th birthday of Professor Hans-H. Brintzinger and in recognition of his significant contributions in the development of early transition metal chemistry and its application to olefin polymerization catalysis.

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systems is attributed to the reduction of steric crowding at the d^0 metal center due to the constrained geometry introduced by the short silyl bridge, which produces a significant decrease in the (ring centroid)–M–N angle [9] relative to the typical (ring centroid)–M–(ring centroid) angle of 125–135° in bent metallocenes [10].

In view of these recent developments, we have initiated an effort to prepare a series of monocyclopentadienyl Group 4 metal complexes, in which a cyclopentadienyl ring of the parent metallocene dichloride is replaced by a π-donor ligand that behaves as a less-electron donating, anionic equivalent. One suitable ligand for this purpose is the dialkylamido anion, NR_2^-, which donates a maximum of four electrons and can be prepared from a wide range of secondary amines. The incorporation of the dialkylamido ligand into the coordination sphere is expected to enhance the metal's Lewis acidity and, depending on the size of the substituent R, reduce the steric congestion at the electrophilic metal center relative to that associated with bent metallocenes. In this paper, we report the synthesis and structural characterization of $(C_5R_5)M[N(^iC_3H_7)_2]Cl_2$ (R = H, Me; M = Ti, Zr) and examine the stereoelectronic influence of the type of cyclopentadienyl ring and the metal on the molecular structure of these 14-electron monocyclopentadienyl Group 4 amido complexes.

2. Experimental details

2.1. Reagents

Reagent grade hydrocarbon and ethereal solvents were purified using standard methods [11] and distilled under nitrogen. Na/K alloy was used to dry pentane, toluene, and tetrahydrofuran. These dried solvents were then transferred to storage flasks containing $[(C_5H_5)_2Ti(\mu\text{-}Cl)_2]_2Zn$ [12] and freshly distilled prior to use. Hexamethyldisiloxane was dried over $LiAlH_4$ or CaH_2. Chlorinated solvents such as CH_2Cl_2 and CCl_4 were distilled from P_4O_{10}. The deuterated solvents, C_6H_6-d_6 (Aldrich, 99.5%) and $CHCl_3$-d_1 (Aldrich, 99.8%), were dried over activated 4A molecular sieves prior to use. Starting materials such as $(C_5H_5)TiCl_3$ [13], $(C_5Me_5)TiCl_3$ [14], $Li(C_5Me_5)$ [15], $TiCl_3 \cdot 3THF$ [16], $(C_5H_5)ZrCl_3 \cdot 2THF$ [17], $(C_5Me_5)ZrCl_3$ [18], and $[Li(N(^iC_3H_7)_2)]_n$ [19] were prepared employing literature procedures. $TiCl_3$ (Alfa), $TiCl_4$ (Aldrich), $(C_5H_5)_2TiCl_2$ (Boulder), $ZrCl_4$ (Alfa), ^{n}BuLi (Aldrich, 1.6 M in hexanes), diisopropylamine (Aldrich) and HCl (Matheson) were used without further purification.

2.2. General considerations

All manipulations and reactions were carried out on a double-manifold, high-vacuum line or in a Vacuum Atmospheres glovebox equipped with a HE-493 Dri-Train. Air and moisture sensitive compounds were synthesized using pressure equalizing filter-frits equipped with high vacuum Teflon stopcocks. Nitrogen was purified by passage over reduced BTS catalysts and activated 4A molecular sieves. All glassware was thoroughly oven-dried or flame-dried under vacuum prior to use. NMR sample tubes were sealed under approximately 500 Torr of nitrogen. ^1H and ^{13}C NMR spectra were recorded using a JEOL GX-270 FT-NMR spectrometer operating in the FT mode at 270 MHz (^1H) or 67.5 MHz (^{13}C). The ^1H chemical shifts are referenced to the residual proton peaks of benzene-d_6 at δ 7.15 (vs. TMS) or chloroform-d_1 at δ 7.24 (vs. TMS). The ^{13}C resonances are referenced to the central peak of benzene-d_6 at δ 128.0 (vs. TMS) or chloroform-d_1 at δ 77.0 (vs. TMS). Elemental analyses were performed by Robertson Microlit Laboratories of Madison, New Jersey.

2.3. Synthesis of $(C_5R_5)M[N(^iC_3H_7)_2]Cl_2$, R = H, Me; M = Ti, Zr

2.3.1. Preparation of $(C_5H_5)Ti[N(^iC_3H_7)_2]Cl_2$, 1

Stoichiometric amounts of $(C_5H_5)TiCl_3$ (2.000 g, 9.12 mmol) and $[Li(N(^iC_3H_7)_2)]_n$ (0.977 g, 9.12 mmol) were added to a 100 ml pear shaped flask equipped with a 15 mm solv-seal joint. The flask was then attached to a filter frit assembly and evacuated. Toluene (ca. 50 ml) was transferred into the reaction flask and the reaction mixture was stirred overnight at room temperature. The solution was filtered and the solvent slowly removed under vacuo leaving behind a dark orange/brown solid. The product residue was washed with cold pentane several times to remove soluble impurities. The remaining solid was sublimed under vacuum at 80 °C, yielding the desired product, **1**. Orange crystals of **1** for the X-ray structural analysis were then obtained by slow removal of solvent from a saturated pentane solution. ^1H NMR spectrum in $CDCl_3$ (mult., $^2J_{(H-H)}$ in Hz): δ 6.71 (C_5H_5, s), 4.95 ($\mathrm{C}\mathit{H}\mathrm{Me}_2$, m), 1.34 ($\mathrm{CH}\mathit{Me}_2$, d, 6.4) gated non-decoupled ^{13}C NMR spectrum (mult., $^1J_{(C-H)}$ in Hz): δ 117.2 (C_5H_5, d, 177), 53.9 ($\mathit{C}\mathrm{HMe}_2$, d, 131), 22.9 ($\mathrm{CH}\mathit{Me}_2$, q, 127). Anal. Calc. for $C_{11}H_{19}NTiCl_2$: C, 46.51; H, 6.74; N, 4.93. Found: C, 45.49; H, 6.81; N, 4.60.

2.3.2. Preparation of $(C_5Me_5)Ti[N(^iC_3H_7)_2]Cl_2$, 2

A 0.500 g (1.73 mmol) sample of $(C_5Me_5)TiCl_3$ and 0.185 g (1.73 mmol) of $[Li(N(^iC_3H_7)_2)]_n$ were added to a 100 ml pear shaped flask equipped with a 15 mm solv-seal joint. The flask was attached to a filter-frit assembly and evacuated. Toluene (ca. 40 ml) was transferred by vacuum distillation into the reaction vessel, and the reaction mixture was stirred at room temperature overnight. The solvent was removed under vacuo leaving behind a dark red-brown solid. Approximately 40 ml of pentane were added to the reaction flask via vacuum distillation. The solution was stirred at room temperature for two hours and then filtered. The solvent was slowly removed under vacuo leaving behind dark red crystals suitable for X-ray crystallographic analysis. ^{1}H NMR spectrum in C_6D_6 (mult., $^2J_{(H-H)}$ in Hz): δ 3.80 (C*H*Me$_2$, m, 6.4), 2.15 (C_5Me_5, s) 1.32 (CH*Me*$_2$, d, 6.4); gated non-decoupled ^{13}C NMR spectrum (mult., $^1J_{(C-H)}$ in Hz): δ 133.7 (C_5Me$_5$, s), 50.1 (*C*HMe$_2$, d, 136), 23.3 (CH*Me*$_2$, q, 127), 12.9 (C_5Me_5, q, 127).

2.3.3. Preparation of $(C_5H_5)Zr[N(^iC_3H_7)_2]Cl_2$, 3

Equimolar amounts of $(C_5H_5)ZrCl_3 \cdot 2THF$ (0.610 g, 1.50 mmol) and $[Li(N(^iC_3H_7)_2)]_n$ (0.161 g, 1.50 mmol) were weighed into a 100 ml pear shaped flask equipped with a 15 mm solv-seal joint. The flask was attached to a filter-frit assembly and evacuated. Toluene (ca. 50 ml) was added via vacuum distillation to the reaction flask. The reaction mixture was stirred at room temperature overnight. The solution was filtered and the solvent slowly removed under vacuo leaving behind a white crystalline solid. The product residue was washed three additional times with 20 ml portions of cold pentane to extract all of the product, **3**. Recrystallization from toluene yielded white crystals of **3**. ^{1}H NMR spectrum in $CDCl_3$ (mult., $^2J_{(H-H)}$ in Hz): δ 6.67 (C_5H_5, s), 4.05 (C*H*Me$_2$, sept., 6.2), 1.28 (CH*Me*$_2$, d, 6.2); gated non-decoupled ^{13}C NMR spectrum (mult., $^1J_{(C-H)}$ in Hz): δ 114.1 (C_5H_5, d, 175), 49.0 (*C*HMe$_2$, d, 123),

Table 1
Crystallographic data for the X-Ray structural analyses of **1**–**4**

	1	**2**	**3**	**4**
A. Crystal data				
Compound				
Emp. formula	$C_{11}H_{19}Cl_2NTi$	$C_{16}H_{29}Cl_2NTi$	$C_{11}H_{19}Cl_2NZr$	$C_{16}H_{29}Cl_2NZr$
Dimensions (mm)	0.30 × 0.20 × 0.24	0.46 × 0.50 × 0.56	0.14 × 0.16 × 0.32	0.26 × 0.36 × 0.48
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a (Å)	8.0201(12)	8.301(2)	8.1359(9)	8.4004(6)
b (Å)	9.3605(10)	13.299(3)	9.5618(8)	13.3491(10)
c (Å)	9.6466(10)	17.348(4)	9.7833(10)	17.6909(14)
α (°)	73.7260(9)	90	106.154(10)	90
β (°)	80.072(12)	94.80(2)	99.685(11)	95.836(7)
γ (°)	89.580(14)	90	90.103(10)	90
Volume (Å^3)	684.13(14)	1908.4(8)	719.67(14)	1973.4(3)
Z	2	4	2	4
Formula weight (amu)	284.07	354.20	327.39	397.52
Density (g cm^{-3})	1.379	1.233	1.511	1.338
μ (cm^{-1})	9.86	7.21	11.07	8.20
F(000)	296	752	332	824
B. Data collection and structural analyses				
Scan type	ω, variable	ω, fixed	ω, fixed	ω, variable
Scan rate (° min^{-1})	2.0 to 5.0	5.0	10.0	2.0 to 10.0
2θ range (°)	3.0 to 45.0	3.0 to 45.0	3.0 to 50.0	3.0 to 50.0
Refls sampled	$h\ (-1 \le h \le 8)$ $k\ (-9 \le k \le 9)$ $l\ (-10 \le l \le 10)$	$h\ (0 \le h \le 8)$ $k\ (0 \le k \le 14)$ $l\ (-18 \le l \le 18)$	$h\ (0 \le h \le 9)$ $k\ (-10 \le k \le 10)$ $l\ (-11 \le l \le 11)$	$h\ (-1 \le h \le 9)$ $k\ (-1 \le k \le 15)$ $l\ (-21 \le l \le 21)$
No. of refl.	2209	2669	4176	4587
No. of unique data	1758	2471	2494	3455
Agreement factor	$R_{int} = 0.0174$	$R_{int} = 0.0241$	$R_{int} = 0.045$	$R_{int} = 0.0161$
No. of data ($F > 4\sigma(F)$)	1651	2140	2253	3145
Abs. correction	empirical	none	none	empirical
R indices ($F > 4\sigma(F)$)	$R1 = 0.0324$ $wR2 = 0.0668$	$R1 = 0.0660$ $wR2 = 0.1392$	$R1 = 0.0512$ $wR2 = 0.0663$	$R1 = 0.0460$ $wR2 = 0.1184$
R indices for all data	$R1 = 0.0524$ $wR2 = 0.0739$	$R1 = 0.1374$ $wR2 = 0.1755$	$R1 = 0.1032$ $wR2 = 0.0798$	$R1 = 0.0696$ $wR2 = 0.1340$
R index after merging symmetry-related data	$R1 = 0.0445$	$R1 = 0.1076$	$R1 = 0.0836$	$R1 = 0.0597$
σ_1, *GOF*	1.029	1.049	0.997	1.061
Values of a and b	0.0328, 0.025	0.0763, 0.41	0.0234, 0.0	0.0665, 1.93
No. of variables	144	190	144	190
Data to parameter ratio	11.5 : 1	11.3 : 1	15.6 : 1	16.6 : 1
Largest diff peak and hole	0.245, −0.157	0.348, −0.300	0.380, −0.396	0.527, −0.312

24.2 (CHMe_2, q, 127). Anal. Calc. for $C_{11}H_{19}NZrCl_2$: C, 40.10; H, 6.18; N, 4.27. Found: C, 40.35; H, 6.18; N, 4.08.

2.3.4. *Preparation of $(C_5Me_5)Zr[N(^iC_3H_7)_2]Cl_2$, 4*

Into a 100 ml pear shaped flask equipped with a 15 mm solv-seal joint, 0.499g (1.50 mmol) sample of $(C_5Me_5)ZrCl_3$ and 0.161 g (1.50 mmol) of $[Li(N(^iC_3H_7)_2)]_n$ were weighed. After attaching the flask to a filter-frit assembly and evacuating, 40 ml of toluene was introduced via vacuum distillation. The reaction mixture was stirred at room temperature overnight. The solution was filtered and the solvent slowly removed leaving behind a yellow semi-crystalline residue. The solid was washed three times with 20 ml portions of cold pentane and then sublimed. Recrystallization from pentane provided suitable crystals of **4** for the crystallographic analysis. ^{1}H NMR spectrum in C_6D_6 (mult., $^2J_{(H-H)}$ in Hz): δ 3.23 (CHMe$_2$, sept., 6.2), 1.93 (C_5Me_5, s), 1.14 (CHMe_2, d, 6.2); gated non-decoupled ^{13}C NMR spectrum (mult., $^1J_{(C-H)}$ in Hz): δ 124.4 (C_5Me$_5$, s), 45.7 (CHMe$_2$, d, 127), 24.8 (CHMe_2, q, 126), 12.0 (C$_5Me_5$, q, 126). Anal. Calc. for $C_{16}H_{29}NZrCl_2$: C, 48.34; H, 7.35; N, 3.52. Found: C, 45.27; H, 7.29; N, 2.23. The low C analysis reflects incomplete combustion and is consistent with the formation of zirconium carbide, ZrC.

2.3.5. *X-ray structural analyses of monocyclopentadienyl diisopropylamido complexes of Ti and Zr*

X-ray structure determinations were performed on $(C_5H_5)Ti[N(^iC_3H_7)_2]Cl_2$, **1**, $(C_5Me_5)Ti[N(^iC_3H_7)_2]Cl_2$, **2**, $(C_5H_5)Zr[N(^iC_3H_7)_2]Cl_2$, **3**, and $(C_5Me_5)Zr[N(^iC_3H_7)_2]Cl_2$, **4**. The same general procedure was followed for each X-ray structural analysis. A suitable crystal was sealed in a capillary tube under a nitrogen atmosphere and then optically aligned on the goniostat of a Siemens P4 automated X-ray diffractometer. The unit cell dimensions were initially determined by indexing a set of reflections whose angular coordinates were obtained from a rotation photograph or with the automatic peak search routine provided with XSCANS [20]. The corresponding lattice parameters and orientation matrix for the unit cell were determined from a nonlinear least-squares fit of the orientation angles of at least 20 higher order reflections at 22 °C. The refined lattice parameters and other pertinent crystallographic information are summarized in Table 1.

Intensity data were measured with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) and ω scans. Background counts were measured at the beginning and at the end of each scan with the crystal and counter kept stationary. The intensities of three standard reflections were measured after every 100 reflections. The intensity data were corrected for Lorentz-polarization and crystal decay (when appropriate). An empirical absorption correction was applied based upon PSI scans measured for a minimum of eight reflections with $\chi \approx \pm 90°$ and 2θ ranging from 10° to 45°.

The structure solution in each case was provided by the first E-map calculated on the basis of the phase assignments made by the SHELXTL direct methods structure solution software. The coordinates of all remaining non-hydrogen atoms that were not revealed on the initial E-map were located in subsequent Fourier maps. All hydrogen atoms, with the exception of the agostic methine H atom of **1** and **3**, were idealized with isotropic temperature factors set at 1.2 times that of the adjacent carbon. The initial position for the methine hydrogen atom, H(6A), was resolved in a difference Fourier map and then refined with an isotropic temperature factor. The positions of all the methyl hydrogens were optimized by a rigid rotating group refinement with idealized tetrahedral angles. Full-matrix least-squares refinement, based upon the minimization of $\Sigma w_i |F_0^2 - F_c^2|^2$ with $w_i^{-1} = [\sigma^2(F_0^2) + (aP)^2 + bP]$ where $P = (\mathrm{Max}(F_0^2, 0) + 2F_c^2)/3$, was performed with SHELXL-93 [21] operating on either a Professional Computer Systems 486 66MHz PC or a Silicon Graphics Iris Indigo workstation. The final values of the discrepancy indices are provided in Table 1. Their values were calculated from the expressions $R1 = \Sigma \| F_0 | - | F_c \| / \Sigma | F_0 |$ and $wR2 = [\Sigma(w_i(F_0^2 - F_0^2)^2)/\Sigma(w_i(F_0^2)^2)]^{1/2}$ and the standard deviation of an observation of unit weight σ_1 is equal to $[\Sigma(w_i(F_0^2 - F_c^2)^2)/(n-p)]^{1/2}$, where n is the number of reflections and p is the number of parameters varied during the last refinement cycle.

The refined atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\times 10^3$) for compounds **1**–**4** are summarized in Table 2. Selected interatomic distances and bond angles for these four monocyclopentadienyl Group 4 amido complexes are compared in Table 3.

2.4. *Synthesis and characterization of monocyclopentadienyl Group 4 dialkylamido complexes $(C_5R_5)M[N(^iC_3H_7)_2]Cl_2$, M = Ti, Zr*

A series of monocylopentadienyl Group 4 diisopropylamido complexes $(C_5R_5)M[N(^iC_3H_7)_2]Cl_2$ (R = H, Me; M = Ti, Zr) was prepared by the stoichiometric reaction of $(C_5R_5)MCl_3$ (or its THF adduct) with one equivalent of $[Li(N(^iC_3H_7)_2)]_n$ in toluene Eq. (1). Roesky and his co-workers have employed the analogous synthetic

$$(C_5R_5)MCl_3 + 1/n\big[Li(N(^iC_3H_7)_2)\big]_n \longrightarrow (C_5R_5)M\big[N(^iC_3H_7)_2\big]Cl_2 \qquad (1)$$
$$R = H, Me; M = Ti, Zr$$

strategy to prepare $(C_5R_5)Ti[N(SiMe_3)_2]Cl_2$ (R = H, Me) [22] and $(C_5Me_5)Ti[NH(^tC_4H_9)]Cl_2$ [23]. The cor-

Table 2
Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$Å^2 \times 10^3$] for compounds **1–4**

Atom	x	y	z	U_{eq}
Compound: $(C_5H_5)Ti[N(^iPr)_2]Cl_2$, **1**				
Ti	1792(1)	3130(1)	8246(1)	34(1)
Cl(1)	2178(1)	5632(1)	7102(1)	64(1)
Cl(2)	−1108(1)	2735(1)	8650(1)	55(1)
N	2676(3)	2179(3)	6838(3)	33(1)
C(1)	3365(7)	1545(6)	9808(5)	74(1)
C(2)	4065(5)	2959(7)	9492(5)	79(1)
C(3)	2887(8)	3786(5)	10111(5)	78(1)
C(4)	1477(6)	2857(6)	10778(4)	75(1)
C(5)	1779(7)	1489(5)	10592(4)	71(1)
C(6)	1737(4)	2886(4)	5620(4)	43(1)
C(7)	2890(5)	3824(4)	4252(4)	63(1)
C(8)	617(5)	1763(4)	5300(4)	63(1)
C(9)	3868(4)	1073(3)	6466(4)	39(1)
C(10)	3278(5)	−514(4)	7357(4)	65(1)
C(11)	5678(4)	1433(4)	6517(4)	57(1)
Compound: $(C_5Me_5)Ti[N(^iPr)_2]Cl_2$, **2**				
Ti	743(2)	8793(1)	2208(1)	44(1)
Cl(1)	48(3)	7142(2)	2264(1)	79(1)
Cl(2)	3500(2)	8627(2)	2306(1)	76(1)
N	346(7)	9194(4)	3204(3)	48(2)
C(1)	−1095(12)	9828(7)	1482(4)	62(2)
C(2)	475(16)	10172(7)	1358(5)	87(3)
C(3)	1172(11)	9416(11)	929(6)	90(4)
C(4)	126(13)	8660(7)	815(4)	74(3)
C(5)	−1264(9)	8901(7)	1156(4)	59(2)
C(6)	−2448(15)	10415(9)	1797(5)	159(6)
C(7)	1155(21)	11185(8)	1548(7)	253(11)
C(8)	2825(13)	9492(14)	590(6)	245(10)
C(9)	365(17)	7682(8)	370(5)	179(7)
C(10)	−2793(12)	8279(8)	1111(6)	131(4)
C(11)	−667(12)	8851(7)	3814(5)	91(3)
C(12)	−2366(12)	8754(10)	3526(6)	142(5)
C(13)	−19(13)	7882(7)	4182(5)	114(4)
C(14)	1393(12)	10064(7)	3441(5)	87(3)
C(15)	473(15)	10989(7)	3638(6)	133(5)
C(16)	2719(12)	9790(8)	4062(5)	127(4)
Compound: $(C_5H_5)Zr[N(^iPr)_2]Cl_2$, **3**				
Zr	3260(1)	1864(1)	8267(1)	35(1)
Cl(1)	2760(2)	−712(2)	7150(2)	77(1)
Cl(2)	6258(2)	2263(2)	8683(2)	62(1)
N	2313(5)	2857(4)	6797(4)	35(1)
C(1)	3210(12)	3582(8)	10684(7)	78(2)
C(2)	1638(14)	3496(10)	9918(8)	90(3)
C(3)	976(10)	2136(13)	9673(8)	96(3)
C(4)	2171(14)	1354(8)	10306(8)	84(3)
C(5)	3518(10)	2286(11)	10928(6)	76(2)
C(6)	3241(8)	2134(6)	5606(6)	47(2)
C(7)	2089(8)	1176(6)	4284(6)	73(2)
C(8)	4380(8)	3194(7)	5260(6)	70(2)
C(9)	1141(7)	3939(5)	6424(5)	41(2)
C(10)	1706(8)	5477(5)	7290(6)	69(2)
C(11)	−633(8)	3555(6)	6513(6)	63(2)
Compound: $(C_5Me_5)Zr[N(^iPr)_2]Cl_2$ **4**				
Zr	774(1)	3751(1)	2237(1)	48(1)
Cl(1)	41(2)	2015(1)	2257(1)	91(1)
Cl(2)	3638(2)	3611(1)	2329(1)	84(1)
N	326(5)	4198(3)	3275(2)	56(1)
C(1)	−1137(8)	4806(5)	1446(3)	75(2)
C(2)	408(12)	5175(5)	1333(4)	109(3)
C(3)	1098(7)	4414(9)	917(4)	103(3)
C(4)	50(9)	3655(6)	801(3)	88(2)
C(5)	−1301(7)	3889(5)	1129(3)	70(2)
C(6)	−2487(14)	5383(8)	1758(5)	185(6)
C(7)	1076(22)	6180(7)	1535(7)	310(13)
C(8)	2682(10)	4503(15)	591(6)	279(10)
C(9)	305(17)	2690(8)	371(5)	220(8)
C(10)	−2816(10)	3261(8)	1076(6)	159(4)
C(11)	−688(9)	3880(6)	3849(4)	102(2)
C(12)	−2403(10)	3877(9)	3573(5)	176(6)
C(13)	−171(12)	2891(6)	4213(5)	132(3)
C(14)	1367(9)	5041(5)	3483(4)	97(2)
C(15)	546(14)	5998(6)	3634(5)	144(4)
C(16)	2705(10)	4799(7)	4080(4)	130(3)

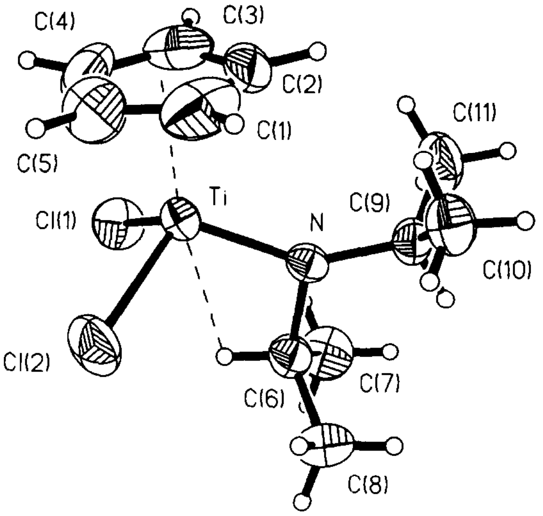

Fig. 1. Perspective view of the molecular structure of $(C_5H_5)Ti[N(^iC_3H_7)_2]Cl_2$, **1**, with the non-hydrogen atom labeling scheme. The thermal ellipsoids are scaled to enclose 50% probability.

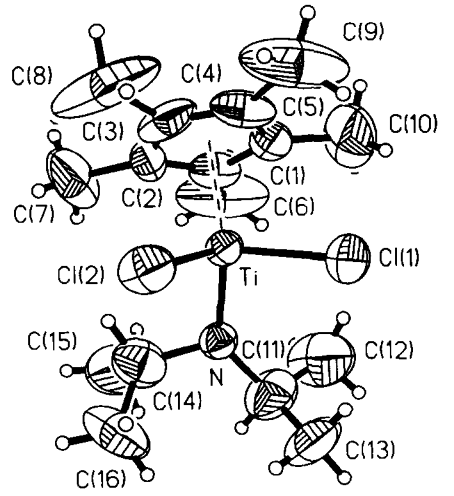

Fig. 2. Perspective view of the molecular structure of $(C_5Me_5)Ti[N(^iC_3H_7)_2]Cl_2$, **2**, with the non-hydrogen atom labeling scheme. The thermal ellipsoids are scaled to enclose 50% probability.

responding metathetical reactions of $(C_5Me_5)TiCl_3$ with one, two and three equivalents of $LiNMe_2$ has been shown by Mena and his co-workers [24] to afford $(C_5Me_5)Ti(NMe_2)_nCl_{3-n}$ ($n = 1, 2, 3$) in excellent yields. The steric bulk of the isopropyl substituents is apparently sufficient to minimize the possibility of dimer formation for the Zr compounds **3** and **4**. In general, the metathetical reactions (1) proceed cleanly and afford **1**–**4** in good yield (60–80%). Complexes **1**–**4** are readily purified by recrystallization or sublimation and have been characterized by ^1H and ^{13}C NMR measurements and elemental analyses. The NMR spectra of **1**–**4** provide no indication of ligand scrambling in solution that would lead to the formation of $(C_5R_5)_2MCl_2$.

The solution NMR spectra of **1**–**4** are relatively simple. The cyclopentadienyl ring proton resonance of **1** and **3** appears at δ 6.71 and 6.67 respectively, whereas the singlet for the methyl proton resonance of the C_5Me_5 ligand in **2** and **4** is located at δ 2.15 and 1.93, respectively. In the gated non-decoupled ^{13}C NMR spectrum of **1** and **3**, the cyclopentadienyl carbon resonance is identified by its characteristic doublet of pseudo-quintets with $^1J_{(C-H)}$ ranging from 175 to 177 Hz. For compounds **2** and **4**, the ^{13}C NMR resonances of the C_5Me_5 ligand consist of a downfield singlet for the internal ring carbons and an upfield binomial quartet with $^1J_{(C-H)} = 127$ Hz for the methyl carbons.

The isopropyl substituents of **1**–**4** exhibit characteristic NMR resonance patterns. In the ^1H NMR spectra the isopropyl groups display an upfield doublet due to the coupling ($^3J_{(H-H)} \sim 6$ Hz) of the six methyl protons with the methine proton and the expected downfield septet for the methine proton. In the gated non-decoupled ^{13}C NMR spectra, the methyl and secondary carbons of each isopropyl substituent appear as a quartet and doublet, respectively. Whereas $^1J_{(C-H)}$ for the chemically-equivalent methyl carbons remains fairly constant, the value of $^1J_{(C-H)}$ for the secondary carbon is 8–9 Hz larger for the Ti compounds, **1** and **2**, compared to the respective Zr congeners, **3** and **4**.

2.5 Description of the molecular structures of monocyclopentadienyl Ti and Zr amido complexes

The molecular structures of the four diisopropylamido compounds, **1**–**4**, were determined by X-ray crystallography. These analyses provide the opportunity to evaluate the effect of the metal and the stereoelectronic influence of the type of cyclopentadienyl ligand on the molecular geometry of these 14-electron complexes. Perspective views of the molecular structures of **1**–**4** are depicted in Figs. 1–4, respectively, with the non-hydrogen labeling scheme. Each compound is mononuclear and is characterized by a pseudotetrahedral geometry with a metal coordination sphere defined by a π-bonded cyclopentadienyl ligand, two chlorides, and the N-donor of the diisopropylamido ligand. The structures are well-behaved except for the apparent librational motion of the C_5Me_5 ring which is characterized by large in-plane thermal displacements for its five methyl carbons in **2** and **4**. Selected interatomic distances and bond angles are summarized in Table 3.

The Ti–N distances of 1.865(2) and 1.865(5) Å in **1** and **2** respectively, and the Zr–N distances of 1.988(4)

Table 3
Selected interatomic distances (Å) and bond angles (deg) for **1**–**4** [a]

	Compound			
	1	**2**	**3**	**4**
A. Interatomic distances (Å)				
M–N	1.865(2)	1.865(5)	1.988(4)	2.003(4)
M–Cp(c)	2.035	2.077	2.191	2.215
M–Cl	2.290(1)	2.274(2)	2.403(2)	2.399(2)
	2.305(1)	2.291(2)	2.416(2)	2.401(2)
M···H(6A)	2.25		2.28	
range M–C(Cp)	2.332(4)–2.357(4)	2.342(7)–2.433(7)	2.471(7)–2.493(6)	2.462(5)–2.555(5)
range C–C	1.356(6)–1.379(6)	1.332(13)–1.414(12)	1.341(9)–1.395(10)	1.345(11)–1.421(10)
B. Bond angles (°)				
Cp(c)–M–N	116.2	129.5	114.5	128.0
Cp(c)–M–Cl	112.3	109.0	111.9	108.3
	111.6	111.7	110.9	111.0
Cl(1)–M–Cl(2)	103.38(4)	99.2(1)	104.92(6)	100.41(7)
M–N–C	146.1(2)	137.0(5)	147.0(3)	137.1(4)
	101.4(2)	109.5(5)	99.6(3)	107.4(4)
C–N–C	112.4(2)	113.5(6)	113.4(6)	115.5(5)
Cp(c)–M···H(6A)	171		169	
range C–C–C	106.9(4)–109.0(4)	105.9(8)–109.1(8)	106.5(5)–109.3(7)	104.7(6)–109.4(6)

[a] Cp(c) denotes the centroid of the corresponding C_5H_5 or C_5Me_5 ring.

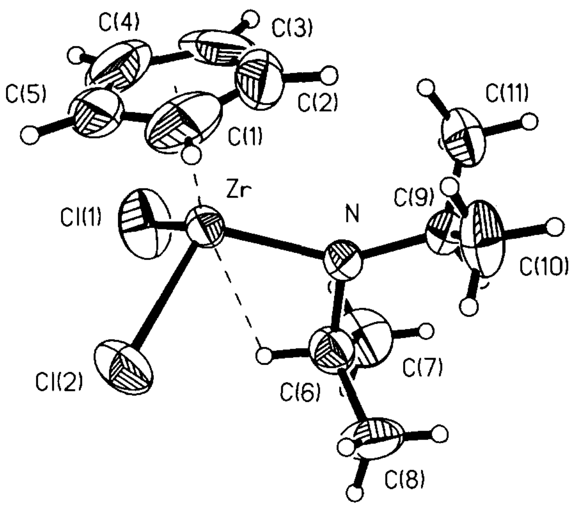

Fig. 3. Perspective view of the molecular structure of $(C_5H_5)Zr[N(^iC_3H_7)_2]Cl_2$, 3, with the non-hydrogen atom labeling scheme. The thermal ellipsoids are scaled to enclose 50% probability.

and 2.003(4) Å in 3 and 4, respectively, are consistent with the presence of a M–N double bond. Using Pauling's covalent radii [25], the estimated values for Ti–N and Zr–N single bonds are 2.02 and 2.15 Å, respectively. In comparison to other mononuclear Ti complexes containing terminal dialkylamido ligands, the Ti–N bonds of 1, 2 are slightly shorter than the Ti–N bond of 1.879(3) Å in $(C_5H_5)Ti[N(SiMe_3)_2]Cl_2$ [22] and are considerably shorter than the average Ti–N bond of 1.940(10) Å in $Ti[N(SiMe_3)_2]_3Cl$ [26] and the two independent Ti–N bonds of 1.912(9), 1.923(14) Å in the tris(dimethylamido) complex, $(C_5Me_5)Ti(NMe_2)_3$ [26]. The Zr–N bonds of 3, 4 are also substantially shorter than their respective averaged distances of 2.070(3) and 2.080(5) Å in $Zr[N(SiMe_3)_2]_3X$ (X = Cl [26], Me [27]). The $N(p_\pi) \rightarrow M(d_\pi)$ bonding interaction associated with a terminal dialkylamido ligand arises from π-donation of the out-of-plane N lone pair and should be accompanied by a nearly trigonal planar geometry at the sp^2 hybridized N atom. Although the individual bond angles about the amido N deviate substantially from 120° in **1–4**, their sum does not provide any evidence of pyramidalization at N.

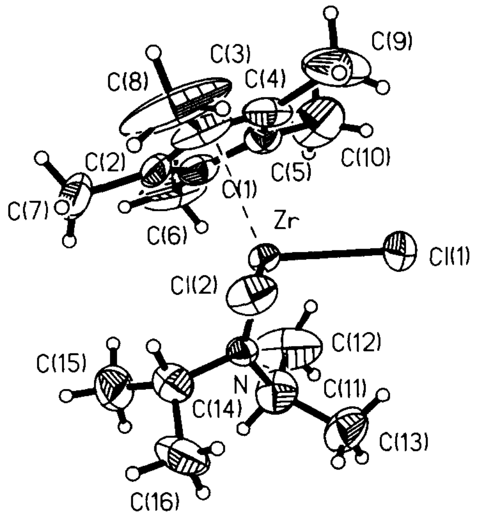

Fig. 4. Perspective view of the molecular structure of $(C_5Me_5)Zr[N(^iC_3H_7)_2]Cl_2$, 4, with the non-hydrogen atom labeling scheme. The thermal ellipsoids are scaled to enclose 50% probability.

The π-donating ability of the diisopropylamido ligand, relative to the cyclopentadienyl or permethylcyclopentadienyl ligand, is reflected by the Cp(c)–M and M–Cl distances. The Cp(c)–Ti distances of 2.035 Å and 2.077 Å in 1 and 2, respectively, are ca. 0.02 Å and 0.05 Å shorter than the Cp(c)–Ti distances of 2.059 Å in $(C_5H_5)_2TiCl_2$ [28] and 2.128 Å in $(C_5Me_5)_2TiCl_2$ [29], respectively. A comparable 0.02 Å reduction in the Cp(c)–Zr distance also accompanies the replacement of a cyclopentadienyl ring in Cp_2ZrCl_2 [30] with the diisopropylamido ligand in 3. Similarly, the Ti–Cl distances of **1** and **2** are 0.06–0.08 Å shorter and the Zr–Cl distances of **3** and **4** are 0.03–0.06 Å shorter than the corresponding M–Cl bond distances reported in related bent metallocene dichlorides [28–31]. The relative decreases in the Cp(c)–Ti and Ti–Cl distances observed for $(C_5R_5)Ti[N(^iC_3H_7)_2]Cl_2$, however, are notably smaller in magnitude those observed for the related monocyclopentadienyl aryloxide compounds $(C_5R_5)Ti[OAr]Cl_2$, in which the Cp(c)–Ti and Ti–Cl distances range from 2.00–2.03 Å and 2.25–2.27 Å, respectively [32,33]. These collective structural results indicate that a diisopropylamido ligand is a stronger π-donor than the aryloxide ligand but a weaker π-donor than either the Cp or Cp* ligand in these monocyclopentadienyl Group 4 complexes. The lower π-donating ability of the diisopropylamido or the aryloxide ligand is compensated by a commensurate decrease in the M–Cl distances, reflecting an enhancement in the effective π-donor strength of the two remaining chloride ligands.

An examination of the angular parameters about the Group 4 metal in $(C_5R_5)M[N(^iC_3H_7)_2]Cl_2$ and $(C_5R_5)_2MCl_2$ complexes also reveals that the diisopropylamido ligand of **1–4** is sterically less-demanding than either the C_5H_5 or C_5Me_5 ligand. The Cp(c)–M–N angles of 116.2° in **1** and 114.5° in **3** are significantly smaller than the Cp(c)–M–Cp(c) angles of 131.0° in Cp_2TiCl_2 [28] and 126.6° in Cp_2ZrCl_2 [30], but are 10–15° larger than the corresponding Cp(c)–M–N bond angles observed for the more open mononuclear ansa-monocyclopentadienyl Group 4 amido complexes, $\{[(\eta^5\text{-}C_5R_4)SiR'_2(NR'')]ML_2\}_n$ (n = 1 or 2) [7]. The replacement of the C_5H_5 ligand with a C_5Me_5 ligand in $(C_5R_5)M[N(^iC_3H_7)_2]Cl_2$ produces a significant increase in the corresponding Cp(c)–M–N bond angle to 129.5° in **2** and to 128.0° in **4**. For each pair of complexes, this increase in the Cp(c)–M–N bond is a consequence of the greater steric bulk of the C_5Me_5 ligand and is accompanied by a modest reduction in the Cl–M–Cl bond angle.

Finally, the solid state structures of $CpTi[N(^iC_3H_7)_2]Cl_2$ and $CpZr[N(^iC_3H_7)_2]Cl_2$ are characterized by a β-agostic interaction involving the methine C–H bond of an isopropyl group. The $M \cdots H(6A)$ distance is ca. 2.25 Å. This interaction places this methine H essentially *trans* to the Cp ligand ($Cp(c) \cdots M \cdots H(6A)$ angle: (171°, **1**; 169°, **3**) and is characterized by a highly unsymmetrical disposition of the isopropyl substituents of the amido ligand. Although this agostic interaction is clearly evident in the crystal structures of **1** and **3**, no additional resonances or a reduced $^1J_{(C-H)}$ coupling constant involving the methine hydrogens are observed in the solution NMR spectra of these compounds. The absence of a similar β-agostic interaction in the corresponding solid state structures of **2** and **4** probably reflects the reduction in Lewis acidity and greater steric congestion arising from the introduction of the stronger π-donating and sterically more demanding C_5Me_5 ligand into the metal coordination sphere.

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Supplementary material available

Tables of interatomic distances, thermal parameters, and hydrogen atom coordinates and structure factor tables for the crystallographic analyses of **1–4** are available from the authors.

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