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Note

Reactivity studies of a four-coordinate methyl chloro aluminium aminophenolate complex with $B(C_6F_5)_3$

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Abstract

The X-ray characterized four-coordinate aminophenolate aluminium complex {6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}Al(Me)(Cl) (**1**), which is readily available by reaction of the corresponding aminophenolate Li salt with $MeAlCl_2$, slowly reacts with $B(C_6F_5)_3$ to yield a 1/1 mixture of the Al methyl cation {6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}Al(Me)$(THF)^+$ (**2**, as $MeB(C_6F_5)_3^-$ salt) and the Al dichloro derivative {6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}$AlCl_2$ (**3**). This reaction most likely proceeds via a Me^- abstraction/ligand exchange sequence.

Keywords: Aluminium; Cationic; Lewis acid; Aminophenolate

1. Introduction

Cationic aluminium species have recently received an increased interest because their enhanced Lewis acidity versus that of neutral analogues may be of potential interest in catalysis as well as in the mediation of other reactions requiring a Lewis acid species [1]. In this regard, some of these cations have already been used as alkene oxide [2], (D,L)-lactide [3b], ε-caprolactone [4] and ethylene [5] polymerization catalysts. Among this class of compounds, four-coordinate Al alkyl cations of the type $\{LX\}Al(R)(L)^+$ (LX^- = bidentate monoanionic ligand, L = labile ligand), have been the most studied as they combine a low-coordination with a cationic metal center, thus resulting in highly Lewis acidic species [2e,5b]. The interest in these cations has been triggered by the fact that they were shown to be readily accessible via an alkyl abstraction reaction of neutral precursors $\{LX\}AlR_2$ with reagents such as $B(C_6F_5)_3$ in the presence of a Lewis base L [5b].

In contrast with the numerous studies on the ionization chemistry of $\{LX\}AlR_2$ derivatives with $B(C_6F_5)_3$, the reactivity of $\{LX\}Al(X)(R)$ derivatives ($X \neq$ alkyl) with the latter borane has never been investigated although this approach may, in principle, constitute a straightforward way to access $\{LX\}Al(X)(L)^+$ (via a R^- abstraction reaction) [6]. In this regard, we are interested in the synthesis of Al chloro cations of the type $\{LX\}Al(Cl)(L)^+$ via reaction of $\{LX\}Al(Cl)(R)$ derivatives with $B(C_6F_5)_3$. Low-coordinate Al chloro cationic species, nearly unknown to date with the exception of studies by Bertrand et al. on that matter [3], may be of interest as they could exhibit an enhanced Lewis acidity vs. that of Al alkyls $\{LX\}Al(R)(L)^+$ and thus be of potential use in catalysis [3b].

For our studies, the choice of a sterically bulky bidentate *N*,*O*-aminophenolate ligand seemed appropriate since this class of LX^- ligand has been shown to be suitable for the obtention of stable Al alkyls cations $\{LX\}Al(R)(L)^+$ [7]. Here, we report the results of our reactivity studies on the ionization of a mono-chloro aminophenolate Al methyl complex with $B(C_6F_5)_3$.

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2. Results and discussion

2.1. Synthesis and structure of the mono-chloro aminophenolate Al complex {6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}Al(Me)(Cl) (1)

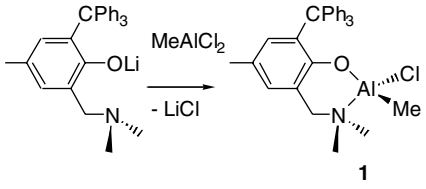
The neutral Al complex **1** was synthesized via a classical salt metathesis route involving the reaction of the corresponding aminophenolate lithium salt and $AlMeCl_2$. Thus, the reaction of the lithium salt [6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O]Li, generated in situ by deprotonation of the aminophenol ligand 6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2OH with ^{n}BuLi at RT in pentane, with an equimolar amount of $AlMeCl_2$ yields the four-coordinate Al complex {6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}Al(Me)(Cl) (**1**, Scheme 1), which was isolated in good yield (78%) as a colorless crystalline solid.

The molecular structure of the Al complex **1** was determined by X-ray crystallography analysis, thus establishing its monomeric nature as well as the effective chelation of one aminophenolate to the Al center (Fig. 1). Overall, compound **1** exhibits similar structural and geometrical features as those of related aminophenolate Al dialkyl complexes [2e]. The Al–O and Al–N bond distances in **1** (1.7206(16) and 1.972(3) Å, respectively) are slightly shorter than those in the related aminophenolate Al dimethyl complex {6-($CH_2NC_5H_{10}$)-2-^{t}Bu-4-C_6H_2O}$AlMe_2$ (1.768(2) and 2.019(2) Å, respectively) [2e], which may reflect the more electron deficient and Lewis acidic Al center in **1**.

The NMR data for **1** are consistent with a C_1-symmetric structure for this complex in solution and thus with its state structure being retained in solution at RT.

2.2. Reaction of the Al complex 1 with $B(C_6F_5)_3$

The reaction of the aminophenolate complex **1** with $B(C_6F_5)_3$ was investigated to probe the ability of **1** to be ionized (via a Me^- abstraction reaction) and to tentatively access an Al chloro cation via this route.



Scheme 1.

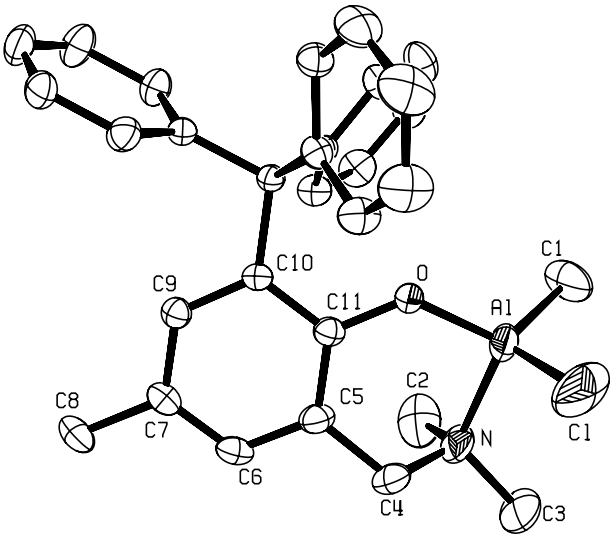
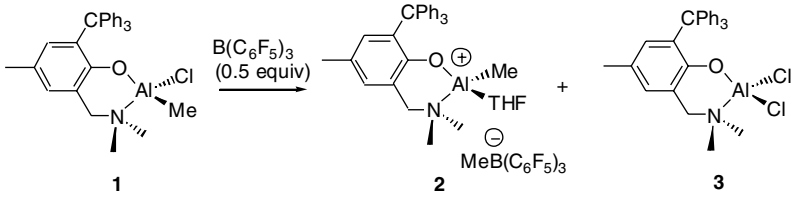


Fig. 1. Molecular structure of the Al complex **1** as determined by X-ray crystallography with a partial labelling for clarity. The hydrogen atoms are also omitted for clarity. Selected bond distances (Å): Al–O = 1.721(2), Al–C(1) = 1.947(4), Al–N = 1.972(3), Al–Cl = 2.134(1). Selected bond angles (°): O–Al–C(1) = 118.3(1), O–Al–N = 97.99(9), O–Al–Cl = 109.25, C(1)–Al–Cl = 113.3(1).

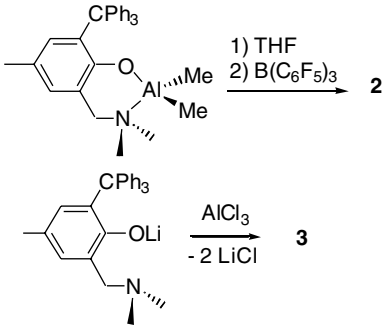
The reaction of complex **1** with 1 equivalent of $B(C_6F_5)_3$ in the presence of 1 equivalent of THF (CD_2Cl_2, RT, 18 h) affords the quantitative conversion to a 1/1 mixture of the Al-THF methyl cation {6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}Al(Me)(THF)$^+$ (as $MeB(C_6F_5)_3^-$ salt (**2**) Scheme 2) and the neutral Al dichloro derivative {6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}$AlCl_2$ (**3**, Scheme 1), along with 0.5 equivalent of unreacted $B(C_6F_5)_3$, as monitored by ^{1}H and ^{19}F NMR [8]. As can be expected, this reaction proceeds in a similar manner when performed with 0.5 equivalent of $B(C_6F_5)_3$.

The identity of the Al complexes **2** and **3** was confirmed by their independent synthesis. Thus, the Al cation **2** could be generated by ionization of the Al dimethyl complex {6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}$AlMe_2$ with $B(C_6F_5)_3$ in the presence of THF, while the Al dichloro derivative **3** was synthesized by a salt metathesis reaction between an equimolar amount of [6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O]Li and $AlCl_3$ and was isolated in a moderate yield (Scheme 3).

The borane $B(C_6F_5)_3$ thus appears to slowly ionize complex **1** via a Me^- abstraction reaction, as evidenced by the presence of the $MeB(C_6F_5)_3^-$ anion in the reaction mixture [9]; however, the Al chloro cation expected to be derived



Scheme 2.



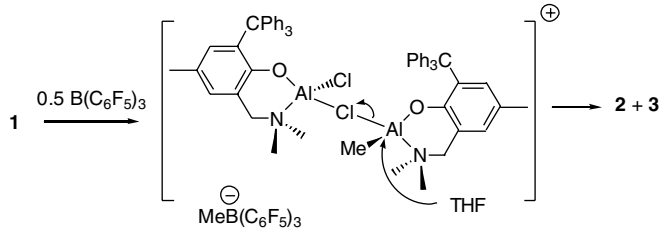
Scheme 3.

from it is not observed at any point along the reaction process, as deducted from a careful ^{1}H NMR monitoring of the reaction at RT. This suggests that the putative Al chloro cation, if formed, reacts quite fast. The formation of complexes **2** and **3** as well as the stoichiometry of the reaction strongly suggests a ligand exchange reaction involving unreacted **1** and an Al cationic species derived from Me^- abstraction at **1** by $B(C_6F_5)_3$.

A possible mechanism for this ionization reaction may involve an initial Me^- abstraction by $B(C_6F_5)_3$ at the Al center of **1** to form a putative transient μ-Cl dinuclear Al cation (Scheme 4), which, upon coordination of THF to the *Al*ClMe metal center, would yield a 1/1 ratio of the Al-THF methyl cation **2** and the neutral dichloro derivative **3**. The latter species is formed irreversibly as it does not further react with $B(C_6F_5)_3$; this feature is most likely the driving force of the reaction.

Although we have no experimental evidence for the proposed chloro-bridged Al dinuclear cation, this proposal is consistent with the reaction outcome, its stoichiometry (2/1 ratio in **1** vs. $B(C_6F_5)_3$) as well as with the known ability of Al complexes to form μ-Cl-typed aggregates. In addition, although μ-Cl Al cations of the type conjectured here have not been previously observed in group 13 chemistry, related dinuclear cations such as $[Cp_2Zr(Cl)\text{-}(\mu\text{-}Cl)\text{-}(Cl)ZrCp_2]^+$ have been spectroscopically characterized by Brintzinger and al. in cationic zirconium metallocene chemistry [10].

In summary, the ionization reaction of the mono-chloro Al methyl complex **1** with $B(C_6F_5)_3$ in the presence of THF yields the Al methyl cation **2** along with the neutral dichloro derivative **3** via a presumably Me^- abstraction/ligand exchange reaction sequence. The Al chloro cation



Scheme 4.

$\{6\text{-}(CH_2NMe_2)\text{-}2\text{-}CPh_3\text{-}4\text{-}Me\text{-}C_6H_2O\}Al(Cl)(THF)^+$ was never observed in the reaction mixture. These results imply that the alkyl abstraction route, successful to access Al cationic alkyls from $\{LX\}AlR_2$, may not be a viable way to generate Al chloro cations of the type $\{LX\}Al(Cl)(L)^+$.

3. Experimental section

3.1. General procedures

All experiments were carried out under N_2 using standard Schlenk techniques or in a Mbraun Unilab glovebox. Toluene, pentane and diethyl ether were distilled from Na/benzophenone and stored over activated molecular sieves (4 Å) in a glovebox prior to use. CH_2Cl_2, CD_2Cl_2 were distilled from CaH_2 and stored over activated molecular sieves (4 Å) in a glovebox prior to use. C_6D_6 was degassed under a N_2 flow and stored over activated molecular sieves (4 Å) in a glovebox prior to use. The aminophenol derivative 6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2OH was prepared following a literature procedure [2e]. $B(C_6F_5)_3$ was purchased from Strem and extracted with dry pentane prior to use. All other chemicals were purchased from Aldrich and were used as received except for NMe_2Ph, which was stored over activated molecular sieves (4 Å) prior to use. NMR spectra were recorded on Bruker AC 200 or 400 MHz NMR spectrometers, in Teflon-valved J-Young NMR tubes at ambient temperature, unless otherwise indicated. ^{1}H and ^{13}C chemical shifts are reported vs. $SiMe_4$ and were determined by reference to the residual ^{1}H and ^{13}C solvent peaks. ^{11}B and ^{19}F chemical shifts are reported versus BF_3–Et_2O in CD_2Cl_2 and neat $CFCl_3$, respectively. Elemental analysis was performed by the microanalysis laboratory of the Université Pierre et Marie Curie (Paris, France).

3.2. [6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O]Li

In a glovebox, *n*-BuLi (0.62 mL of a 2.5 M hexane solution, 1.56 mmol) was added dropwise to a precooled (−40 °C) pentane suspension of the aminophenol 6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2OH (579 mg, 1.42 mmol) under vigorous stirring. After the addition, the mixture was left under stirring for 12 h, after which the resulting colorless suspension was filtered through glass frit. The obtained colorless solid was washed with pentane and dried and was further used as is (477 mg, 81% yield). ^{1}H NMR (200 MHz, C_6D_6): δ 7.34 [d, ^4J(HH) = 2.0 Hz, 1H, O-*Ph*], 7.30–6.84 (m, 15H, C*Ph*$_3$), 6.83 [d, ^4J(HH) = 2.0 Hz, 1H, O-*Ph*], 3.67 (br, 2H, PhCH_2), 2.23 (s, 3H, *Me*Ph), 1.54 (s, 6H, NMe_2).

3.3. {6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O}AlMeCl (**1**)

In a glovebox, Cl_2AlMe (0.71 mL of a 1 M hexanes solution, 0.71 mmol) was rapidly added via a pipette to a precooled (−40 °C) toluene solution (5 mL) of 6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2OLi (295 mg, 0.71 mmol).

The reaction mixture was allowed to warm to room temperature and stirred for 18 h. The resulting colorless light suspension was then filtered through glass frit and the filtrate evaporated to dryness under vacuum to yield a colorless residue. Recrystallization of this residue from a 1/1 toluene/Et_2O mixture at −40°C afforded pure **1** as a colorless solid (210 mg, 55% yield). Anal. Calc. for $C_{30}H_{31}AlClNO$: C, 74.45; H, 6.46. Found: C, 74.96; H, 6.52. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.21–7.13 (m, 15H, C*Ph*$_3$), 6.99 [d, ^4J(HH) = 2.0 Hz, 1H, O-*Ph*], 6.77 [d, ^4J(HH) = 2.0 Hz, 1H, O-*Ph*], 4.28 [d, ^2J(HH) = 14.0 Hz, 1H, PhC*H*$_2$], 3.35 [d, ^2J(HH) = 14.0 Hz, 1H, PhC*H*$_2$], 2.50 (s, 3H), 2.16 (s, 3H), 2.10 (s, 3H), −1.11 (s, 3H, Al*Me*). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 154.5 (Ph), 146.8 (Ph), 137.5 (Ph), 132.7 (Ph), 131.6 (Ph), 131.5 (Ph), 129.2 (Ph), 127.4 (Ph), 125.6 (Ph), 120.5 (Ph), 64.1 (*C*Ph$_3$), 62.0 (Ph*C*H$_2$), 44.9 (N*Me*), 42.3 (N*Me*), 20.9 (Ph*Me*), −13.7 (Al*Me*).

3.4. [{6-(CH$_2$NMe$_2$)-2-CPh$_3$-4-Me-C$_6$H$_2$O}Al(Me)(THF)][MeB(C$_6$F$_5$)$_3$] (2)

In a glovebox, in a small Schlenk flask, the Al dimethyl compound {6-(CH$_2$NMe$_2$)-2-CPh$_3$-4-Me-C$_6$H$_2$O}AlMe$_2$ (88.0 mg, 0.19 mmol) was dissolved in CH_2Cl_2 (1 mL) and an equimolar amount of THF (15.4 μL, 0.19 mmol) was added. $B(C_6F_5)_3$ (97.2 mg, 0.19 mmol) was introduced and the resulting colorless solution was stirred at room temperature for 30 min, after which it was evaporated to dryness in vacuo to yield a colorless foam. Trituration of the foamy residue with cold pentane (precooled at −40 °C) provoked the precipitation of a colorless solid. The mixture was then filtered through frit under reduced pressure and the obtained solid was further dried to afford pure **2**. Anal. Calc. for $C_{53}H_{42}AlBF_{15}NO_2$: C, 60.76; H, 4.04. Found: C, 59.91; H, 3.85. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.23–6.88 (m, 16H, C*Ph*$_3$ and O-*Ph*), 6.87 [d, ^4J(HH) = 2.0 Hz, 1H, O-*Ph*], 3.81 (br s, THF, 4H), 3.72 (br s, 2H, PhC*H*$_2$), 2.41 (br s, N*Me*$_2$, 6H), 2.20 (s, *Me*Ph, 3H), 1.94 (br s, THF, 4H), 0.48 (*Me*B), −0.92 (Al*Me*). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 151.6 (Ph), 148.1 [d, ^1J(CF) = 242 Hz, *C*$_6$F$_5$], 145.5 (Ph), 137.3 [d, ^1J(CF) = 255 Hz, *C*$_6$F$_5$], 136.8 (Ph), 136.0 [d, ^1J(CF) = 238 Hz, *C*$_6$F$_5$], 133.2 (Ph), 130.5 (Ph), 129.4 (Ph), 128.8 (Ph), 126.9 (Ph), 125.5 (Ph), 119.0 (Ph), 71.3 (br s, THF), 63.1 (Ph*C*H$_2$ or *C*Ph$_3$), 62.9 (Ph*C*H$_2$ or *C*Ph$_3$), 44.0 (br s, N*Me*$_2$), 25.5 (THF), 20.5 (Ph*Me*), 10.0 (*Me*B), −17.8 (Al*Me*). ^{19}F NMR (376 MHz, CD_2Cl_2): δ −133.5 [d, ^3J(FF) = 19 Hz, *o*-C$_6$*F*$_5$], −165.7 [t, ^3J(FF) = 20 Hz, *m*-C$_6$*F*$_5$], −168.2 [m, ^3J(FF) = 19 Hz, *p*-C$_6$*F*$_5$].

3.5. {6-(CH$_2$NMe$_2$)-2-CPh$_3$-4-Me-C$_6$H$_2$O}AlCl$_2$ (3)

The dichloro derivative **3** was generated using the same procedure as that for complex **1** using an equimolar amount of [6-(CH$_2$NMe$_2$)-2-CPh$_3$-4-Me-C$_6$H$_2$O]Li (250.0 mg, 0.603 mmol) and $AlCl_3$ (80.4 mg, 0.603 mmol). Pure **3** was obtained after recrystallization of the crude product from toluene at −40 °C. Anal. Calc. for $C_{29}H_{28}AlCl_2NO$: C, 69.05; H, 5.59. Found: C, 69.24; H, 5.41. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.32–7.18 (m, 15H, C*Ph*$_3$), 7.09 [d, 1H, ^4J(HH) = 2.0 Hz, O-*Ph*], 6.81 [d, 1H, ^4J(HH) = 2.0 Hz, O-*Ph*], 3.91 (s, 2H, Ph-C*H*$_2$), 2.43 (s, 6H, N*Me*$_2$), 2.18 (s, 3H, Ph-*Me*). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 152.9 (O-*Ph*), 145.6 (Ph), 136.4 (Ph), 130.5 (Ph), 128.6 (Ph), 127.8 (Ph), 127.0 (Ph), 126.7 (Ph), 124.9 (Ph), 119.5 (Ph), 63.0 (*C*Ph$_3$), 62.3 (Ph*C*H$_2$), 44.5 (N*Me*$_2$), 20.2 (*Me*Ph).

3.6. NMR-scale reaction of the Al complex 1 with B(C$_6$F$_5$)$_3$ in the presence of THF

In a glovebox, the mono-chloro Al compound **1** (31.4 mg, 0.065 mmol), $B(C_6F_5)_3$ (33.1 mg, 0.065 mmol) and THF (5.3 μL, 0.065 mmol) were charged in a small vial sample and dissolved in CD_2Cl_2. Hexamethylbenzene, used as an internal standard (0.3 equivalents, 3.2 mg, 0.02 mmol) was also added to the sample. The resulting colorless solution was then transferred to a J-Young NMR tube. The reaction was monitored by ^{1}H and ^{19}F NMR spectroscopy showing the slow formation of a 1/1 mixture of the Al-THF cation {6-(CH$_2$NMe$_2$)-2-CPh$_3$-4-Me-C$_6$H$_2$O}Al(Me)(THF)$^+$ (**2**) and the Al dichloro complex {6-(CH$_2$NMe$_2$)-2-CPh$_3$-4-Me-C$_6$H$_2$O}AlCl$_2$ (**3**, 95% conversion based on the internal standard after 18 h at RT). After this time, the Al complex **1** has completely reacted, whereas the ^{19}F NMR spectrum of the reaction mixture only exhibits resonances for a 1/1 mixture of $B(C_6F_5)_3$ and the anion $MeB(C_6F_5)_3^-$.

3.6.1. Crystal data for 1

Crystals of **1** suitable for X-ray diffraction were obtained at −35 °C from a saturated 1/1 Et_2O–toluene solution of **1**.

Compound **1**: $C_{30}H_{31}AlClNO$, $M = 483.99$ g mol^{-1}; colorless prismatic crystal; $0.10 \times 0.08 \times 0.06$ mm^3; monoclinic; space group $P2_1/n$; $a = 8.950(5)$ Å, $b = 24.015(5)$ Å, $c = 14.220(5)$ Å; $\beta = 104.66(5)°$; $Z = 4$; $D_{calc} = 1.087$ g cm^{-3}; μ(Mo Kα) = 0.179 mm^{-1}; a total of 23 811 reflections; $1.70 < \theta < 30.03$, 8628 independent reflections with 5915 having $I > 2\sigma(I)$; 307 parameters; final results: $R(F) = 0.1090$; $R_w(F) = 0.0767$, Goodness-of-fit = 0.865, maximum residual electronic density = 0.884 e Å^{-3}. Selected crystals were mounted on a Nonius Kappa-CCD area detector diffractometer (Mo Kα, $\lambda = 0.71073$ Å). The complete conditions of data collection (Denzo software) and structures refinements are given below. The cell parameters were determined from reflections taken from one set of ten frames (1.0° steps in phi angle), each at 20 s exposure. The structures were solved using direct methods (SIR97) and refined against F^2 using the SHELXL97 software. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated according to stereo-chemistry and refined using a riding model in SHELXL97. All hydrogen atoms were placed from Fourier differences and refined isotropically.

Acknowledgements

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Appendix A. Supplementary data

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 610951 for compound **1**. 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 http://www.ccdc.cal.ac.uk).

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.07.001.

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[6] $B(C_6F_5)_3$ is one of the best suited reagents for alkyl anion abstraction from the dialkyl Group 4 metallocenes and related compounds. For a review on reactions involving $B(C_6F_5)_3$ as a Lewis acid reagent: see, G. Erker, Dalton Trans. (2005) 1883, In our case, it was anticipated that the greater stability of the $RB(C_6F_5)_3^-$ vs. $ClB(C_6F_5)_3^-$ anion should favor the formation of $\{LX\}AlCl^+$ cations in the reaction between {LX}AlClR aluminium derivatives and $B(C_6F_5)_3$.
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[8] The reaction of the Al compound **1** with $B(C_6F_5)_3$ in the absence of THF or any external Lewis base yielded an intractable mixture of products.
[9] We should point out that the mono-chloro Al complex **1** is stable in CD_2Cl_2 for days at 40 °C and thus does not undergo any ligand exchange (to yield the corresponding Al dimethyl complex and the Al chloro complex **3**, as may be thought given the outcome of the reaction between **1** and $B(C_6F_5)_3$). The Me^- abstraction by $B(C_6F_5)_3$ thus initially occurs at the Al metal center of **1**.
[10] O. Wrobel, F. Schaper, U. Wieser, H. Gregorius, H.H. Brintzinger, Organometallics 22 (2003) 1320.