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Syntheses and X-ray structures of some pyrrolylaldiminate metal complexes

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Abstract

Several pyrrolylaldiminate complexes of Group 1, 4 and 13 metals are reported. The reaction of 5-*tert*-butyl-2-[(2,6-diisopropylphenyl)aldimino]pyrrole (HL) with NaH produced LNa(THF) (**1**). In situ lithiation of HL followed by addition of one equivalent of MCl_x (M = Zr, $x = 4$; M = Hf, $x = 4$, M = Al, $x = 3$) afforded the corresponding pyrrolylaldiminate complexes, $MLCl_2(\mu\text{-}Cl)_2Li(OEt_2)_2$ (M = Zr, **3**; Hf, **4**) and $AlLCl_2$ (**5**). Alkylation of **5** with MeMgBr generated $AlLMe_2$ (**6**). In addition to the spectroscopic data, complexes **3**–**6** were characterized by X-ray crystallography.

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Keywords: Zirconium; Hafnium; Aluminum; Pyrrolylaldiminate

1. Introduction

Metal complexes containing chelating nitrogen ligands with bulky substituents continue to constitute an active area of exploratory research [1]. Extensive studies in this field have primarily focused on the development of well-defined metal complexes as catalysts for olefin polymerization [2–5]. Monoanionic bidentate nitrogen ligands are of current interest, particularly for the low-valent, low-coordinate metal complexes of hard transition and main group elements, from which intriguing structures and reactivity have emerged significantly. Representative examples of such ligands are depicted in Scheme 1 [6–14].

The pyrrolylaldiminate ligands are closely related to the salicylaldiminate ligands, which have evolved in metal complexes that exhibit specific chemical transformations in both stoichiometric and catalytic manner [15,16]. Metal complexes of pyrrolylaldiminate, however, have received much less attention. Several reports recently describe the formation of mono- and bis-chelate complexes of Group 2, 4, 6, 8, 9, 10, 12 and 13 metals [17–24]. Perhaps the most phenomenal examples are the titanium derivatives of the type $[2\text{-}C_4H_3N(CH{=}NR)]_2TiCl_2$ ($R = C_6H_5$, *cyclo*-C_6H_{11}), which lead to cyclic olefin copolymerization in a living fashion [25]. We became interested in a more sterically demanding ligand, 5-*tert*-butyl-2-[(2,6-diisopropylphenyl)-aldimino]pyrrole (HL), for inorganic and organometallic chemistry. The steric properties provided by the *tert*-butyl and isopropyl groups are anticipated to preclude possible side reactions on the pyrrole ring, to offer partial protection to the metal center where possible, and to discourage the formation of bis-chelate complexes. Roesky and co-workers [17] recently described the isolation of aluminum complexes containing L^- [26], but the solid-state structures have not been reported. Herein we present the syntheses of some mono-pyrrolylaldiminate derivatives of Group 1, 4 and

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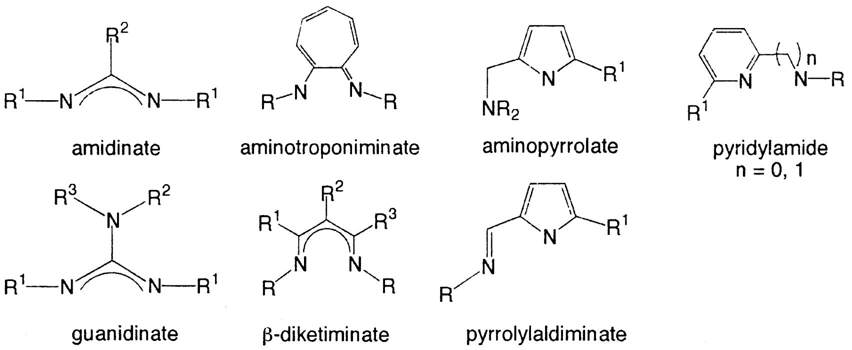


Scheme 1. Representative examples of monoanionic bidentate N-ligands.

13 metals, along with the X-ray structures of Zr, Hf, and Al complexes.

2. Experimental

2.1. General procedures

Unless otherwise specified, all experiments were performed under nitrogen using standard Schlenk or glovebox techniques. All solvents were reagent grade or better and purified by standard methods. Molecular sieves and Celite were activated in vacuo (10^{-3} Torr) for 24 h at 175 and 125 °C, respectively. All NMR solvents were sparged with nitrogen and dried over activated 4 Å molecular sieves for days prior to use. All other chemicals were used as received from commercial vendors. The NMR spectra were recorded on Varian instruments. Chemical shifts (δ) are listed as parts per million downfield from tetramethylsilane and coupling constants (J) are given in hertz. ^{1}H-NMR spectra are referenced using the residual solvent peak at δ 7.16 for C_6D_6, and δ 7.27 for $CDCl_3$. ^{13}C-NMR spectra are referenced using the residual solvent peak at δ 128.39 for C_6D_6, and δ 77.23 for $CDCl_3$. The assignment of the carbon atoms for all new compounds is based on the DEPT ^{13}C-NMR spectroscopy. Routine coupling constants are not listed. All NMR spectra were recorded at room temperature in specified solvents. Elemental analysis was performed on a Heraeus CHN–O rapid analyzer. Because complexes **1**–**6** are all sensitive to air and moisture, satisfactory analysis was hampered for some compounds.

2.2. Synthesis of NaL(THF) (1)

Solid NaH (45 mg, 1.875 mmol, 1.16 equivalents) was suspended in THF (5 ml) and cooled to −35 °C. A solution of HL (500 mg, 1.610 mmol) in THF (8 ml) at −35 °C was added dropwise. Gas evolved upon addition. The reaction mixture was stirred at room temperature overnight. The resulting red solution was passed through a pad of Celite to remove the excess NaH. All volatiles were removed. The reddish brown solid residue was washed with pentane (5 ml) and dried in vacuo to afford the title compound as an off-white solid; yield 625 mg (96%). Colorless crystals may be obtained by recrystallization from diethyl ether. ^{1}H-NMR (C_6D_6, 200 MHz) δ 7.88 (s, 1H, $C\mathit{H}{=}N$), 7.11–7.24 (m, 3H), 7.04 (m, 1H), 6.60 (m, 1H), 3.42 (m, 4H, $OC\mathit{H}_2CH_2$), 3.18 (septet, $J = 8$ Hz, 2H, $C\mathit{H}Me_2$), 1.46 (s, 9H, $C\mathit{Me}_3$), 1.34 (m, 4H, $OCH_2C\mathit{H}_2$), 1.17 (d, $J = 8$ Hz, 12H, $CH\mathit{Me}_2$).

2.3. Synthesis of $ZrLCl_2(\mu\text{-}Cl)_2Li(OEt_2)_2$ (3)

To a diethyl ether solution (5 ml) of HL (200 mg, 0.64 mmol) was added *n*-BuLi (0.40 ml, 1.6M solution in hexanes, 0.64 mmol) at −35 °C. The solution was naturally warmed to room temperature and stirred for 2 h. The solution was cooled to −35 °C again and added to a white suspension of $ZrCl_4$ (150 mg, 0.64 mmol) in diethyl ether (8 ml) at −35 °C with vigorous stirring. The reaction mixture was stirred at room temperature for 20 h and filtered through a pad of Celite, which was further washed with diethyl ether until the washings were colorless. The ether filtrate was concentrated in vacuo and cooled to –35 °C to yield a yellow crystalline solid; yield 160 mg (49%). ^{1}H-NMR (C_6D_6, 200 MHz) δ 7.58 (s, 1H, $C\mathit{H}{=}N$), 6.93–6.99 (m, 3H), 6.70 (d, $J = 3.8$ Hz, 1H, pyrrole CH), 6.25 (d, $J = 3.8$ Hz, 1H, pyrrole CH), 4.06 (septet, $J = 8$ Hz, 2H, $C\mathit{H}Me_2$), 3.35 (q, 8H, $O(C\mathit{H}_2CH_3)_2$), 1.61 (s, 9H, $C\mathit{Me}_3$), 1.53 (d, $J = 8$ Hz, 6H, $CH\mathit{Me}_2$), 1.15 (d, $J = 8$ Hz, 6H, $CH\mathit{Me}_2$), 0.93 (t, 12H, $O(CH_2C\mathit{H}_3)_2$); $^{13}C\{^1H\}$-NMR (C_6D_6, 125 MHz) δ 168.8, 162.0 ($CH{=}N$), 144.8, 134.7, 128.6, 127.9 (CH), 127.7 (CH), 124.3 (CH), 113.3 (CH), 66.7 ($O(\mathit{C}H_2\mathit{C}H_3)_2$), 35.0 ($\mathit{C}Me_3$), 32.6 ($\mathit{C}H_3$), 28.6 ($\mathit{C}HMe_2$), 25.8 ($\mathit{C}H_3$), 24.4 ($\mathit{C}H_3$), 14.7 ($\mathit{C}H_3$). Anal.

Calc. for $C_{29}H_{49}Cl_4LiN_2O_2Zr$: C, 46.95; H, 6.15; N, 4.38. Found: C, 47.02; H, 6.85; N, 4.29%.

2.4. Synthesis of $HfLCl_2(\mu\text{-}Cl)_2Li(OEt_2)_2$ (**4**)

To a diethyl ether solution (5 ml) of HL (200 mg, 0.64 mmol) was added *n*-BuLi (0.40 ml, 1.6 M solution in hexanes, 0.64 mmol) at −35 °C. The solution was naturally warmed to room temperature and stirred for 2 h. The solution was cooled to −35 °C again and added to a white suspension of $HfCl_4$ (206 mg, 0.64 mmol) in diethyl ether (8 ml) at −35 °C with vigorous stirring. The reaction mixture was stirred at room temperature for 20 h and filtered through a pad of Celite, which was further washed with diethyl ether until the washings were colorless. The ether filtrate was concentrated in vacuo and cooled to −35 °C to yield a yellow crystalline solid; yield 403 mg (85%). ^1H-NMR (C_6D_6, 500 MHz) δ 7.72 (s, 1H, C*H*=N), 7.11–7.17 (m, 3H), 6.67 (d, $J = 4$ Hz, 1H, pyrrole CH), 6.30 (d, $J = 4$ Hz, 1H, pyrrole CH), 4.10 (septet, $J = 7$ Hz, 2H, C*H*Me_2), 3.26 (br s, 8H, $O(CH_2CH_3)_2$), 1.66 (s, 9H, CMe_3), 1.49 (d, $J = 7$ Hz, 6H, CH*Me*$_2$), 1.11 (d, $J = 7$ Hz, 6H, CH*Me*$_2$), 0.90 (t, 12H, $O(CH_2CH_3)_2$); $^{13}C\{^1H\}$-NMR (C_6D_6, 125 MHz) δ 169.5, 162.0 (*C*H=N), 144.3, 135.0, 128.7, 127.9 (CH), 127.8 (CH), 124.4 (CH), 113.7 (CH), 66.4 ($O(CH_2CH_3)_2$), 35.0 (*C*Me_3), 32.6 (*C*H_3), 28.6 (*C*HMe_2), 26.0 (*C*H_3), 24.5 (*C*H_3), 14.9 (*C*H_3).

2.5. Synthesis of $AlLCl_2$ (**5**)

To a toluene solution (17 ml) of HL (2.0 g, 6.44 mmol) was added *n*-BuLi (4.03 ml, 1.6 M solution in hexanes, 6.44 mmol) at −35 °C. The solution was naturally warmed to room temperature and stirred for 2 h. The solution was cooled to −35 °C again and added to a white suspension of $AlCl_3$ (0.859 g, 6.44 mmol) in toluene (13 ml) at −35 °C. The reaction mixture was stirred at room temperature for 36 h and filtered through a pad of Celite, which was further washed with toluene until the washings were colorless. The toluene filtrate was concentrated in vacuo and cooled to −35 °C to yield a red crystalline solid; yield 2.31 g (3 crops, 88%). ^1H-NMR (C_6D_6, 200 MHz) δ 7.28 (s, 1H, CH=N), 7.03–7.15 (m, 3H), 6.62 (d, $J = 4.4$ Hz, 1H, pyrrole CH), 6.21 (d, $J = 4.4$ Hz, 1H, pyrrole CH), 3.43 (septet, $J = 8$ Hz, 2H, C*H*Me_2), 1.37 (s, 9H, C*Me*$_3$), 1.30 (d, $J = 8$ Hz, 6H, CH*Me*$_2$), 0.91 (d, $J = 8$ Hz, 6H, CH*Me*$_2$). $^{13}C\{^1H\}$-NMR (C_6D_6, 75 MHz) δ 167.5 (C_{Aryl}), 161.2 (*C*H = N), 144.8 (C_{Aryl}), 138.9 (C_{Aryl}), 134.1 (C_{Aryl}), 129.0 (C_{Aryl}), 126.9 (C_{Aryl}), 125.0 (C_{Aryl}), 115.4 (C_{Aryl}), 34.4 (*C*Me_3), 31.3 (C*Me*$_3$), 29.1 (*C*HMe_2), 26.2 (CH*Me*$_2$), 23.9 (CH*Me*$_2$). Anal. Calc. for $C_{21}H_{29}AlCl_2N_2$: C, 61.92; H, 7.18; N, 6.88. Found: C, 59.70; H, 7.97; N, 6.32%.

2.6. Synthesis of $AlLMe_2$ (**6**)

To a diethyl ether solution (6 ml) of $AlLCl_2$ (200 mg, 0.49 mmol) was added MeMgBr (0.33 ml, 3 M solution in Et_2O, 0.99 mmol, 2 equivalents) at −35 °C. The reaction mixture was naturally warmed to room temperature and stirred for 24 h. Diethyl ether was removed in vacuo. The solid residue was extracted with pentane (7 ml). The pentane extract was filtered through a pad of Celite. Pentane was removed in vacuo to yield a pale yellow crystalline solid; yield 143 mg (80%). Recrystallization from a concentrated Et_2O solution at −35 °C gave X-ray quality crystals. ^1H-NMR (C_6D_6, 500 MHz) δ 7.46 (s, 1H, CH = N), 7.12 (m, 1H), 7.07 (m, 2H), 6.80 (d, $J = 3.6$ Hz, 1H, pyrrole CH), 6.36 (d, $J = 3.6$ Hz, 1H, pyrrole CH), 3.22 (septet, $J = 6.5$ Hz, 2H, C*H*Me_2), 1.37 (s, 9H, C*Me*$_3$), 1.22 (d, $J = 6.5$ Hz, 6H, CH*Me*$_2$), 0.93 (d, $J = 6.5$ Hz, 6H, CH*Me*$_2$), −0.22 (s, 6H, AlMe). $^{13}C\{^1H\}$-NMR (C_6D_6, 125 MHz) δ 164.1 (C_{Aryl}), 159.8 (*C*H=N), 144.2 (C_{Aryl}), 141.4 (C_{Aryl}), 135.2 (C_{Aryl}), 128.1 (C_{Aryl}), 124.6 (C_{Aryl}), 123.4 (C_{Aryl}), 113.2 (C_{Aryl}), 34.1 (*C*Me_3), 31.4 (C*Me*$_3$), 28.6 (*C*HMe_2), 26.4 (CH*Me*$_2$), 23.5 (CH*Me*$_2$), −8.0 (br, Al*Me*).

2.7. X-ray crystallographic studies

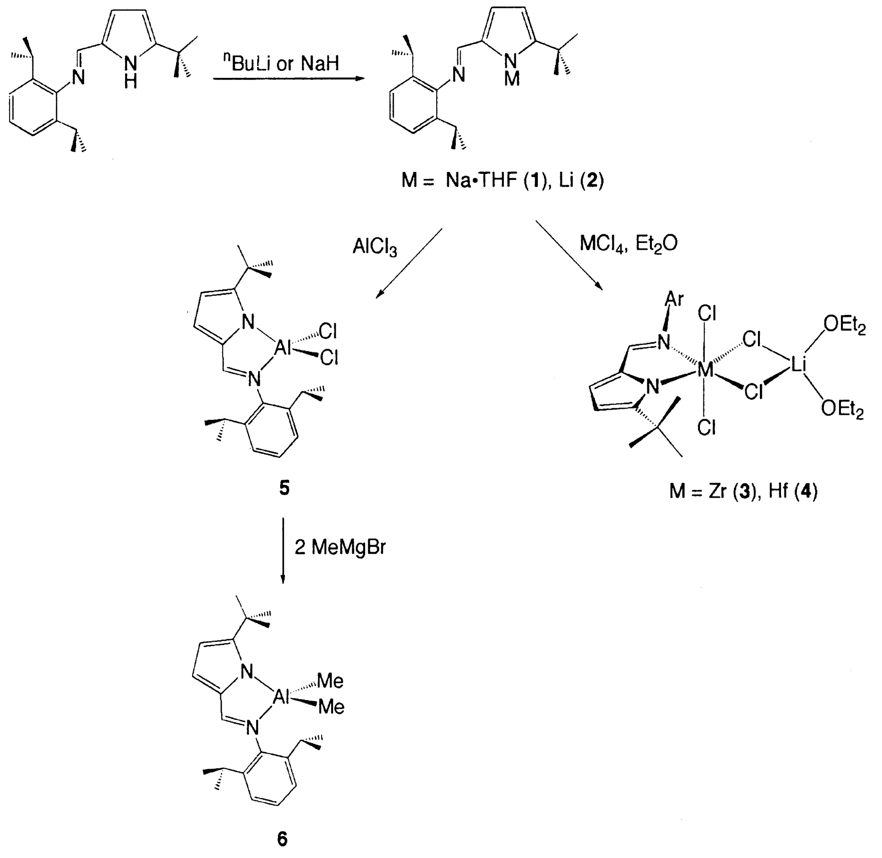
Table 1 summarizes the crystallographic data for all structurally characterized compounds. Data for compounds **3** and **4** were collected on a Bruker SMART 1000 CCD diffractometer with graphite monochromated Mo–K_α radiation ($\lambda = 0.7107$ Å). Structures were solved by direct methods and refined by full matrix least squares procedures against F^2 using SHELXTL. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions. Data for compounds **5** and **6** were collected using Mo–K_α radiation ($\lambda = 0.71069$ Å) on a Rigaku AFC7S diffractometer. Structures were solved by direct methods and refined by full-matrix least-squares procedures against F using TEXSAN. All no*n*-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions. In **5** the isopropylmethyl groups are disordered in the ratio 50:25:25 over three conformations.

3. Results and discussion

The ligand HL was readily prepared by a standard condensation method from the reaction of 2,6-diisopropylaniline with 5-*tert*-butylpyrrole-2-carbaldehyde [20,27]. Deprotonation of HL proceeds cleanly with alkali metal alkyl or hydride, affording the corresponding metal derivatives. For instance, addition of a solution of HL in THF to NaH suspended in THF at −35 °C afforded LNa(THF) (**1**, Scheme 2) quantita-

Table 1
Crystallographic data for compounds **3–6**

	3	**4**	**5**	**6**
Formula	$C_{29}H_{49}Cl_4LiN_2O_2Zr$	$C_{29}H_{49}Cl_4LiN_2O_2Hf$	$C_{21}H_{29}AlCl_2N_2$	$C_{23}H_{35}AlN_2$
M	697.66	784.93	407.36	366.52
Crystal size (mm^3)	0.52 × 0.30 × 0.08	0.38 × 0.28 × 0.14	0.4 × 0.4 × 0.8	0.4 × 0.6 × 0.8
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
Unit cell dimensions				
a (Å)	10.874(2)	10.8405(7)	10.218(2)	16.166(2)
b (Å)	14.363(3)	14.3285(9)	18.428(2)	16.422(2)
c (Å)	23.036(5)	23.0097(15)	13.044(2)	8.760(2)
γ (°)	93.56(3)	93.4160(10)	108.04(2)	90.0
V (Å^3)	3590.9(13)	3567.7(4)	2335.3(7)	2325.4(7)
Z	4	4	4	4
D_{calc} (g cm^{-3})	1.159	1.461	1.159	1.047
$2\theta_{max}$ (°)	55.04	55.04	52.0	52.0
T (K)	150(2)	150(2)	298(2)	298(2)
Diffractometer	Bruker SMART 1000 CCD	Bruker SMART 1000 CCD	Rigaku AFC7S	Rigaku AFC7S
Total reflections	22256	12665	5015	2625
Independent reflections	8177	7786	4747	2625
T_{max}, T_{min}	0.9486, 0.6712	0.9486, 0.7683	1.0000, 0.9787	1.0000, 0.9784
Absorption coefficient/mm^{-1}	0.630	3.249	3.22	0.95
R_{int}	0.0596	0.0383	0.030	
Goodness-of-fit	0.815	1.006	1.68	1.60
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0408$, $wR_2 = 0.0581$	$R_1 = 0.0325$, $wR_2 = 0.0657$	$R_1 = 0.0506$, $wR_2 = 0.0749$	$R_1 = 0.0407$, $wR_2 = 0.0529$
R indices (all data)	$R_1 = 0.0949$, $wR_2 = 0.0640$	$R_1 = 0.0639$, $wR_2 = 0.1047$	$R_1 = 0.1444$, $wR_2 = 0.0947$	$R_1 = 0.1390$, $wR_2 = 0.0688$



Scheme 2.

tively as colorless crystals. The reaction of HL with *n*-BuLi gave what we formulated as LiL (**2**), which proved to be a useful starting material for metathesis reactions with metal chlorides.

Treatment of one equivalent of **2** to $ZrCl_4$ suspended in Et_2O at −35 °C led to the formation of large yellow crystals after standard work-up. An X-ray study of a single crystal showed it to be an 'ate' complex $ZrLCl_2(\mu\text{-}Cl)_2Li(OEt_2)_2$ (**3**). The hafnium analogue, $HfLCl_2(\mu\text{-}Cl)_2Li(OEt_2)_2$ (**4**), was synthesized accordingly and structurally characterized. Attempts to prepare the bis-pyrrolylaldiminate complexes of Zr and Hf were not successful, likely as a reflection of the steric size of the ligand. This result is consistent with those reported by Bochmann et al. that the less sterically demanding pyrrolylaldiminate ligand $[2\text{-}C_4H_3N(CH{=}NC_6H_3{}^iPr_2)]^-$ forms bis-chelate complexes of Zr [20] and those reported by Fujita et al. [18] that Ti complexes readily adopt two $[2\text{-}C_4H_3N(CH{=}NC_6H_5)]^-$ ligands that are sterically much smaller. The reaction of **2** (one or two equivalents) with $TiCl_4$ under the condition similar to those for **3** and **4** led to intractable materials that cannot be identified so far.

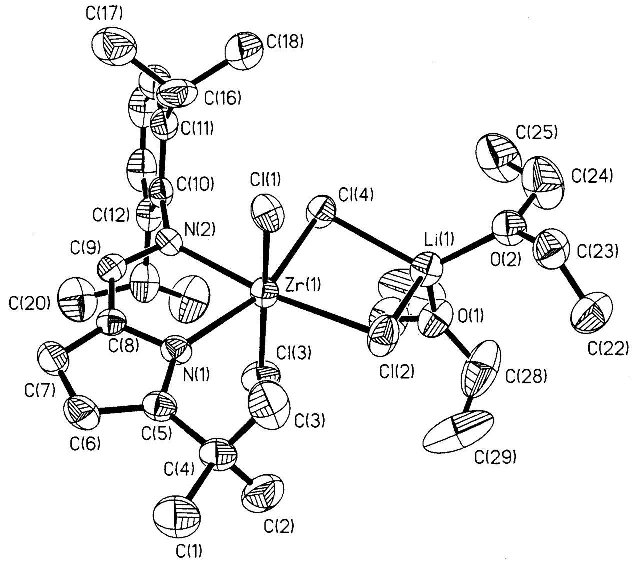


Fig. 1. Molecular structure of $ZrLCl_2(\mu\text{-}Cl)_2Li(OEt_2)_2$ (**3**).

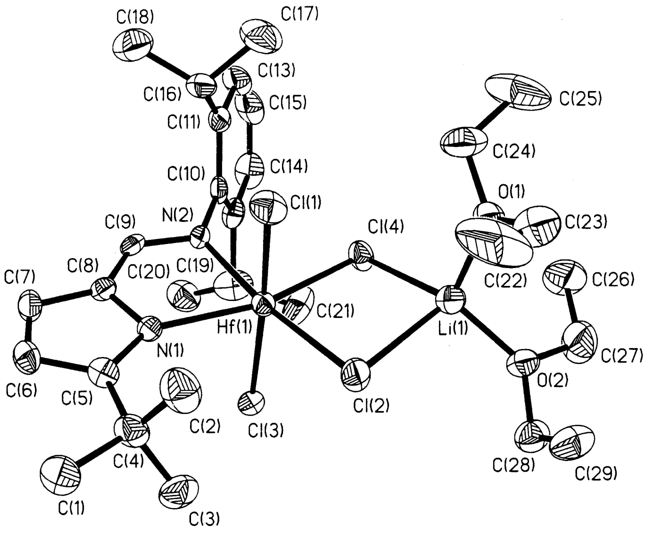


Fig. 2. Molecular structure of $HfLCl_2(\mu\text{-}Cl)_2Li(OEt_2)_2$ (**4**).

The X-ray structures of **3** and **4** are shown in Figs. 1 and 2, respectively. Crystallographic details are summarised in Table 1, and selected bond lengths and angles for **3** and **4** are listed in Tables 2 and 3, respectively. The two structures resemble each other closely; both are found to have a six-coordinate metal center surrounded by one bidentate pyrrolylaldiminate ligand and four chlorine atoms in a distorted octahedral structure. The pyrrolylaldiminate bite angles of 76.58(9)° in **3** and 77.9(2)° in **4** are far smaller than the ideal 90° for an octahedral structure, but larger than those found in $[2\text{-}C_4H_3N(CH{=}NC_6H_3{}^iPr_2)]_2Zr(NMe_2)_2$ (70.16° average) [20] and $[2\text{-}C_4H_3N(CH{=}NC_6H_5)]_2TiCl_2$ (75.86° average) [18]. As expected, the distances of $M{-}N_{pyrrole}$ are shorter (by about 0.05 Å in both **3** and **4**) than those of $M{-}N_{imine}$, consistent with the formally anionic feature of the former donor. The bond distances of $M{-}Cl_{bridging}$ are slightly longer than those of $M{-}Cl_{terminal}$. The five-membered metallacycles are virtually planar. The diisopropylphenyl ring is nearly perpendicular to the metallacycle plane. For both **3** and **4**, the coordination sphere is found to be more open on the *tert*-butyl substituted pyrrole side than the arylated imine part, as evidenced by, for example, the C(5)–N(1)–Zr(1) angle being about 10.4° larger than C(10)–N(2)–Zr(1). The lithium atom is separated from the metal center at a distance that no chemical bonding is possible. The lithium atoms in **3** and **4** are both distorted from the ideal tetrahedral with angles ranging from ca.

Table 2
Selected bond lengths (Å) and bond angles (°) for $ZrLCl_2(\mu\text{-}Cl)_2Li(OEt_2)_2$ (**3**)

Bond lengths			
Zr(1)–N(1)	2.221(2)	Zr(1)–N(2)	2.273(2)
Zr(1)–Cl(3)	2.4104(10)	Zr(1)–Cl(1)	2.4313(10)
Zr(1)–Cl(4)	2.4784(9)	Zr(1)–Cl(2)	2.4819(10)
Zr(1)–Li(1)	3.485(6)		
Bond angles			
N(1)–Zr(1)–N(2)	76.57(9)	N(1)–Zr(1)–Cl(3)	87.97(7)
N(2)–Zr(1)–Cl(3)	92.46(6)	N(1)–Zr(1)–Cl(1)	85.77(7)
N(2)–Zr(1)–Cl(1)	92.09(6)	Cl(3)–Zr(1)–Cl(1)	171.21(3)
N(1)–Zr(1)–Cl(4)	159.69(7)	N(2)–Zr(1)–Cl(4)	83.14(6)
Cl(3)–Zr(1)–Cl(4)	93.83(4)	Cl(1)–Zr(1)–Cl(4)	94.19(4)
N(1)–Zr(1)–Cl(2)	113.05(7)	N(2)–Zr(1)–Cl(2)	170.37(6)
Cl(3)–Zr(1)–Cl(2)	88.34(3)	Cl(1)–Zr(1)–Cl(2)	88.43(3)
Cl(4)–Zr(1)–Cl(2)	87.23(3)	Cl(4)–Li(1)–Cl(2)	89.47(18)
Li(1)–Cl(2)–Zr(1)	90.17(13)	Li(1)–Cl(4)–Zr(1)	90.65(13)
C(5)–N(1)–Zr(1)	143.0(2)	C(10)–N(2)–Zr(1)	132.66(18)

Table 3
Selected bond lengths (Å) and bond angles (°) for $HfLCl_2(\mu\text{-}Cl)_2Li(OEt_2)_2$ (**4**)

Bond lengths			
Hf(1)–N(1)	2.214(6)	Hf(1)–N(2)	2.262(6)
Hf(1)–Cl(1)	2.403(2)	Hf(1)–Cl(3)	2.4236(19)
Hf(1)–Cl(2)	2.4662(19)	Hf(1)–Cl(4)	2.4660(18)
Hf(1)–Li(1)	3.458(12)		
Bond angles			
N(1)–Hf(1)–N(2)	77.9(2)	N(1)–Hf(1)–Cl(1)	88.10(16)
N(2)–Hf(1)–Cl(1)	92.25(15)	N(1)–Hf(1)–Cl(3)	85.95(15)
N(2)–Hf(1)–Cl(3)	92.26(15)	Cl(1)–Hf(1)–Cl(3)	171.62(7)
N(1)–Hf(1)–Cl(2)	111.01(17)	N(2)–Hf(1)–Cl(2)	171.10(15)
Cl(1)–Hf(1)–Cl(2)	88.21(8)	Cl(3)–Hf(1)–Cl(2)	88.43(7)
N(1)–Hf(1)–Cl(4)	161.45(17)	N(2)–Hf(1)–Cl(4)	83.59(15)
Cl(1)–Hf(1)–Cl(4)	93.71(7)	Cl(3)–Hf(1)–Cl(4)	93.82(7)
Cl(2)–Hf(1)–Cl(4)	87.51(6)	Cl(4)–Li(1)–Cl(2)	89.6(4)
Li(1)–Cl(2)–Hf(1)	90.0(3)	Li(1)–Cl(4)–Hf(1)	90.1(3)
C(5)–N(1)–Hf(1)	144.6(5)	C(10)–N(2)–Hf(1)	132.9(4)

89° to 124°, the most acute being associated with the two bridging chlorine atoms.

The metathesis reaction of **2** with $AlCl_3$ in toluene produced red crystalline $AlLCl_2$ (**5**) in 88% yield. Again, attempts to synthesize the bis-pyrrolylaldiminate derivatives were not successful. Addition of two equivalents of **2** to $AlCl_3$ led to **5** as the only isolable product, which is in contrast to the formation of $[2\text{-}C_4H_3N(CH{=}NC_6H_3{}^iPr_2)]_2AlCl$ [17] where less sterically demanding pyrrolylaldiminate ligand is employed. No reaction was observed between **5** and **2**, even under forcing conditions. Alkylation of **5** proceeds smoothly. Treatment of two equivalents of MeMgBr or MeLi to **5** afforded $AlLMe_2$ (**6**) as pale yellow crystals in 80% yield. Attempts to prepare AlLMeCl by reactions of **5** with one equivalent of MeMgBr led to the isolation of **6** in considerable yield. The dichloride complex **5** does not react with the dimethyl complex **6** under the condition employed. Compound **6** is thermally stable; no decomposition was observed when a C_6D_6 solution was heated at 80 °C for 72 h.

The solid-state structures of **5** and **6** were also determined by X-ray crystallographic studies. The ORTEP diagrams are presented in Figs. 3 and 4, and selected bond lengths and angles are listed in Tables 4 and 5. Crystals of **5** were grown from a concentrated toluene solution at −35 °C, while those of **6** from diethyl ether. As depicted in Figs. 3 and 4, both are found to be monomeric, four-coordinate species with the aluminum center in a distorted tetrahedral structure. The pyrrolylaldiminate bite angles of 88.2(2)° in **5** and 85.5(2)° in **6** are far smaller than the ideal tetrahedral angle (109.47°), but notably larger than those found in the tetrahedral bis-pyrrolylaldiminate complexes of Mg (84.72° average) [17] and Fe (81.89° average) [20]. The Cl(1)–Al(1)–Cl(2) angle of 110.85(9)° in **5** is essentially typical for a tetrahedral structure, whereas the C(1)–Al(1)–C(2) angle of 115.7(4)° in **6** is wider. This result is consistent with the Bent's rule [28] that the more electronegative chlorine atoms in **5** prefer the hybrid orbitals of Al having less s character, thereby resulting in a smaller bond angle (electronegativity: Cl 3.16, C 2.55) [29]. The averaged Al–Cl distance of 2.11 Å in **5** is comparable to the averaged Al–$Cl_{terminal}$ distance of 2.07 Å in Al_2Cl_6 [30]. The Al–Me distances in **6** (1.943 Å average) also compare well with the Al–$Me_{terminal}$ distances in Al_2Me_6 (1.97 Å average) [30]. Remaining parameters of **5** and **6** are unexceptional or similar to those observed for **3** and **4**.

The solution NMR data of **3-6** are all consistent with the corresponding solid-state structures. The imine

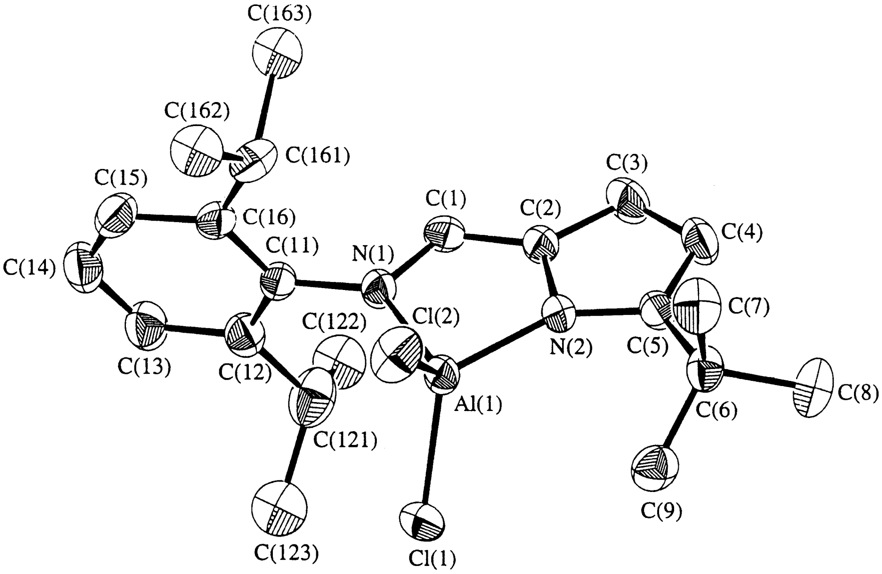


Fig. 3. Molecular structure of $AlLCl_2$ (**5**).

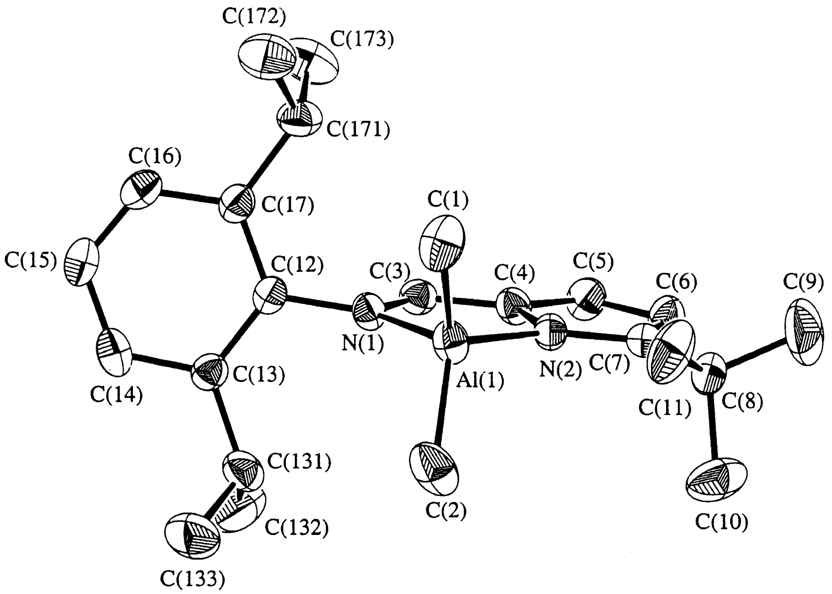


Fig. 4. Molecular structure of $AlLMe_2$ (**6**).

proton of the pyrrolylaldiminate ligand is shifted upfield as compared to that of HL, whereas the aromatic hydrogen atoms on the pyrrole ring show downfield shift. The isopropyl methyl groups are diastereotopic in each compound, likely as a consequence of restricted rotation about the $N-C_{ipso}$ bond [31]. A variable-temperature NMR study of **6** in C_6D_6 indicates that the two doublet resonances for the diastereotopic $CHMe_2$ groups do not show the propensity to exchange at temperatures below 80 °C. Room temperature NMR spectra of **6** are consistent with a molecule having a C_s symmetry as two chemically equivalent Al–*Me* groups are observed.

4. Conclusion

We have prepared and structurally characterized a variety of mono-pyrrolylaldiminate complexes. The steric significance of the *tert*-butyl group in the pyrrolylaldiminate ligand is demonstrated. As a result, the Group 4 chemistry described here is in contrast to that found in a closely related system reported by Bochmann et al [20]. The X-ray structural analyses of the aluminum derivatives **5** and **6** show them to be monomeric four-coordinate species. Further studies directed to the synthesis of other pyrrolylaldiminate derivatives and the application of these compounds on catalysis are currently underway.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 205820 for **3**, 205818 for **4**, 205819 for **5** and 205817 for **6**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK

Table 4
Selected bond lengths (Å) and bond angles (°) for $AlLCl_2$ (**5**)

Bond lengths			
Al(1)–Cl(1)	2.111(2)	Al(1)–Cl(2)	2.102(2)
Al(1)–N(1)	1.911(4)	Al(1)–N(2)	1.867(4)
N(1)–C(1)	1.319(5)	N(1)–C(11)	1.439(6)
N(2)–C(2)	1.392(6)	N(2)–C(5)	1.368(6)
C(1)–C(2)	1.394(7)		
Bond angles			
Cl(1)–Al(1)–Cl(2)	110.85(9)	Cl(1)–Al(1)–N(1)	108.8(2)
Cl(1)–Al(1)–N(2)	117.5(1)	Cl(2)–Al(1)–N(1)	114.2(1)
Cl(2)–Al(1)–N(2)	115.3(1)	N(1)–Al(1)–N(2)	88.2(2)
Al(1)–N(1)–C(11)	131.4(3)	Al(1)–N(2)–C(5)	145.1(3)

Table 5
Selected bond lengths (Å) and bond angles (°) for $AlLMe_2$ (**6**)

Bond lengths			
Al(1)–N(1)	1.976(4)	Al(1)–N(2)	1.923(4)
Al(1)–C(1)	1.950(7)	Al(1)–C(2)	1.936(7)
N(1)–C(3)	1.303(7)	N(1)–C(12)	1.446(7)
N(2)–C(4)	1.408(6)	N(2)–C(7)	1.362(6)
C(3)–C(4)	1.390(7)		
Bond angles			
N(1)–Al(1)–N(2)	85.5(2)	N(1)–Al(1)–C(1)	109.8(3)
N(1)–Al(1)–C(2)	112.6(2)	N(2)–Al(1)–C(1)	116.7(3)
N(2)–Al(1)–C(2)	112.8(3)	C(1)–Al(1)–C(2)	115.7(4)
Al(1)–N(1)–C(12)	131.1(3)	Al(1)–N(2)–C(7)	144.6(4)

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