

Fluoroaryl-substituted ketiminate complexes of aluminum

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Abstract

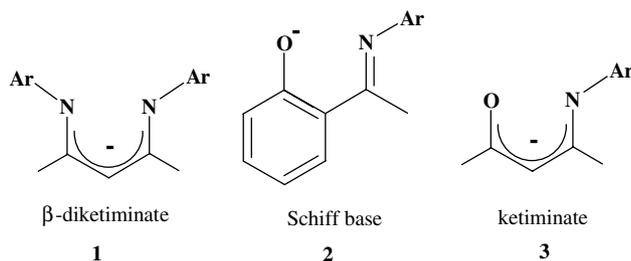
The ketiminate complex $\text{AlCl}[\text{OC}(\text{Me})\text{CHC}(\text{Me})\text{N}(p\text{-C}_6\text{H}_4\text{F})_2$ (**4**) has been prepared from the β -aminoenone, $\text{O}=\text{C}(\text{Me})\text{CH}=\text{C}(\text{Me})\text{N}(\text{H})(p\text{-C}_6\text{H}_4\text{F})$ (**3**) by lithiation of **3** with *n*-BuLi, followed by reaction with AlCl_3 and by the reaction of **3** with Me_2AlCl . A second compound, $[\text{AlCl}_2\{\text{O}=\text{C}(\text{Me})\text{CH}=\text{C}(\text{Me})\text{N}(\text{H})(p\text{-C}_6\text{H}_4\text{F})\}_4][\text{AlCl}_4]$ (**5**), was also isolated from the AlCl_3 reaction. The structures of **4** and **5** were determined by X-ray diffraction analysis.

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1. Introduction

Due to their pronounced Lewis acidity and ready availability, aluminum complexes continue to assume a role of considerable importance, not only for organic synthesis [1], but also in the field of catalysis [2]. In addition to the strongly electrophilic character of the aluminum atom itself, the supporting ligands of these complexes can be used to fine-tune both the steric and electronic properties at the metal center. In this context, β -diketiminates (**1**) and Schiff base ligands (**2**) have found extensive



use in organoaluminum chemistry, both with respect to polymerization catalysis [3] and also for the stabilization of unusual aluminum valence states and coordination numbers [4]. Few studies, however, have focused on aluminum complexes with ketiminate ligands [5]. The monoanionic ketiminate ligand (**3**) normally binds to metals in a similar fashion to β -diketiminates and Schiff bases. As a consequence of the formation of a six-membered chelate ring, the ligation of a ketiminate causes the metal center to be surrounded by bulky substituents on only one side of the ring, thus leaving the other side relatively open. Moreover, ligands of the type O–N are particularly interesting because the oxygen atom provides a site for strong coordination whereas the nitrogen atom is typically less strongly bound, thus resulting in ligand hemilability and potentially interesting catalytic behavior [6]. In order to develop catalytic systems with enhanced activities at the metal centers, it has become increasingly desirable to introduce electron-withdrawing substituents into the coordination sphere [7]. We have recently developed a new method for the synthesis of α -diimines and β -ketiminates bearing fluorinated aryl substituents [8] and in the present contribution

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we explore the use of ligand **3** (Ar = *p*-fluorophenyl) in the context of aluminum chemistry.

2. Experimental

2.1. General

All manipulations and reactions were performed under a dry, oxygen-free, catalyst-scrubbed argon atmosphere using standard Schlenk techniques or under a dry, oxygen-free, helium atmosphere in a Vacuum Atmospheres drybox. All glassware was oven-dried and vacuum- and argon flow-degassed before use. Toluene and diethyl ether were distilled under N₂ from sodium benzophenone ketyl and degassed prior to use. The syntheses of the ligands are described in a previous paper [8]; Me₂AlCl and AlCl₃ were purchased from commercial sources and used without further purification.

2.2. Physical measurements

Low-resolution CI mass spectra were obtained on a Finnigan MAT TSQ-700 mass spectrometer, and high-resolution CI mass spectra were measured on a VG Analytical ZAB-VE sector instrument. All MS analyses were performed on samples that had been sealed in glass capillaries under argon in a drybox. Solution-phase NMR spectra were recorded at 298 K on a GE Varian Unity 300 instrument (¹H, 300 MHz; ¹⁹F, 282 MHz; ²⁷Al, 78 MHz) at the University of Texas at Austin or the Los Alamos National Laboratory (LANL). All NMR samples were run immediately following removal from the drybox. Benzene-d₆ and chloroform-d were vacuum distilled under argon from sodium benzophenone ketyl prior to use. The ¹H NMR chemical shifts are reported relative to tetramethylsilane (δ 0.00) and referenced to solvent. The ¹⁹F NMR chemical shifts are reported relative to freon-11 (δ 0.00) and referenced to C₆H₅CF₃ (δ -63.5 at LANL) or to freon-11 (δ 0.00 at UT-Austin). The ²⁷Al NMR chemical shifts are reported relative to [Al(H₂O)₆]³⁺ (δ 0.00).

2.3. X-ray structure determination of complexes **4** and **5**

Crystals of suitable quality were collected under an argon atmosphere from Schlenk-type flasks, and covered immediately with degassed perfluorinated polyether oil. The X-ray data were collected on a Nonius Kappa CCD diffractometer at 153 K using an Oxford Cryostream low-temperature device and graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). A correction was applied for Lorentz polarization. All structures were solved by direct methods, and refined by full-matrix

least squares on F^2 using the Siemens SHELX PLUS 5.0 (PC) software package [9]. All non-hydrogen atoms were allowed anisotropic thermal motion and all hydrogen atoms, which were included in calculated positions (C–H 0.96 Å), were refined using a riding model and a general isotropic thermal parameter. The crystal and structure refinement details are presented in Table 1.

2.4. AlCl[OC(Me)CHC(Me)N(*p*-C₆H₄F)]₂ (**4**)

2.4.1. Method 1

A solution of *n*-BuLi (2.56 mmol) in hexanes was added slowly to a solution of O=C(Me)CH=C(Me)N(H)(*p*-C₆H₄F) (0.50 g, 2.56 mmol) in 20 ml of diethyl ether at 0 °C. The reaction mixture was allowed to come to room temperature over a period of 3 h, after which time the volatiles were removed in vacuo. The “O=C(Me)CH=C(Me)N(Li)(*p*-C₆H₄F)” in 70 ml of diethyl ether was added slowly to a solution of AlCl₃ (0.34 g, 2.55 mmol) in 20 ml of diethyl ether at 0 °C. The reaction mixture was allowed to come to room temperature and stirred overnight, after which time the volatiles were removed in vacuo, and the resulting pale yellow residue was extracted with toluene (75 ml). After filtration through a glass frit covered with a pad of diatomaceous earth, the yellow filtrate was concentrated and maintained at ambient temperature for 1 week which resulted in the formation of a crop of colorless crystals of **4** (0.02 g, 2% yield, m.p. 118–124 °C). ¹H NMR (C₆D₆, 25 °C): δ 7.1 (m, 8H, $w_{1/2} = 30$ Hz, aryl-ring protons), 5.4 (s, 2H, CH), 2.2 (s, 6H, CH₃CN), 2.0 (s, 6H, CH₃CO). ¹⁹F NMR (CDCl₃, 25 °C): δ -118.0 (m, $w_{1/2} = 12$ Hz). ²⁷Al NMR (C₆D₆, 25 °C): δ 91 (broad, $w_{1/2} = 100$ Hz). MS (CI⁺, CH₄): *m/e* 447 (M + H), 411 (M - Cl), 194 [O=C(Me)CH=C(Me)-N(H)(*p*-C₆H₄F) + H]. HRMS (CI, CH₄) Calc. for C₂₂H₂₂AlClF₂N₂O₂: 447.123154. Found: 447.122689.

2.4.2. Method 2

A solution of O=C(Me)CH=C(Me)N(H)(*p*-C₆H₄F) (0.32 g, 1.63 mmol) in 3 ml of toluene was added to a solution of Me₂AlCl (0.15 g, 1.62 mmol) in 3 ml of toluene. Following the cessation of gas evolution, the reaction mixture was stirred overnight at ambient temperature. Crystals of **4** formed upon slow evaporation of the solvent. (0.12 g, 33% yield). The spectroscopic data were identical with those listed above for Method 1.

2.5. [AlCl₂{O=C(Me)CH=C(Me)N(H)(*p*-C₆H₄F)}₄]-[AlCl₄] (**5**)

The solution from which the crystals of **4** were grown (by Method 1) was transferred to a separate Schlenk flask. The solvent was removed in vacuo and the yellow

Table 1
Crystal and structure refinement data for **4** and **5**

Compound	4	5
Empirical formula	C ₂₂ H ₂₂ AlClF ₂ N ₂ O ₂	C ₄₉ H ₄₉ Al ₂ Cl ₆ F ₄ N ₄ O ₄
Formula weight	446.85	1100.58
Temperature (K)	153(2)	153(2)
Wavelength (Å)	0.71069	0.71069
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	P1̄
Unit cell dimensions		
<i>a</i> (Å)	12.140(5)	11.425(5)
<i>b</i> (Å)	12.201(5)	15.731(5)
<i>c</i> (Å)	14.121(5)	17.238(5)
α (°)	90	88.003(5)
β (°)	92.150(5)	78.409(5)
γ (°)	90	74.750(5)
Volume	2090.1(14)	2927.5(18)
<i>Z</i>	4	2
<i>D</i> _{calc.} (mg m ⁻³)	1.420	1.249
Absorption coefficient (mm)	0.264	0.378
<i>F</i> (000)	928	1134
Crystal size (mm)	0.20 × 0.20 × 0.20	0.2 × 0.2 × 0.2
θ Range for data collection	3.34–27.62°	2.96–28.32°
Index ranges	−15 ≤ <i>h</i> ≤ 14, −15 ≤ <i>k</i> ≤ 15, −14 ≤ <i>l</i> ≤ 18	−14 ≤ <i>h</i> ≤ 14, −20 ≤ <i>k</i> ≤ 16, −22 ≤ <i>l</i> ≤ 22
Reflections collected	7153	21380
Independent reflections [<i>R</i> _{int}]	2421 [0.0845]	13866 [0.0302]
Completeness to θ_{\max}	99.3%	95.0%
Maximum/minimum transmission	0.9490 and 0.9490	0.8863
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	2421/0/181	13866/0/887
Goodness-of-fit on <i>F</i> ²	1.144	1.031
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0694, <i>wR</i> ₂ = 0.1360	<i>R</i> ₁ = 0.0952, <i>wR</i> ₂ = 0.2242
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1023, <i>wR</i> ₂ = 0.1472	<i>R</i> ₁ = 0.1524, <i>wR</i> ₂ = 0.2619
Largest peak and hole (e Å ⁻³)	0.460 and −0.424	2.397 and −1.792

residue was taken into the drybox. Following the addition of 3 ml of C₆D₆, a crop of yellow crystals of **5** formed over a period of 5 min. (0.15 g, 5%, m.p. 178–182 °C). ¹H NMR (C₆D₆, 25 °C): δ 12.3 (br, 4H, NH), 6.5 (m, 16H, *w*_{1/2} = 43 Hz, aryl-ring protons), 4.7 (s, 4H, CH), 2.3 (s, 12H, CH₃C–N), 1.2 (s, 12H, CH₃C=O). ¹⁹F NMR (CDCl₃, 25 °C): δ −113.7 (m, *w*_{1/2} = 10 Hz). ²⁷Al (CDCl₃, 25 °C): δ 86 (sharp; (AlCl₄)[−]), 2 (sharp; (AlCl₂(ligand)₄)⁺). MS (Cl⁺, CH₄): *m/e* 642 (M – Cl–ligand), 485 [M–(2 ligand)], 194 [O=C(Me)CH=C(Me)–N(H)(*p*-fluorophenyl) + H].

3. Results and discussion

Treatment of the free ligand O=C(Me)CH=C(Me)–N(H)(*p*-C₆H₄F) with *n*-BuLi afforded the lithiated intermediate, “O=C(Me)CH=C(Me)N(Li)(*p*-C₆H₄F)”, which in turn was allowed to react in situ with 1 equivalent of AlCl₃. Although the reagents were employed in 1:1 stoichiometry, a disubstituted product, AlCl[OC(Me)CHC(Me)N(*p*-C₆H₄F)]₂ (**4**), was isolated. The empirical composition of **4** was indicated by the detection of a peak corresponding to the molecular ion at *m/e* 447 in the Cl⁺ mass spectrum, along with a satisfactory HRMS

for the same ion. Confirmation of the proposed composition was provided by X-ray crystallography (see Tables 1 and 2).

Individual molecules of **4** possess a twofold rotation axis that lies along the Al(1)–Cl(1) bond and renders the two chelate rings equivalent (Fig. 1). The aluminum atom is five-coordinate and adopts a trigonal bipyramidal geometry in which the two nitrogen atoms occupy the axial positions as evidenced by the fact that the N(1)–Al(1)–N(2) angle deviates only slightly from linearity [172.44(4)°]. The equatorial plane comprises one chlorine and two oxygen atoms, for which the sum of bond angles is 360.00(8)°. The N–C–C–O chelate rings are close to planar as reflected by the sum of bond angles (718.78°). There is a slight deviation of the oxygen atom (0.078 Å) from the mean plane of each ring. The chelate rings are delocalized as evidenced by the pattern of bond lengths, [1.314(3) Å, O(1)–C(4); 1.350(4) Å, C(4)–C(3); 1.431(4) Å, C(3)–C(2); 1.320(4) Å, C(2)–N(1)]. Compared with the free ligand [8], lengthening of the O(1)–C(4) and C(3)–C(2) bonds and a shortening of the N(1)–C(2) bond takes place upon coordination.

In an effort to prepare an aluminum ketimate complex with a 1:1 stoichiometry, 1 equivalent of the protonated form of the free ligand, O=C(Me)CH=C–

Table 2
Selected bond lengths (Å) and angles (°)

Compound 4			
<i>Bond lengths</i>			
Cl(1)–Al(1)	2.1925(18)	C(13)–C(12)	1.361(4)
Al(1)–O(1)	1.774(2)	C(13)–C(14)	1.371(4)
Al(1)–N(1)	2.034(2)	C(15)–C(10)	1.385(4)
N(1)–C(2)	1.320(4)	C(15)–C(14)	1.388(4)
N(1)–C(10)	1.445(3)	C(4)–C(5)	1.497(4)
F(13)–C(13)	1.370(3)	C(12)–C(11)	1.392(4)
O(1)–C(4)	1.314(3)	C(2)–C(1)	1.501(4)
C(3)–C(4)	1.350(4)	C(10)–C(11)	1.385(4)
C(3)–C(2)	1.431(4)		
<i>Bond angles</i>			
O(1)–Al(1)–O(1A)	122.64(15)	C(4)–O(1)–Al(1)	132.98(18)
O(1)–Al(1)–N(1A)	86.40(9)	C(4)–C(3)–C(2)	124.8(3)
O(1A)–Al(1)–N(1A)	89.97(9)	C(12)–C(13)–F(13)	118.5(3)
O(1)–Al(1)–N(1)	89.97(9)	C(12)–C(13)–C(14)	123.3(3)
O(1A)–Al(1)–N(1)	86.40(9)	F(13)–C(13)–C(14)	118.3(3)
N(1A)–Al(1)–N(1)	172.44(15)	C(10)–C(15)–C(14)	121.0(3)
O(1)–Al(1)–Cl(1)	118.68(8)	O(1)–C(4)–C(3)	123.7(3)
O(1A)–Al(1)–Cl(1)	118.68(8)	O(1)–C(4)–C(5)	113.7(3)
N(1A)–Al(1)–Cl(1)	93.78(7)	C(13)–C(12)–C(11)	118.3(3)
N(1)–Al(1)–Cl(1)	93.78(7)	N(1)–C(2)–C(3)	121.4(3)
C(2)–N(1)–C(10)	116.5(2)	N(1)–C(2)–C(1)	121.9(3)
C(2)–N(1)–Al(1)	125.87(19)	C(11)–C(10)–N(1)	121.1(3)
C(10)–N(1)–Al(1)	117.66(17)	C(15)–C(10)–N(1)	119.7(2)
Compound 5			
<i>Bond lengths</i>			
C(22)–C(50)	1.377(7)	C(53)–C(57)	1.371(9)
C(22)–C(44)	1.392(7)	C(57)–F(3)	1.352(6)
C(22)–N(15)	1.422(6)	O(7)–Al(2)	1.867(3)
C(24)–O(12)	1.280(5)	O(11)–Al(2)	1.889(3)
C(24)–C(42)	1.392(6)	O(12)–Al(2)	1.867(3)
C(24)–C(49)	1.491(7)	O(13)–Al(2)	1.885(3)
C(37)–C(15)	1.328(6)	Al(2)–Cl(1)	2.2686(19)
C(37)–C(42)	1.405(7)	Al(2)–Cl(2)	2.4238(19)
C(37)–C(59)	1.498(7)	Al(4)–Cl(4)	2.082(3)
C(44)–C(46)	1.390(8)	Al(4)–Cl(06)	2.101(3)
C(46)–C(57)	1.377(9)	Al(4)–Cl(07)	2.103(4)
C(50)–C(53)	1.401(8)	Al(4)–Cl(3)	2.135(3)
<i>Bond angles</i>			
C(50)–C(22)–N(15)	119.0(5)	O(12)–Al(2)–O(11)	88.34(13)
C(44)–C(22)–N(15)	120.7(5)	O(7)–Al(2)–O(11)	88.73(14)
O(12)–C(24)–C(42)	119.4(4)	O(13)–Al(2)–O(11)	168.65(14)
O(12)–C(24)–C(49)	119.4(4)	O(12)–Al(2)–Cl(1)	91.77(11)
C(42)–C(24)–C(49)	121.2(4)	O(7)–Al(2)–Cl(1)	98.16(11)
N(15)–C(37)–C(42)	121.6(4)	O(13)–Al(2)–Cl(1)	95.38(11)
N(15)–C(37)–C(59)	118.7(4)	O(11)–Al(2)–Cl(1)	95.91(10)
F(3)–C(57)–C(46)	117.8(6)	Cl(4)–Al(4)–Cl(06)	108.54(16)
C(37)–N(15)–C(22)	127.7(4)	Cl(4)–Al(4)–Cl(07)	109.75(16)
C(24)–O(12)–Al(2)	148.2(3)	Cl(06)–Al(4)–Cl(07)	109.57(17)
O(12)–Al(2)–O(13)	169.89(15)	Cl(4)–Al(4)–Cl(3)	106.65(19)
O(12)–Al(2)–O(13)	92.50(14)	Cl(06)–Al(4)–Cl(3)	109.37(14)
O(7)–Al(2)–O(13)	88.50(14)	Cl(07)–Al(4)–Cl(3)	112.85(19)

(Me)N(H)(*p*-C₆H₄F), was allowed to react with Me₂AlCl. However, both methyl groups underwent a methane elimination reaction and the product was shown to be **4** on the basis of spectroscopic data and X-ray crystallography. It is worth noting that the yield of **4** from the methane elimination route (Method 2) is

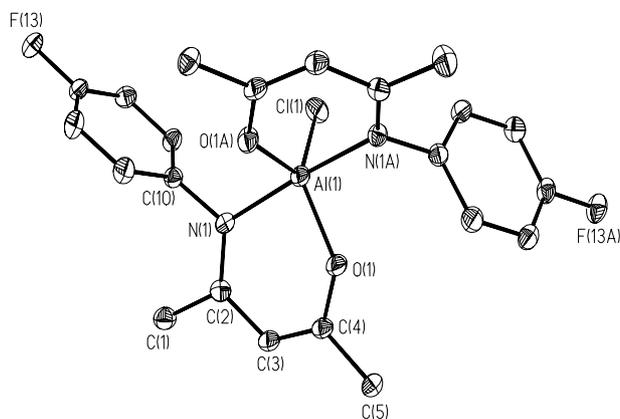
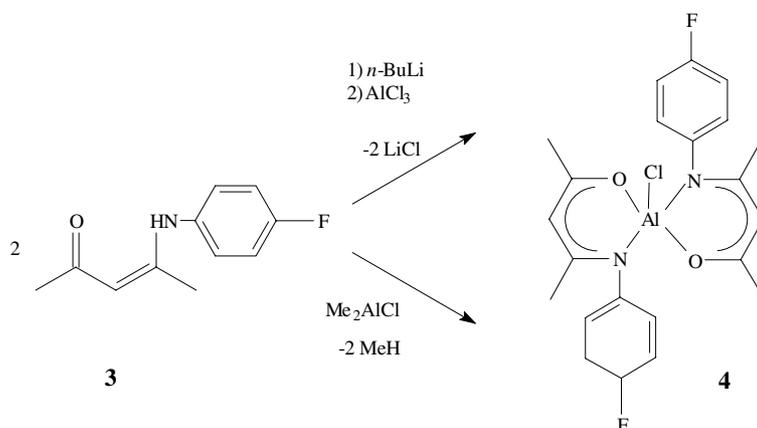


Fig. 1. Molecular structure of AlCl[OC(Me)CHC(Me)N(*p*-C₆H₄F)]₂, (**4**), showing the atom numbering scheme. The thermal ellipsoids are shown at the 30% probability level. All hydrogen atoms have been omitted for clarity.

significantly better than that realized by salt elimination (Method 1). The two approaches are summarized in Scheme 1.

Yu et al. [5] have reported similar reactions with the bulkier ketiminate ligand [OC(Me)CHC(Me)N(2,6-*i*-Pr₂C₆H₃)][−]. However, there are significant differences in our results. For instance, and probably on account of the bulkier aryl ligand, these authors were able to obtain both 1:1 and 2:1 ligand:aluminum stoichiometry products either by the methane elimination or by salt elimination methodology. There is also a significant difference in the two AlCl(ketiminate)₂ structures.

Both structures feature trigonal bipyramidal aluminum centers. However, in contrast to **4**, which has axially disposed nitrogens, in the case of AlCl[OC(Me)CHC(Me)N(2,6-*i*-Pr₂C₆H₃)], the axial positions are occupied by oxygen atoms with an O–Al–O bond angle of 168.8(5)°. A further chemical difference relates to the fact that a second product was isolated from the reaction of O=C(Me)CH=C(Me)–N(H)(*p*-C₆H₄F) with AlCl₃. The ²⁷Al NMR assay of this product (**5**) evidenced sharp resonances at δ 86 and 2, the first of which is indicative of the presence of [AlCl₄][−] and the second of which falls in the region anticipated for hexacoordinate aluminum [10]. The ¹H and ¹⁹F NMR spectra of **5** were similar to those of the free ligand, albeit shifted due to coordination to aluminum. Of particular significance was the presence of a peak at δ 12.3 in the ¹H spectrum thus indicating that the amido protons were still present. In order to elucidate the structure of **5**, it was necessary to appeal to X-ray crystallography. The solid state of **5** comprises an equimolar mixture of [AlCl₂{O=C(Me)CH=C(Me)N(H)(*p*-C₆H₄F)}₄]⁺ and [AlCl₄][−] ions and there are no unusually short interionic contacts. The structure of **5** is illustrated in Fig. 2. The geometry around the aluminum center Al(2) is octahedral and the average O–Al–O bond angle in the AlO₄ equatorial plane is 89.52(14)°. The Cl(1)–Al(2)–Cl(2)



Scheme 1.

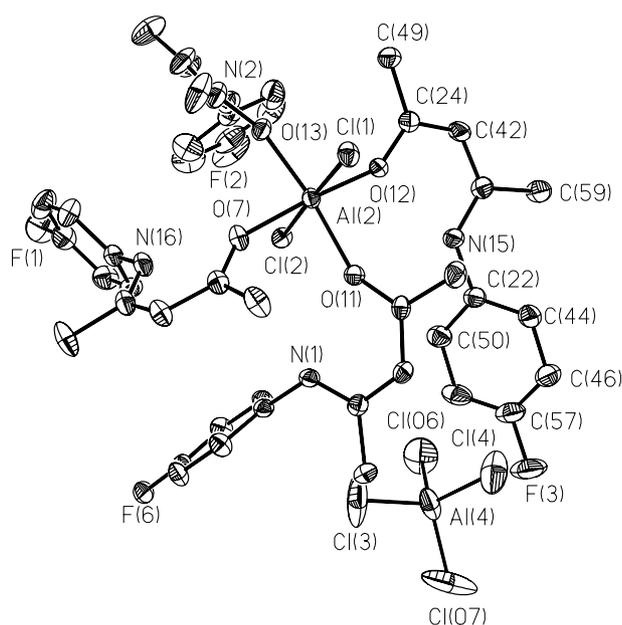
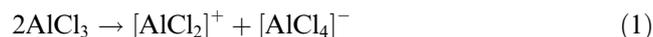


Fig. 2. Molecular structure of $[\text{AlCl}_2\{\text{O}=\text{C}(\text{Me})\text{CH}=\text{C}(\text{Me})\text{N}(\text{H})(p\text{-C}_6\text{H}_4\text{F})\}_4][\text{AlCl}_4]$, (**5**), showing the atom numbering scheme. A benzene of crystallization has been omitted for clarity. The thermal ellipsoids are shown at the 30% probability level. All hydrogen atoms have been omitted for clarity.

bond angle is $175.53(4)^\circ$ and the average aluminum–chlorine bond length of $2.347(19) \text{ \AA}$ is slightly longer than that observed for **4**. The Al–oxygen bond lengths, which average $1.877(3) \text{ \AA}$, are slightly longer than that determined for **4**, suggestive of a donor–acceptor rather than a σ -type Al–O bond. This view was confirmed by the detection of the amino proton atom on N(1) as well as being consistent with the assignment of the +3 oxidation state Al(2). The bond lengths observed for the β -aminoenone ligand compare reasonably well with those reported for the free ligand [8], the main difference being an increase of the C=O bond length from $1.252(1)$ to $1.280(5) \text{ \AA}$ upon coordination. The adjacent C(24)–

C(42) bond [$1.392(6) \text{ \AA}$] is $\sim 0.03 \text{ \AA}$ shorter than in the free ligand ($1.426(2) \text{ \AA}$) while the other C–C bond, C(42)–C(37), undergoes a 0.02 \AA increase upon coordination, as does the C–N bond. There are no main group examples of cations of the type $[\mathbf{5}]^+$ in which β -aminoenone ligands bind to the metal atom via the ketone functionality rather than as bidentate ketiminate ligands. There are, however, examples of this type of bonding in titanium and zirconium chemistry [11,12]. These Group 4 derivatives were prepared by treatment of the respective metal tetrahalide with two equivalents of the free ligand, thus forming the MCl_4L_2 complexes ($\text{M} = \text{Ti}, \text{Zr}$; $\text{L} = \beta$ -aminoenone). Both complexes feature octahedral geometries; however, unlike $[\mathbf{5}]^+$, they are neutral compounds.

The formation of **5** can best be understood on the basis of the autoionization reaction shown in Equation 1. The cation $[\text{AlCl}_2]^+$ is a strong Lewis acid that readily coordinates with the keto



functionality of the free ligand in preference to undergoing a hydrogen chloride elimination reaction. This type of autoionization is observed frequently in systems where halide abstraction reactions are possible since they do not involve the transfer of lone pairs and are therefore defined by Lewis acid and base chemistry [13]. Clearly, for this type of reaction to occur in the observed manner it requires the absence of the lithiated β -aminoenone ligand. Either the ligand was reprotonated, or more likely, the lithiation of the starting β -aminoenone did not go to completion.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre, CCDC Nos. 256864 and 256865 for compounds

4 and 5, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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