Neutral and Cationic Methylaluminium Complexes of 2-Anilinotropone Ligands: Synthesis, Characterization, and Reactivity toward Ethylene

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Some new aluminium complexes bearing bidentate monoanionic 2-anilinotroponate ligands have been synthesized and characterized. Reaction of 2-(2,6-diisopropylanilino)tropone or 2-(perfluoroanilino)tropone with $AlMe_3$ (1 equiv.) gave, by methane elimination, compounds [2-(2,6-diisopropylanilino)tropone]$AlMe_2$ (**1**) and [2-(perfluoroanilino)tropone]$AlMe_2$ (**2**), respectively, as yellow solids. Reaction of **1** with 1 equiv. of the ligand furnished, by protodealumination of a second Al–CH_3 bond, the [2-(2,6-diisopropylanilino)tropone]$_2$AlMe derivative **3**. The structure of **3** has been determined by single-crystal X-ray diffraction, showing a five-coordinate aluminium atom with a distorted trigonal-bipyramidal geometry. Compounds **1** and **3** underwent methyl abstraction reactions with $B(C_6F_5)_3$; the resulting cationic species was trapped in the presence of THF in dichloromethane solution. The reactivity of the synthesized compounds in ethylene polymerisation has also been explored.

Introduction

Organometallic aluminium complexes are widely employed in organic synthesis and in catalysis.[1] In particular, organoaluminium compounds are currently used in polymerisation chemistry, e.g. in cationic,[2,3] anionic,[4−6] and ring-opening polymerisation.[7] In addition, alkylaluminium complexes have long been known to catalyse olefin oligomerizations,[8] and are the preferred cocatalysts in various important industrial processes catalysed by transition metals, such as the Ziegler−Natta olefin polymerisation,[9] the Wilke alkene dimerization[10] and the Ziegler nickel effect.[11]

The disclosure by Coles and Jordan in 1997 that certain cationic methylaluminium amidinate compounds promote ethylene polymerisation, although with low activity,[12] has encouraged a growing interest in exploring the reactivity of various aluminium compounds. Dialkylaluminium compounds bearing monoanionic chelating ligands, such as the *N*,*N* bidentate aminotroponiminate,[13] the tridentate *N*,*N*,*N* pyridylaminoamide[14] or the tridentate *O*,*N*,*N* and *O*,*N*,*O* pendant arm Schiff-base ligands[15] showed, after activation with the ionising agents traditionally used in homogeneous Ziegler−Natta catalysis {i.e. $B(C_6F_5)_3$ or $[(C_6H_5)_3C][B(C_6F_5)_4]$}, some activity for ethylene polymerisation catalysis. In this regard, we reported recently the synthesis of alkylaluminium compounds bearing phenoxy-imine or *N*,*N* imino-amide ligands that undergo decomposition reactions after alkyl abstraction with $B(C_6F_5)_3$; the cationic species were instead obtained in the presence of THF. Toluene solutions of the aluminium salicylaldiminate compounds, if activated with $B(C_6F_5)_3$, polymerise ethylene to solid polyethylene with low activity.[16] Furthermore, the simple bis(dichloroaluminium)ethane[17] and alkylaluminium compounds themselves,[18] activated with ionising agents, can catalyse the polymerisation of ethylene, also with low activity.

Although cationic alkyl complexes have been isolated and characterized, it is still unclear if they are directly responsible for the catalytic activity. Monitoring the reaction of alkylaluminium aminotroponiminate cationic complex with [D$_4$]ethylene, Jordan excluded that intact cationic species are the active ethylene polymerisation catalysts, while their main reaction is a β-H transfer to generate the corresponding cationic aluminium hydride.[13b] In fact, according to recent theoretical studies on ethylene polymerisation at aluminium centres, mononuclear aluminium species are unlikely to produce polymers, because chain transfer is too easy relative to propagation.[19] Therefore, more complex structures for the active species have to be considered. Computational studies showed that dinuclear species could be involved and, recently,[19c] an aluminium bis(iminophosphorano)methanediide complex, based on a spirocyclic carbon centre subtended by two $AlMe_2$ units, was shown to polymerise ethylene with higher activity.[20]

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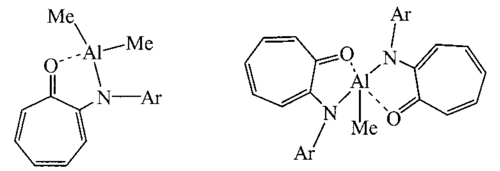
We report here the synthesis and characterization of some new aluminium complexes carrying bidentate monoanionic anilinotropone ligands[21] (Scheme 1), along with their reactivity with ion-generating activators, and some preliminary data on their reactivity in ethylene polymerisation.



1 Ar = 2,6-(C_6H_3)*i*Pr_2
2 Ar = C_6F_5

3 Ar = 2,6-(C_6H_3)*i*Pr_2

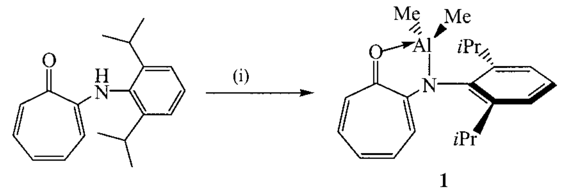
Scheme 1

Results and Discussion

Synthesis of [2-(Anilino)tropone]$AlMe_2$ Derivatives

Recently, Brookhart has described neutral anilinotropone-based nickel(II) compounds[22] that can polymerise ethylene in the absence of an activator, with an activity higher than the analogous neutral nickel salicylaldiminate compounds reported by Grubbs.[23] We therefore synthesized the [2-(anilino)tropone]dimethylaluminium derivatives **1** and **2** to test their reactivity with olefins.

Treatment of 2-(2,6-diisopropylanilino)tropone[21] with $AlMe_3$ (1 equiv.) in toluene at 0 °C for 2 h produces [2-(2,6-diisopropylanilino)tropone]$AlMe_2$ (**1**) as a yellow solid. The reaction proceeds by protodealumination of the Al−CH_3 bond, with concomitant elimination of methane (Scheme 2), as evidenced by ^1H and ^{13}C NMR analysis. In the ^1H NMR spectrum ([D_6]benzene, room temperature) the N*H* singlet (δ = 8.86 ppm) of the ligand disappears, while a new singlet appears at high field [δ = −0.21 ppm (6 H)] accounting for the Al*Me*$_2$ protons. Similarly, in the ^{13}C NMR spectrum ([D_6]benzene, room temperature) a new signal at δ = −8.3 ppm is observed, which is attributable to Al*Me*$_2$ carbon atoms. The signal of the carbonyl carbon atom shifts from δ = 177.3 ppm in the free ligand to δ = 173.7 ppm in the aluminium compound **1**, indicating a change in electronic density after coordination to Al. The ^1H NMR spectrum has one signal for the Al*Me*$_2$ protons, one multiplet for C*H*Me_2 [δ = 3.09 ppm (2 H)] and two doublets for the methyl groups of CH*Me*$_2$ [δ = 1.21 ppm (6 H) and 0.89 ppm (6 H)]. The ^{13}C NMR spectrum confirms this picture: one signal for *C*HMe_2 (δ = 28.7 ppm), two signals for the methyl carbon atoms of CH*Me*$_2$ (δ = 25.9 and 24.5 ppm), one signal for the Al*Me*$_2$ groups. This pattern is compatible with a mirror symmetry passing through the tropone seven-membered ring, and perpendicular to the 2,6-disubstituted phenyl group; the Al*Me*$_2$ groups are equivalent, therefore they should lie symmetrically above and below the plane. Thus, the molecule belongs to the C_s symmetry group.



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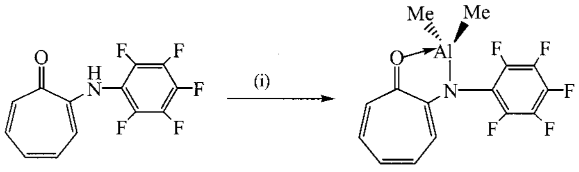
Scheme 2. Reaction conditions: (i): $AlMe_3$, toluene, 0 °C

The compound was further characterized by both FT-IR spectroscopy and EI mass spectrometry. The slight difference in the FT-IR spectrum between the stretching frequency of the carbonyl group in **1** (1598 cm^{-1}) and in the ligand (1601 cm^{-1}) could be explained by considering that in **1** the carbonyl group is reasonably coordinated to the metal atom while in the free ligand the C=O group is involved in hydrogen bonding with the NH group. The molecular ion peak in the EI mass spectrum is at *m*/*z* = 336.

The reaction of 2-(perfluoroanilino)tropone with $AlMe_3$ (1 equiv.) in toluene, at 0 °C, proceeds similarly (Scheme 3), affording [2-(perfluoroanilino)tropone]$AlMe_2$ (**2**) as a yellow solid, which has been characterized by ^1H and ^{13}C NMR analysis and EI mass spectrometry. The NMR spectroscopic data are compatible with a mirror symmetry passing through the seven-membered tropone ring and perpendicular to the perfluorophenyl group, as hypothesized for **1**.



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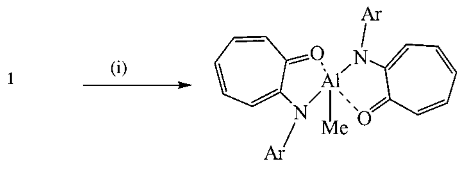
Scheme 3. Reaction conditions: (i): $AlMe_3$, toluene, 0 °C

Synthesis of [2-(2,6-Diisopropylanilino)tropone]$_2$AlMe (3)

The title compound was initially obtained as a secondary product in a preparation of **1**, upon accidentally using an excess of ligand, and was identified by NMR spectroscopy in [D_6]benzene solution. Compound **1** can be converted quantitatively into **3** by simply adding 1 equiv. of the ligand in toluene solution at room temperature (Scheme 4).



3 Ar = 2,6-(C_6H_3)*i*Pr_2

Scheme 4. Reaction conditions: (i): 2-(2,6-diisopropylanilino)tropone, toluene, room temperature

Compound **3** has been fully characterised by ^{1}H and ^{13}C NMR spectroscopy, elemental analyses, EI MS, FT-IR spectroscopy, and single-crystal X-ray diffraction. Diagnostic signals in the ^{1}H NMR spectrum ([D$_6$]benzene, room temperature; Figure 1) are a singlet at $\delta = -0.06$ ppm (3 H), attributable to the Al*Me* protons, four doublets at $\delta = 0.99, 1.03, 1.06, 1.48$ ppm (6 H each) that are attributable to the CHMe_2 protons, and two multiplets for C*H*Me$_2$ at $\delta = 3.07$ (2 H) and 3.37 ppm (2 H). The ^{13}C NMR spectrum exhibits resonances for the corresponding carbon atoms: one signal at $\delta = -6.7$ ppm, attributable to Al*Me*, four signals for the methyl carbon atoms at $\delta = 23.9, 25.4, 25.5$ and 26.5 ppm, and two signals at $\delta = 28.8$ and 29.8 ppm for the *C*HMe$_2$ carbon atoms. This picture is consistent with a C_2 symmetry of the molecule in solution.

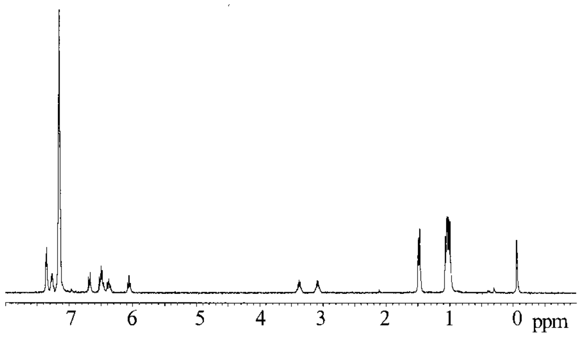


Figure 1. ^{1}H NMR spectrum of **3** (C_6D_6, room temperature)

The compound was further characterized by EI mass spectrometry, which shows the molecular ion peak at *m*/*z* = 603 [M]$^+$ and a peak at *m*/*z* = 587 [M − CH$_3$]$^+$. In the FT-IR spectrum, the stretching frequency of the carbonyl group appears at 1597 cm^{-1}.

Complex **3** crystallized as regular yellow prisms from toluene at −20 °C. The molecular structure of **3** (Figure 2) and the corresponding selected interatomic distances and angles (Table 1) are reported here. The X-ray structure determination shows that the space group is *C*2/*c*, with a crystallographic twofold axis parallel to the *b* axis and passing through the Al atom and methyl group C atom. Therefore the C_2 molecular axis, observed in solution, is preserved in the crystal. The unit cell contains four molecules of **3** and eight molecules of toluene disordered over a mirror plane; this feature affects the overall quality of the structural data.

The compound contains a five-coordinate Al atom with a highly distorted, approximate trigonal-bipyramidal geometry (tbp).[24] The O atoms occupy the apical positions, while the N atoms and the methyl group carbon atom lie in the equatorial plane; the C_2 molecular axis bisects the angle between the two N atoms.

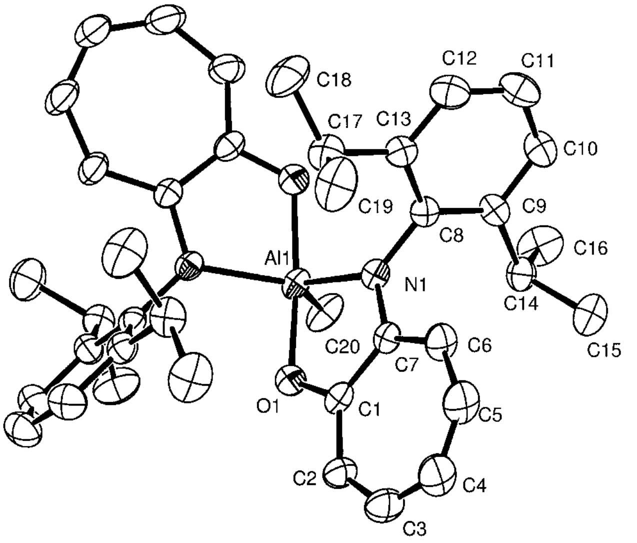
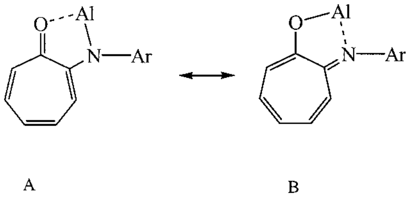


Figure 2. Molecular structure of **3**; thermal ellipsoids are drawn at 20% probability; H atoms omitted for clarity

Table 1. Selected bond lengths [Å] and angles [°]; symmetry-equivalent atoms indicated with the letter "e"

Al(1)−O(1)	1.865(3)	N(1)−Al(1)−O(1)	80.85(16)
Al(1)−N(1)	1.956(4)	N(1)−Al(1)−O(1e)	91.43(16)
Al(1)−C(20)	1.981(6)	O(1)−Al(1)−O(1e)	164.0(2)
O(1)−C(1)	1.292(5)	N(1)−Al(1)−N(1e)	122.3(2)
N(1)−C(7)	1.335(5)	N(1)−Al(1)−C(20)	118.84(12)
N(1)−C(8)	1.429(6)	O(1)−Al(1)−C(20)	97.99(11)
C(1)−C(2)	1.405(6)		
C(1)−C(7)	1.432(6)		
C(2)−C(3)	1.415(7)		
C(3)−C(4)	1.367(8)		
C(4)−C(5)	1.377(8)		
C(5)−C(6)	1.370(6)		
C(6)−C(7)	1.435(6)		

The seven-membered tropone ring is almost planar with rmsd 0.024 Å; carbon atoms C1 and C7 deviate most from the seven-atoms least-squares plane by 0.039(4) and −0.034(4) Å, respectively. A comparison between the carbon−heteroatom bond lengths in compound **3** and in the free ligand[22] evidenced that the C1−O1 bond [1.292(5) Å] is longer than in the free ligand (1.252 Å), while C7−N1 [1.335(5) Å] is statistically almost the same as in the free ligand (1.355 Å). Some contribution from resonance form B in Scheme 5 cannot be excluded.



Scheme 5

The aniline six-membered ring is almost perfectly planar (rmsd 0.005 Å), with the N1, C14, and C17 atoms practically lying in the same plane. The aniline ring forms a dihedral angle of 58.6(1)° with the plane defined by the tropone seven-membered ring.

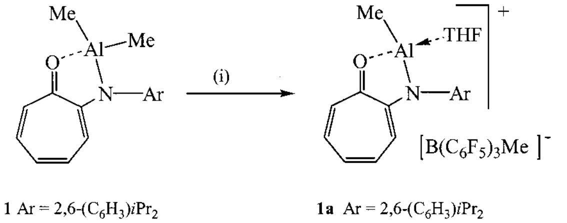
Five-coordinate aluminium complexes play an important role as initiators for the controlled polymerisation of polar monomers. Complexes bearing tetradentate macrocyclic or chelating ligands (such as porphyrins,[25] salen-type ligands[26]), or bulky monoanionic bidentate ligands,[27] catalyse the living ring-opening polymerisation of propene oxide. The generation of highly electrophilic cationic species and their catalytic application has also been explored.[7b,28]

Generation of Cationic Species and Their Reactivity Toward Ethylene

For catalytic applications, cationic aluminium species are more attractive than neutral ones, because of their increased Lewis acidity. The stability of group-13 alkyl cations depends strongly on the ancillary ligand and the kind of counter anion. Bochmann has described the preparation of the bis(cyclopentadienyl)aluminium cation from the corresponding methyl compound after reaction with $B(C_6F_5)_3$;[3] however, simple alkylaluminium compounds, if treated with the activators commonly used in homogeneous olefin polymerisation catalysis {i.e. $B(C_6F_5)_3$ or $[(C_6H_5)_3C][B(C_6F_5)_4]$}, undergo degradation reaction with cleavage of a $B-C_6F_5$ bond.[29] The cationic alkylaluminium species was trapped in the presence of bases[7a] or using coordinating solvents, such as diethyl ether and THF.[30]

We have generated cationic complexes from the synthesized aluminium compounds by NMR tube reactions with $B(C_6F_5)_3$. When **1** and $B(C_6F_5)_3$ are mixed in C_6D_6 at room temperature, a brown oil precipitates, thus preventing NMR solution analysis. The reaction was consequently studied in CD_2Cl_2 solution. After in situ treatment of **1** with of $B(C_6F_5)_3$ (1 equiv.), the ^1H NMR spectrum shows a resonance at $\delta = +0.45$ ppm, which is attributable to the *free* anion $[\mathit{Me}B(C_6F_5)_3]^-$,[31] therefore indicating that the main reaction is methyl abstraction by $B(C_6F_5)_3$. The initially formed cationic species is degraded rapidly, generating a mixture of unidentified organometallic species. Ethylene was added to a freshly prepared solution of **1** and $B(C_6F_5)_3$ in CD_2Cl_2; monitoring the reaction at room temperature showed that ethylene was consumed and that a solid polymer was formed.

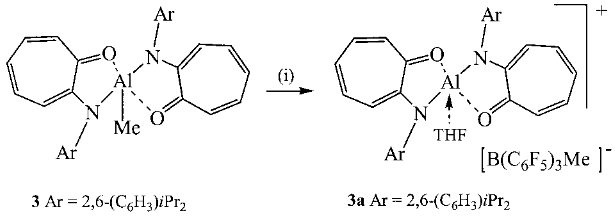
Attempts to isolate and better characterize the cationic species in the absence of bases were unsuccessful. Trapping of the cationic species was instead achieved in the presence of THF. When $B(C_6F_5)_3$ (1 equiv.) was added to a CD_2Cl_2 solution of **1** containing THF (1 equiv.), the THF-coordinated methyl cation of $\{[2\text{-}(2,6\text{-diisopropylanilino})\text{tropone}]\text{AlMe(THF)}\}^+[\text{MeB}(C_6F_5)_3]^-$ (**1a**) was formed (Scheme 6). Characteristic ^1H NMR resonances are the signals at $\delta = -0.27$ ppm for $\text{Al}\mathit{Me}^+$ (3 H) and at $\delta = 0.45$ ppm for $\text{B}\mathit{Me}$ (3 H). The pattern of signals in the ^1H NMR spectrum is consistent with the C_1 symmetry group (i.e. two signals for the $\text{C}\mathit{H}\text{Me}_2$ groups and four doublets for the methyl groups of $\text{CH}\mathit{Me}_2$). Accordingly, the THF methylenic hydrogen atoms in α-positions with respect to the oxygen atom are diastereotopic, and appear as two multiplets at $\delta = 4.40$ (2 H) and 4.26 ppm (2 H); the β-hydrogen atoms, instead, appear as a multiplet centred at $\delta = 2.25$ ppm (4 H). After addition of a further equivalent of THF, the THF methylenic hydrogen atoms in α-positions with respect to the oxygen atom coalesce in a multiplet centered at $\delta = 4.20$ ppm, and the numbers and multiplicity of the signals are the same as in the neutral starting compound, i.e. one signal for the $\text{C}\mathit{H}\text{Me}_2$ and two doublets for the methyl groups of the $\text{CH}\mathit{Me}_2$. Such behaviour can, probably, be explained by assuming, in the presence of excess THF, there is a rapid exchange process between free and bound THF.



Scheme 6. Reaction conditions: (i): $B(C_6F_5)_3$, THF in CD_2Cl_2

Attempts to generate clean cationic species from the monomethylaluminium compound **3** with $B(C_6F_5)_3$ in the absence of coordinating agents were unsuccessful, leading always to a mixture of unidentified species. Addition of ethylene to a freshly prepared solution of **3** and $B(C_6F_5)_3$ did not result in monomer consumption or production of solid polymer, unlike the behaviour of **1** in the analogous experiment (see above). Since compounds **1** and **3** were prepared using the same reagents, but in different stoichiometric ratios, the implication of some metal impurity in the polymerization activity of the aluminium species **1** can be ruled out.[19] In fact, while the reaction of **1** with $B(C_6F_5)_3$ (1 equiv.) generates a cationic methylaluminium compound, abstraction of the methyl group from **3** generates a cationic species that lacks any $Al-C$ bond suitable for chain growth by ethylene insertion.

The cationic species $\{[2\text{-}(2,6\text{-diisopropilanylino})\text{tropone}]_2\text{Al(THF)}\}^+[\text{MeB}(C_6F_5)_3]^-$ (**3a**) was cleanly generated by the reaction of **3** with of $B(C_6F_5)_3$ (1 equiv.) in the presence of THF (1 equiv.) in CD_2Cl_2 (Scheme 7). The product was characterized by ^1H and ^{13}C NMR spectroscopy at room temperature.



Scheme 7. Reaction conditions: (i): $B(C_6F_5)_3$, THF in CD_2Cl_2

In the ^1H NMR spectrum, the singlet of $\text{Al}\mathit{Me}$ of the neutral starting compound **3** disappears, while a new signal appears at $\delta = 0.45$ ppm, which is attributable to the "free" anion $[\mathit{Me}B(C_6F_5)_3]^-$, indicating that alkyl abstraction has occurred. The numbers of signals (i.e. four doublets for the $\mathrm{CH}\mathit{Me}_2$ protons, and two multiplets for $\mathrm{C}\mathit{H}\mathrm{Me}_2$ in the ^{1}H NMR spectrum; four signals for the methyl carbon atoms and two signals for the isopropylic $\mathit{C}\mathrm{HMe}_2$ carbon atom in the ^{13}C NMR spectrum) indicate that the cation preserves the C_2 symmetry observed in solution in the neutral compound. Integration shows that the cation is supported by one molecule of coordinated THF. Interestingly, the THF methylenic hydrogen atoms in α-positions with respect to the oxygen atom, being diastereotopic, appear as two multiplets at $\delta = 4.38$ (2 H) and 3.93 ppm (2 H); the β-hydrogen atoms, instead, appear as a multiplet centred at $\delta = 2.13$ ppm (4 H) (Figure 3). This suggests that the THF molecule substitutes the methyl group of the corresponding neutral compound, and therefore is situated on the C_2 symmetry axis.

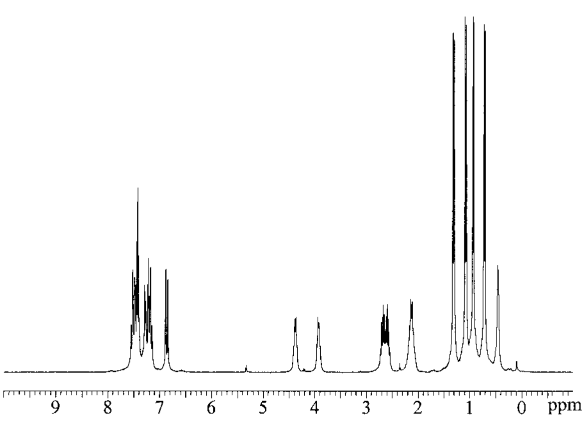


Figure 3. ^{1}H NMR spectrum of **3a** (CD_2Cl_2, room temperature)

Conclusions

Two new 4-coordinate aluminium complexes, namely [2-(2,6-diisopropylanilino)tropone]AlMe_2 (**1**) and [2-(perfluoroanilino)tropone]AlMe_2 (**2**), have been synthesized. A five-coordinate bis[2-(2,6-diisopropylanilino)tropone]AlMe derivative (**3**) has also been synthesized and characterized by single-crystal X-ray diffraction studies, which indicate a distorted trigonal-bipyramidal geometry around Al. Compounds **1** and **3** undergo methyl abstraction reactions with $B(C_6F_5)_3$; the resulting cationic species are stable in the presence of THF in dichloromethane solution. The reactivity of the synthesized compounds in ethylene polymerisation has also been explored. Interestingly, after reaction with $B(C_6F_5)_3$, compound **1** polymerizes ethylene to give a solid polymer, whereas compound **3** does not. This finding indicates that polymerization does not occur at a different metal contaminant.[19]

As Lewis acids, neutral, but especially cationic aluminium compounds, should be useful as catalysts to polymerize substrates containing a Lewis-basic atom. Experiments are in progress to ascertain if these compounds could be involved in the polymerization of polar monomers.

Experimental Section

General: Sensitive materials were manipulated under dry nitrogen using Schlenk or glove-box techniques. Toluene, heptane, and THF were heated under reflux in the presence of sodium and benzophenone and distilled under nitrogen prior to use. AlMe_3 was purchased from Aldrich and used as received. The 2-(2,6-diisopropylanilino)tropone and (perfluoroanilino)tropone ligands,[21] and $B(C_6F_5)_3$[30] were synthesized according to literature procedures. NMR spectra were recorded with a Bruker Avance 400 MHz spectrometer; chemical shifts were referenced to the residual protio impurity of the deuterated solvent. EI MS data were obtained with a Finnigan Thermoquest GCQ Plus 2000 spectrometer, using a direct exposure probe. Infrared spectra were recorded with a FT-IR Bruker Vector 22.

[2-(2,6-Diisopropylanilino)tropone]$\mathbf{AlMe_2}$ (1): A toluene solution of 0.21 M AlMe_3 (4 mL, 0.85 mmol) was slowly added to a solution of 2-(2,6-diisopropylanilino)tropone (240 mg, 0.85 mmol) in toluene (15 mL) at 0 °C with stirring. The solution was then stirred for 2 h. Subsequently, the volatiles were removed under reduced pressure to give the product as an orange solid (yield 229 mg, 80%). ^{1}H NMR (400 MHz, C_6D_6): $\delta = 7.17$ (d, 2 H, C*H*), 7.07 (d, 1 H, C*H*), 6.55 (m, 1 H, C*H*), 6.44 (d, 1 H, C*H*), 6.34 (m, 1 H, C*H*), 6.11 (t, 1 H, C*H*), 3.09 [m, 2 H, $\mathrm{C}\mathit{H}(\mathrm{CH}_3)_2$], 1.21 [d, 6 H, $\mathrm{CH}(\mathrm{C}\mathit{H}_3)_2$], 0.89 [d, 6 H, $\mathrm{CH}(\mathrm{C}\mathit{H}_3)_2$], −0.21 [s, 6 H, $\mathrm{Al}(\mathrm{C}\mathit{H}_3)_2$] ppm. ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 7.38-7.28$ (m, 3 H, C*H*), 7.28 (t, 2 H, C*H*), 6.87 (t, 2 H, C*H*), 6.57 (d, 1 H, C*H*), 2.93 [m, 2 H, $\mathrm{C}\mathit{H}(\mathrm{C}\mathit{H}_3)_2$], 1.20 [d, 6 H, $\mathrm{CH}(\mathrm{C}\mathit{H}_3)_2$], 0.99 [d, 6 H, $\mathrm{CH}(\mathrm{C}\mathit{H}_3)_2$], −0.74 [s, 6 H, $\mathrm{Al}(\mathrm{C}\mathit{H}_3)_2$] ppm. ^{13}C NMR (100 MHz, C_6D_6): $\delta = 173.7$ (C=O), 167.4 (C−N), 144.4, 139.9 (*C*H), 138.4 (*C*H), 126 (*C*H), 125.7 (*C*H), 123.6 (*C*H), 122.3 (*C*H), 28.7 [$\mathit{C}\mathrm{H}(\mathrm{CH}_3)_2$], 25.9 [$\mathrm{CH}(\mathit{C}\mathrm{H}_3)_2$], 24.5 [$\mathrm{CH}(\mathit{C}\mathrm{H}_3)_2$], −8.3 [$\mathrm{Al}(\mathit{C}\mathrm{H}_3)_2$] ppm. EI MS (35 eV): *m*/*z* = 336 $[M]^+$, 324 $[M - CH_3]^+$. FT-IR: $\tilde{\nu} = 1598$ (C=O) cm^{-1}. $C_{21}H_{28}AlNO$ (337.44): calcd. C 74.75, H 8.36, N 4.15; found C 74.54, H 8.56, N 4.29.

[2-(Perfluoroanilino)tropone]$\mathbf{AlMe_2}$ (2): A solution of 2-(perfluoroanilino)tropone (300 mg, 1.04 mmol) in dry toluene (10 mL) was added dropwise to a toluene solution of 0.26 M AlMe_3 (10 mL, 1.14 mmol) at 0 °C. The solution was then stirred for 2 h and left to reach room temperature. The resulting solution was subsequently concentrated and cooled to −20 °C; compound then **2** precipitated as an orange powder; yield 150 mg (42%). ^{1}H NMR (400 MHz, C_6D_6): $\delta = 6.99$ (d, 1 H, C*H*), 6.52 (t, 2 H, C*H*), 6.18 (t, 2 H, C*H*), −0.17 [s, 6 H, $\mathrm{Al}(\mathrm{C}\mathit{H}_3)_2$]. ^{13}C NMR (100 MHz, C_6D_6): $\delta = 175.1$ (C-1), 165.8 (C-2), 139.7 (*C*H), 139.1 (*C*H), 126.2 (*C*H), 124.3 (*C*H), 118.9 (*C*H), −9.3 [$\mathrm{Al}(\mathrm{CH}_3)_2$] ppm. EI MS(35 eV): *m*/*z* = 346 $[M]^+$, 328 $[M - CH_3]^+$.

[2-(2,6-Diisopropylanilino)tropone]$\mathbf{_2}$AlMe (3): [2-(2,6-Diisopropilanilino)tropone]AlMe_2 (82 mg, 0.24 mmol) was dissolved in dry toluene (10 mL). A solution of 2-(2,6-diisopropylanilino)tropone (68 mg, 0.24 mmol) in toluene (5 mL) was then added and the resulting solution stirred at room temperature for 2 h. The volatiles were then removed under reduced pressure to give the product as an orange solid in almost quantitative yield. ^{1}H NMR (400 MHz, C_6D_6): $\delta = 7.34$ (d, 4 H, C*H*), 7.26 (m, 2 H, C*H*), 6.68 (d, 2 H, C*H*), 6.49 (m, 4 H, C*H*), 6.47 (t, 2 H, C*H*), 6.04 (t, 2 H, C*H*), 3.37 [m, 2 H, $\mathrm{C}\mathit{H}(\mathrm{CH}_3)_2$], 3.07 (m, 2 H, $\mathrm{C}\mathit{H}(\mathrm{CH}_3)_2$], 1.48 [d, 6 H, $\mathrm{CH}(\mathrm{C}\mathit{H}_3)$], 1.06 [d, 6 H, $\mathrm{C}\mathit{H}(\mathrm{C}\mathit{H}_3)$], 1.03 [d, 6 H, $\mathrm{C}\mathit{H}(\mathrm{C}\mathit{H}_3)$], 099 [d, 6 H, $\mathrm{C}\mathit{H}(\mathrm{C}\mathit{H}_3)$], −0.06 (s, 3 H, $\mathrm{AlC}\mathit{H}_3$) ppm. ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 7.32-7.03$ (m, 10 H, C*H*), 6.70 (m, 4 H, C*H*), 6.46 (d, 2 H, C*H*), 3.05 [m, 2 H, $\mathrm{C}\mathit{H}(\mathrm{CH}_3)_2$], 2.77 [m, 2 H, $\mathrm{C}\mathit{H}(\mathrm{CH}_3)_2$], 1.27 [d, 6 H, CH(C*H*$_3$)], 1.16 [d, 6 H, CH(C*H*$_3$)], 1.05 [d, 6 H, CH(C*H*$_3$)], 0.78 [d, 6 H, CH(C*H*$_3$)], −0.83 (s, 3 H, AlC*H*$_3$) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 175.2 (C=O); 166.6 (C−N); 144.4, 143.8, 142.3, 138.4, 137.5, 127.0, 125.5, 124.4, 124.1, 122.5, 121.1; 29.8 and 28.8 [*C*H(CH$_3$)$_2$]; 26.5, 25.5, 25.4, and 23.9 [CH(*C*H$_3$)$_2$]; −6.7 (Al*C*H$_3$) ppm. EI MS(35 eV): *m/z* = 603 [M]$^+$, 587 [M − CH$_3$]$^+$. FT-IR: $\tilde{\nu}$ = 1597 (C=O) cm^{-1}. $C_{39}H_{47}N_2O_2Al$ (602.79): calcd. C 77.71, H 7.86, N 4.65; found C 77.23, H 8.16, N 4.34.

Generation of {[2-(2,6-Diisopropylanilino)tropone]AlMe(THF)}$^+$-[MeB(C_6F_5)$_3$]$^-$ (1a): Compound **1** (17 mg, 50 µmol) was dissolved in CD_2Cl_2 (0.5 mL). THF (4 µL, 50 µmol) and B(C_6F_5)$_3$ (26 mg, 50 µmol) were then added sequentially, and the so-obtained solution was analysed by NMR spectroscopy at room temperature. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.76 (m, 2 H, C*H*), 7.66 (m, 1 H, C*H*), 7.46−7.35 (m, 4 H, C*H*), 6.99 (d, 1 H, C*H*), 4.40 (m, 2 H, OC*H*$_2$), 4.26 (m, 2 H, O-C*H*$_2$), 2.66 (m, 1 H, C*H*(CH$_3$)$_2$], 2.57 (m, 1 H, C*H*(CH$_3$)$_2$], 2.25 (s, 4 H, C*H*$_2$), 1.21 (d, 6 H, CHC*H*$_3$), 1.01 (d, 3 H, CHC*H*$_3$), 0.92 (d, 3 H, CHC*H*$_3$), 0.45 (s, 3 H, BC*H*$_3$), −0.27 (s, 3 H, AlC*H*$_3$) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 169.4 (C=O), 168.0, 144.4, 143.8, 142.3, 141.3, 134.5, 133.2, 129.5, 128.0, 126.6, 125.8, 125.3, 76.2 (O*C*H$_2$), 29.2 (2 peaks overlapped, *C*H), 25.9 (*C*H$_2$CH$_2$O), 25.0, 24.8, 23.9 (CH*C*H$_3$), 10.0 (B*C*H$_3$) ppm. Successively, one further eqivalent of THF was added to the solution, and the sample analysed by NMR spectroscopy at room temperature. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.65 (m, 2 H, C*H*), 7.55 (m, 1 H, C*H*), 7.46−7.27 (m, 4 H, C*H*), 6.90 (d, 1 H, C*H*), 4.20 (s, 8 H, OC*H*$_2$), 2.60 [m, 2 H, C*H*(CH$_3$)$_2$], 2.11 (s, 8 H, C*H*$_2$), 1.20 (d, 6 H, CHC*H*$_3$), 1.00 (d, 6 H, CHC*H*$_3$), 0.46 (s, 3 H, BC*H*$_3$), −0.48 (s, 3 H, AlC*H*$_3$) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 169.4 (C=O), 167.9, 144.0, 143.2, 142.2, 133.0, 129.4, 127.8, 126.2, 125.3, 125.2; 76.0 (O*C*H$_2$), 29.2 (*C*H), 25.7 (*C*H$_2$CH$_2$O), 25.4, 23.7 (CH*C*H$_3$), 10.2 (B*C*H$_3$), −14.0 (Al*C*H$_3$) ppm.

Generation of {[2-(2,6-Diisopropylanilino)tropone]$_2$Al(THF)}$^+$-[MeB(C_6F_5)$_3$]$^-$ (3a): Compound **3** (15 mg, 25 µmol) was dissolved in CD_2Cl_2 (0.5 mL). Dry THF (2 µL, 25 µmol) and B(C_6F_5)$_3$ (13 mg, 25 µmol) were then added sequentially, and the resulting solution was analysed by NMR spectroscopy at room temperature. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.60−7.10 (m, 14 H) and 6.85 (d, 2 H) (phenyl and tropone *H*), 4.38 (m, 2 H, OC*H*$_a$H$_b$), 3.93 (m, 2 H, OCH$_a$*H*$_b$), 2.67 [m, 2 H, C*H*(CH$_3$)$_2$], 2.59 [m, 2 H, C*H*(CH$_3$)$_2$], 2.13 (m, 4 H, C*H*$_2$), 1.32 [d, 6 H, CH(C*H*$_3$)], 1.08 [d, 6 H, CH(C*H*$_3$)], 0.93 [d, 6 H, CH(C*H*$_3$)], 0.72 [d, 6 H, CH(C*H*$_3$)], 0.45 (s, 3 H, BC*H*$_3$) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 169.9 (*C*=O), 167.4, 143.8, 143.2 (quaternary carbon atoms), 140.8 (*C*H), 140.2 (*C*H), 138.5 (quaternary carbon atom), 130.3 (*C*H), 128.3 (*C*H), 125.4 (*C*H), 123.9 (*C*H), 75.7 (O*C*H$_2$CH$_2$), 29.7 [*C*H(CH$_3$)$_2$], 29.2 [*C*H(CH$_3$)$_2$], 25.9 (OCH$_2$*C*H$_2$), 24.9 [CH(*C*H$_3$)], 23.7 [CH(*C*H$_3$)] ppm.

X-ray Crystallography: A prismatic yellow crystal of **3** (0.56 × 0.48 × 0.40 mm) was selected and mounted in a Lindemann capillary under an inert gas. Diffraction data were then measured at room temperature with a Rigaku AFC7S diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71069 Å). Data reduction was performed with the crystallographic package TEXSAN.[32] The ψ-scan method was used to correct data for absorption. Structures were solved by direct methods using the program SIR92[33] and refined by means of full-matrix least squares based on F^2 including all diffraction data using the program SHELXL-97.[34] The electron density map revealed a disordered toluene molecule. A rigid body refinement was performed for the solvent molecule, considering two distinct toluene molecules with half occupancy. The hydrogen atoms of the methyl groups were assumed to be disordered over two sites rotated 60° to each other. Anisotropic displacement parameters were used for all non-hydrogen atoms except those belonging to the solvent molecule. Hydrogen atoms were positioned geometrically and refined using a riding model. Finally, a total of 226 parameters were refined considering 4174 intensity data. Maximum and minimum residual densities were 0.35 and −0.34 e·Å^{-3}, respectively. Final disagreement indices were R_1 = 0.0829 for 1336 reflections with $F_o > 4\sigma(F_o)$, R_1 = 0.255 and wR_2 = 0.146 for all 4174 data. ORTEP drawings performed by means of the program ORTEP32.[35] Crystallographic data for **3**: Formula: $C_{39}H_{47}AlN_2O_2 \cdot 2C_7H_8$, *M* = 787.03, system: monoclinic, space group *C*2/*c*, *Z* = 4; *a* = 18.321(6), *b* = 10.145(3), *c* = 25.506(7) Å; β = 91.40(3)°, *V* = 4739(2) Å^3, D_x = 1.103 g·cm^{-3}, $\mu_{calcd.}$ = 0.08 mm^{-1}. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-204539. Copies of the data may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 EZ, UK [Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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