New Neutral and Cationic Dialkylaluminium Complexes Bearing Imino-Amide or Imino-Phenoxide Ligands: Synthesis, Characterization and Reactivity With Olefins

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The synthesis and the characterization of some new aluminium complexes carrying bidentate monoanionic imino-amide or imino-phenoxide ligands are described. Reaction of 1-(*o*,*o*′-diisopropylphenylamino)-6-(*o*,*o*′-diisopropylphenylimino)cyclohexene with $AlMe_3$ proceeded by methane elimination to produce the yellow compound dimethylaluminium *N*-(*o*,*o*′-diisopropylphenyl)-6-[*N*-(*o*,*o*′-diisopropylphenyl)-imido]-1-cyclohexen-1-amide (**1**). In contrast, reaction of the same ligand with $AlEt_3$ under the same experimental conditions involved the 1,4-addition of $AlEt_3$ to the α,β-unsaturated imine, and led to the highly crystalline diethylaluminium *N*-(*o*,*o*′-diisopropylphenyl)-2-[(*o*,*o*′-diisopropylphenyl)amino]-3-ethyl-1-cyclohexen-1-amide (**2**). The structures of compounds **1** and **2** were determined by single-crystal X-ray diffraction. Thermolysis of **2** gave rise to ethane elimination, and led to the oily bis(amido) monoethyl derivative. Treatment of the salicylaldimine ligands 3-*t*Bu-2-(OH)C_6H_3CH=N–R with $AlMe_3$ yielded the dimethylaluminium compounds {3-*t*Bu-2-(O)C_6H_3CH=N–R}$AlMe_2$ [R = C_6H_5 (**3**); 2,6-*i*$Pr_2C_6H_3$ (**4**); and C_6F_5 (**5**)]. Compounds **1**, **3**, and **5** underwent methyl abstraction reactions with $B(C_6F_5)_3$; trapping of the cationic species was accomplished in the presence of THF in dichloromethane solution. Preliminary polymerization tests were carried out for the synthesized Al complexes. Toluene solutions of **3**, **4**, and **5**, when activated with 1 equiv. of $B(C_6F_5)_3$, polymerised ethylene (1 atm) to solid polyethylene with low activity.

Introduction

Since the disclosure by Ziegler of the "aufbau" reaction, alkylaluminium compounds have been known as olefin oligomerization catalysts, because of the displacement reaction competing with a "smooth stepwise addition of ethylene".[1] In 1992 Martin demonstrated that the growth reaction of ethylene at bis(dichloroaluminium)ethane and trialkylaluminium produces, with low activity, polyethylene of high molecular weight and thermoplastic character.[2] More recently, Sen et al. reported that simple alkylaluminium compounds, after reaction with the activators commonly used in the homogeneous olefin polymerization catalysis {i.e. $B(C_6F_5)_3$, $[(C_6H_5)_3C][B(C_6F_5)_4]$ or $[(C_6H_5)N(CH_3)_2H][B(C_6F_5)_4]$} are able to catalyse the polymerization of ethylene and propene, although with low activity.[3] The authors hypothesize that neutral aluminium species, such as $[(R)(C_6F_5)_2Al]_x$, are the active catalysts operating in these systems.[3] Actually, the reaction of $AlMe_3$ with $[(C_6H_5)_3C][B(C_6F_5)_4]$ gives the transient species $[AlMe_2]^+[B(C_6F_5)_4]^-$ which immediately decomposes by ligand exchange to $Al(C_6F_5)_3$ and BMe_3.[4,5] Trapping of the cationic alkylaluminium species was achieved in the presence of bases,[6] or using coordinating solvents such as diethyl ether and THF.[7] Base-free cationic species are expected to be highly electrophilic, and therefore more active as olefin polymerization catalysts.

The stability of base-free group-13 alkyl cations seems to be strongly dependent on the ancillary ligand and the kind of counter-anion. Bochmann described the bis(cyclopentadienyl)aluminium cation as an initiator for the carbocationic polymerization of isobutylene,[8] and Jordan reported the synthesis and characterization of several cationic aluminium complexes incorporating chelating nitrogen-based ligands, able to polymerise ethylene.[9] According to Jordan's results, a few related aluminium derivatives carrying chelating monoanionic ligands have also been shown to polymerise ethylene with comparably low activity.[10]

In this paper we report on the synthesis and the characterization of some new aluminium complexes carrying bidentate monoanionic imino-amide or imino-phenoxide ligands (Scheme 1) and some preliminary data on their reactivity with ion-generating activators and the subsequent reactivity in ethylene polymerization.[11]

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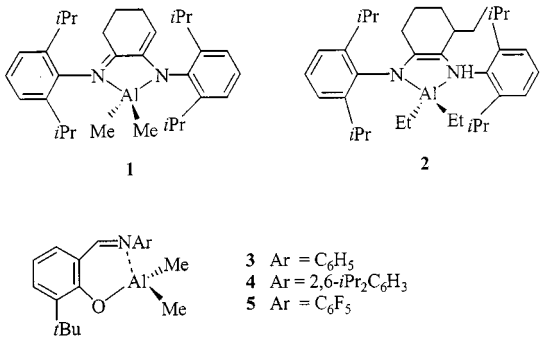
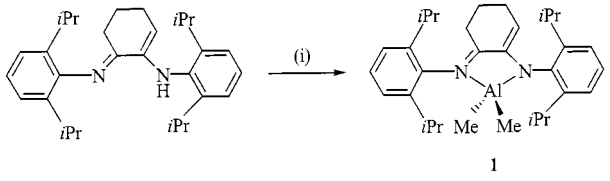


Scheme 1

Results and Discussion

Treatment of 1-(*o*,*o*′-diisopropylphenylamino)-6-(*o*,*o*′-diisopropylphenylimino)cyclohexene[12] with $AlMe_3$ in heptane at room temperature afforded the dimethyl complex **1** as a yellow solid in high yield. The disappearance of the N−*H* signal of the ligand in the ^1H NMR spectrum of **1** ([D_6]benzene, room temperature), and the appearance of a high-field signal (δ = −0.37, 6 H) compatible with Al*Me*$_2$ protons, reveal that the reaction proceeds by protodealumination of the Al−CH_3 bond with concomitant elimination of methane (Scheme 2). Although the molecule belongs to the C_1 symmetry group, the presence of only one signal for the Al*Me*$_2$ protons in the ^1H NMR spectrum, and the signals pattern in the ^{13}C NMR spectrum (i.e. 4 signals for the methyl groups of the isopropyl groups, 2 signals for C*H*Me$_2$) are compatible with the presence of a "pseudo" mirror symmetry passing through the Al and the two nitrogen atoms. This therefore indicates that, under the analysis conditions (i.e. room temperature, benzene solution), the change in conformation of the cyclohexene ring is fast on the NMR time scale.



Scheme 2. Reaction conditions: (i) $AlMe_3$, heptane, room temperature

Crystals of **1** suitable for an X-ray structure determination were grown from toluene at −20 °C. The compound crystallized as prismatic crystals in the monoclinic space group $P2_1/n$, the asymmetric unit containing one discrete molecule of **1** and half of a centrosymmetric disordered toluene molecule. The molecular structure of **1** is shown in Figure 1; selected bond lengths and angles are given in Table 1. The coordination environment about the Al atom is approximately tetrahedral, with Al−CH_3 distances comparable to those observed in analogous β-diketiminato[13] and imino-amide complexes.[14] The Al−N distances differ slightly from each other [1.968(11) and 1.897(10) Å], suggesting a dative and a sigma bond, respectively, as already observed in the just cited imino-amide compounds.[14] Inspection of the bond lengths within the −N1−C1(C6)−C2(C3)−N2− moiety suggests the presence of a partial delocalization.[14,15] The puckering of the cyclohexene ring is described by the deviations of the atoms C3, C4, C5, and C6 from the least-square plane defined by N1, C1, C2, and N2 atoms (rmsd 0.005); these deviations are 0.01(2) Å, 0.45(3) Å, 0.25(3), and 0.02(2) Å, respectively. The Al atom lies under the previously defined plane and deviates by −0.22(2) Å. The aromatic rings C7···C12 and C19···C24 are planar with rmsd of 0.027 and 0.017, respectively, and are almost perpendicular to the Al−N1−C1−C2−N2 ring. The dihedral angles between the five-atom Al−N1−C1−C2−N2 plane and each aromatic ring are 87.8(4)° and 86.6(4)°.

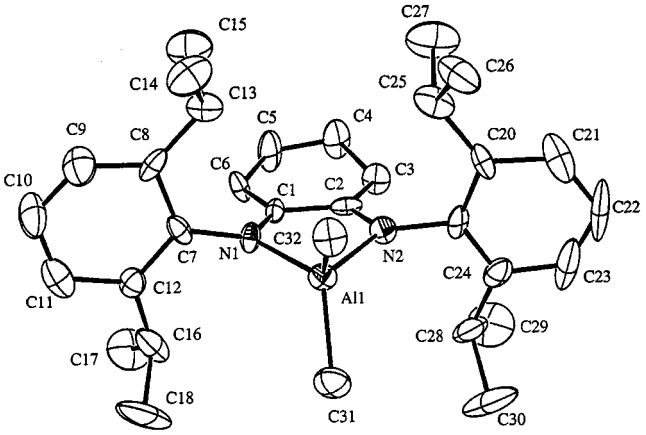


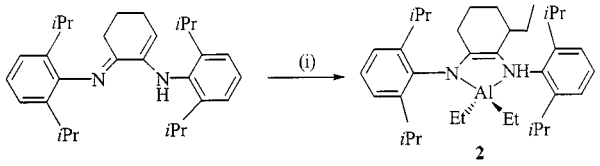
Figure 1. Molecular structure of **1**; thermal ellipsoids are drawn at 20% probability level; hydrogen atoms have been omitted for clarity

Table 1. Selected bond lengths [Å] and angles [°] for compounds **1** and **2**

1	**2**
Al−C31 1.968(12)	Al−C33 1.974(6)
Al−C32 1.961(12)	Al−C35 1.958(6)
Al−N1 1.968(11)	Al−N1 2.045(4)
Al−N2 1.897(10)	Al−N2 1.856(4)
N1−C1 1.344(14)	N1−C1 1.494(5)
N2−C2 1.333(14)	N2−C2 1.393(6)
C1−C2 1.434(15)	C1−C2 1.348(6)
C1−C6 1.385(15)	C1−C6 1.499(6)
C2−C3 1.49(2)	C2−C3 1.494(6)
C3−C4 1.44(2)	C3−C4 1.527(7)
C4−C5 1.43(2)	C4−C5 1.511(7)
C5−C6 1.47(2)	C5−C6 1.521(7)
C31−Al−C32 110.0(6)	C33−Al−C35 112.2(3)
N2−Al−N1 84.2(5)	N2−Al−N1 85.9(2)
N2−Al−C32 114.3(5)	N1−Al−C35 117.0(2)
N2−Al−C31 113.9(5)	N1−Al−C33 102.5(2)
C31−Al− N1 118.0(6)	C33−Al− N2 115.5(2)
C32−Al−N1 114.5(5)	C35−Al−N2 119.8(2)

Interestingly, the reaction of the same ligand with $AlEt_3$ under identical conditions did not afford the expected di-

ethylaluminium imino-amide derivative analogous to **1**, but an orange crystalline solid, characterized by X-ray diffraction and NMR spectroscopy as the diethylaluminium complex **2**, featuring a *C*-alkylated amino-amido ligand (Scheme 3). Particularly diagnostic in the ^{1}H NMR spectrum of **2** ([D$_6$]benzene, 25 °C) (Figure 2) is the broad singlet at δ = 6.55 (1 H, N*H*), indicating that the amine function is not deprotonated, while the signal of the unsaturation on the six-membered carbon ring of the ligand is absent, as a consequence of the ethyl addition. The ethyl groups bound to the aluminium atom are not equivalent, thus resulting in two well-defined patterns of signals at high field; in particular the methylene hydrogen atoms in each ethyl group are diastereotopic and appear as a double quadruplet (δ = 0.18, 2 H, AlCH_2CH$_3$) and two multiplets (δ = 0.52−0.28, 2 H, AlCH'_2CH$_3$).



Scheme 3. Reaction conditions: (i) AlEt$_3$, heptane, room temperature

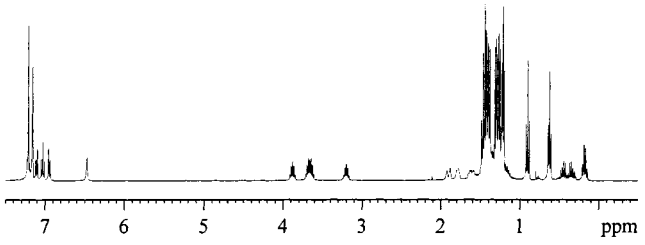


Figure 2. ^{1}H NMR spectrum of **2** (C$_6$D$_6$, room temperature)

This picture is consistent with a C_1 symmetry, that is confirmed by the number of signals in the ^{13}C NMR spectrum [i.e. 4 signals for *C*H(CH$_3$)$_2$, 8 signals for CH(*C*H$_3$)$_2$, 2 signals for AlCH$_2$*C*H$_3$ (δ = 9.6 and 9.0), and 2 broad signals for Al*C*H$_2$CH$_3$ (δ = 0.95 and −0.5)].

Complex **2** was crystallized from toluene at −20 °C. The molecular structure of **2** is shown in Figure 3; selected bond lengths and angles are given in Table 1. The coordination environment about the Al atom is almost tetrahedral with Al−Et bond lengths displaying usual values. The distances Al−N1 and Al−N2 are 2.045(4) Å and 1.856(4) Å, respectively, as observed in analogous aluminium compounds bearing a monoanionic chelating secondary amine-amido ligand.[16] The ligand bite angle N2−Al−N1 measures 85.9(2)° and differs significantly from the values previously observed in analogous secondary amine-amido compounds[16] [88.4(1)−93.6(3)°]. This feature can be ascribed to the different nature of the −N−C−C−N− backbone in compound **2**, which is the only one showing a central double bond. The five atom Al−N1−C1−C2−N2 ring is planar with rmsd = 0.034. The C3 and C6 atoms deviate from the plane by −0.025 and 0.190 Å, respectively. The aromatic rings C9···C14 and C21···C26 are planar with rmsd of 0.004 and 0.007, respectively. The C21···C26 ring lies perpendicularly to the five-atom Al−N1−C1−C2−N2 plane with a dihedral angle between the two mentioned planes of 89.3(1)°. The other aromatic ring cannot assume the same conformation with respect to the five-atom plane because of the steric hindrance of the ethyl group on the cyclohexene ring, thus resulting in a dihedral angle of 83.6(1)°.

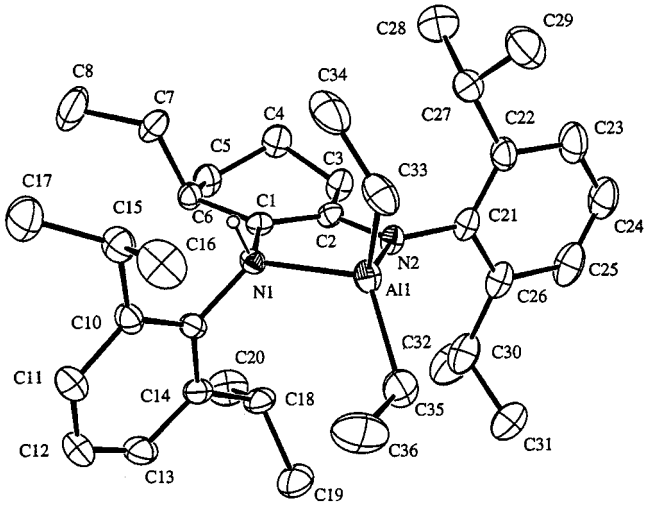
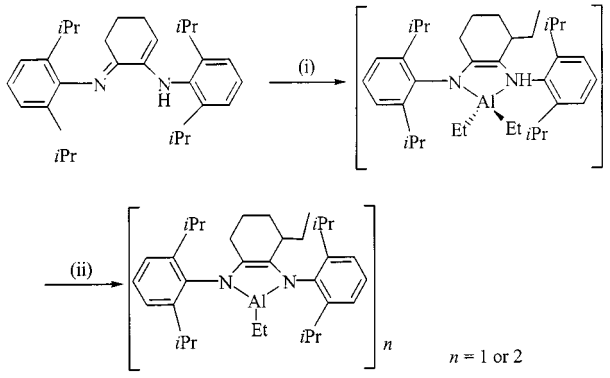


Figure 3. Molecular structure of **2**; thermal ellipsoids are drawn at 20% probability level; hydrogen atoms have been omitted for clarity, with the exception of the amine hydrogen atom

A reasonable reaction pathway leading to compound **2** involves 1,4-addition of AlEt$_3$ to the α,β-unsaturated imine, resulting in alkylation of the cyclohexene moiety of the ligand to give the diethylaluminium amido-amino complex **2**. Although we are not aware of similar reactions for α,β-unsaturated imines, there are many examples of this kind for α,β-unsaturated carbonyl derivatives. Addition of AlR$_2$I to enones, or addition of AlPh$_3$ to chalcone, for example, occurs in this manner almost quantitatively; with α,β-unsaturated ketones, in general, the 1,4-addition of AlR$_3$ can become the principal mode of reaction, and proceeds via initial coordination of the aluminium reagent at the carbonyl group.[17] We hypothesize that, also in our case, the coordination of the AlEt$_3$ is required prior to nucleophilic attack of the ethyl group to the ligand. Actually, the *pre*-coordination of the alkylaluminium compound to the iminic nitrogen atom should increase the electrophilic character of the β-unsaturated carbon atom on the cyclohexene ring, thus supporting the 1,4-addition. Moreover, it is well established that N,N-bidentate ligands, such as the closely related α-diimines, form initial complexes with trialkylaluminium in which only one N-atom is bonded to the aluminium centre.[18]

It is an open question why such a different behaviour is observed by just changing the alkyl group bound to Al from methyl to ethyl. It is, however, evident that the ligand can behave both as a Lewis acid and as a Brønsted acid, and actually nucleophilic addition is observed with AlEt$_3$, while AlMe$_3$ serves as a deprotonating agent.

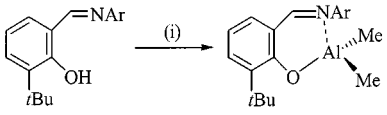
With the aim of obtaining the protodealumination product analogous to **1**, we performed the reaction of the ligand with $AlEt_3$ in refluxing toluene. Removal of volatiles in vacuo left a red oil, that, on the basis of ^1H and ^{13}C NMR analysis, was identified as the bis(amido)monoethylaluminium derivative, possibly derived by thermolysis of **2** by ethane elimination (Scheme 4). Comparing the ^1H NMR spectrum ([D_6]benzene, 25 °C) of the thermolysis product with the ligand spectrum, we noticed the lack of both the resonances of N*H* and =C*H* of the cyclohexene ring. On the other hand, diagnostic signals are a quadruplet at $\delta = 0.33$ (2 H) and a triplet at $\delta = 0.85$ (3 H) attributable to one ethyl group bound to the aluminium atom, and a triplet at $\delta = 0.57$ (3 H) for the CH_3CH$_2$− on the cyclohexene ring. We suppose that, at higher temperatures, the reaction generates first the 1,4-addition product **2**, which rapidly decomposes by ethane elimination resulting in the monoethyl derivative. We cannot determine if the compound is a monomer or a dimer; unfortunately, ^{27}Al NMR experiments were precluded by the probe signal noise.



Scheme 4. Reaction conditions: (i) $AlEt_3$, refluxing toluene; (ii) − C_2H_6

While the five-coordinate alkyl(Salen)group-13 complexes have been largely studied and used in many catalytic reactions,[19] only a few reports concerning the related lower coordinate dialkyl(salicylaldiminato)aluminium compounds have appeared in the literature.[10b,11] We have synthesized the dimethyl(salicylaldiminato)aluminium compounds **3** and **4**, and the perfluoro derivative **5** with the aim to test their reactivity in olefin polymerization. Actually, recent reports by Coates[20a] and by Fujita[20b] described titanium complexes carrying salicylaldiminato ligands with electron-withdrawing substituents that show increased activity in the polymerization of olefins.

Compounds **3**−**5** were prepared in good yields as yellow solids by treating the related ligand with $AlMe_3$ (1:1 ratio) in heptane at room temperature (Scheme 5). Reactions cleanly proceed by protodealumination of the Al−CH_3 bond with concomitant elimination of methane. Products were characterized by ^1H and ^{13}C NMR (room temperature, C_6D_6 solution), revealing similar features. The methyl groups bound to the aluminium atom show characteristic resonances at $\delta \approx -0.30$ in the ^1H NMR spectrum, and between $\delta = -8$ and -9 in the ^{13}C NMR spectrum. No differences were observed for the resonances of the *tert*-butyl substituent on the phenoxy group; for all the complexes the C(CH_3)$_3$ signal appeared at $\delta \approx 1.5$ in ^1H NMR spectrum, while the ^{13}C NMR resonances for *C*Me$_3$ and C*Me*$_3$ are shown at $\delta = 35.7$ and 29.8, respectively. Diagnostic signals for the imine function appear at $\delta \approx 7.5$ in the ^1H NMR spectrum, and between $\delta = 170$ and 180 in the ^{13}C NMR spectrum. Interestingly, in the ^1H NMR spectrum of **5**, the Al*Me* resonance appears as a triplet ($J = 1.4$ Hz), which is probably due to the coupling with the α-fluorine atoms of the C_6F_5 group.

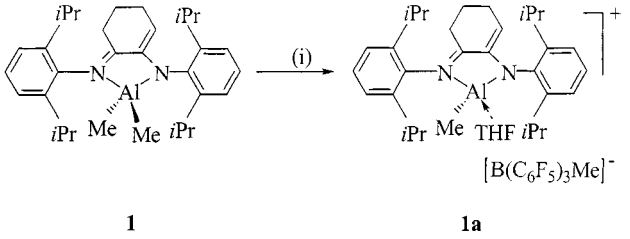


Scheme 5. Reaction conditions: (i) $AlMe_3$, heptane, room temperature

We have explored the generation of 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 red oil precipitated, thus preventing NMR solution analysis. The reaction was consequently studied in CD_2Cl_2 solution. After in situ treatment of **1** with 0.5 equiv. of $B(C_6F_5)_3$, the ^1H NMR spectrum showed, in addition to the signals of the neutral dimethylaluminium starting compound, new resonances attributable to a mixture of organometallic species. Although the ^1H NMR spectrum's region relative to the ligand is quite complicated, the high-field region can be easily interpreted in terms of methyl abstraction by $B(C_6F_5)_3$. Diagnostic resonances are two singlets at $\delta = +0.45$ and -0.42, attributable, by comparison with the data reported in the literature, to the free anion $[MeB(C_6F_5)_3]^-$ [21] and to the methyl group bound to the aluminium cation $AlMe^+$, respectively.[9] Formation of $[MeB(C_6F_5)_3]^-$ was further confirmed by a resonance at $\delta = -15.4$ in the ^{11}B NMR spectrum. After addition of a further amount (0.5 equiv.) of $B(C_6F_5)_3$, the resonances of the neutral starting compound disappeared. Subsequently, ethylene was added to the NMR tube; monitoring of the reaction showed that ethylene was consumed. 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 1 equiv. of THF, the THF-coordinated methyl cation **1a** was formed (Scheme 6). Characteristic resonances are the signals at $\delta = -0.41$ for AlMe^+ (3 H) and at $\delta = 0.48$ (3 H) for B*Me* in the ^1H NMR spectrum; the corresponding ^{13}C NMR resonances appear at $\delta = -13.6$ and 10.3, respectively. As a consequence of the positive charge on the aluminium atom, the resonances of the ligand in the cationic species are shifted to lower field compared to the resonances of the neutral compound in the same solvent (CD_2Cl_2). For instance, the triplet of C*H*= in the cyclohex-

ene ring of the ligand moves from δ = 4.76 for compound **1** to δ = 5.61 for the cation **1a**. Moreover, a C_1 symmetry can be deduced by the number of signals relative to the isopropyl substituents on the aryl groups (i.e. four signals for C*H*Me$_2$ and eight doublets for CH*Me*$_2$). Ethylene (ca. 1.3 equiv.) was added in the NMR tube; reaction of the olefin with the cationic species did not take place under these conditions, as shown by the ^{1}H NMR spectrum. Further investigation is in progress to determine if polymerization of ethylene occurs under more severe conditions.



1 **1a**

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

Attempts to generate clean cationic species from the amino-amide diethylaluminium compound **2** with B(C_6F_5)$_3$ were in vain; reactions always led to a mixture of species, even in the presence of THF.

Similar experiments were performed with the imino-phenoxide compounds **3** and **5**, giving analogous results. Thus, while reaction of **3** with B(C_6F_5)$_3$ in C_6D_6 gives a mixture of species, the cationic species {3-*t*Bu-2-(O)C_6H_3CH=N−C_6H_5}AlMe(THF)$^+$[MeB(C_6F_5)$_3$]$^-$ (**3a**) and {3-*t*Bu-2-(O)C_6H_3CH=N−C_6F_5}AlMe(THF)$^+$[MeB(C_6F_5)$_3$]$^-$ (**5a**) were instead obtained in the presence of THF in CD_2Cl_2 solution. The ^{1}H NMR spectrum of **3a** (CD_2Cl_2, room temperature) shows the Al*Me*$^+$ resonance at lower field in comparison with the resonance of the neutral one in the same solvent (δ = −0.15 vs. −0.82, respectively), as a consequence of the positive charge on the aluminium atom. Resonances relative to the imino-phenoxide ligand show an analogous shift; particularly, the C*H*=N signal moves from δ = 8.35 to 8.72. In addition, the aromatic hydrogen atom signals on the phenoxy group are split in a wider range (δ = 7.82−6.80). Signals for the THF coordinated to the aluminium atom appear at δ = 4.22 and 2.14 (OC*H*$_2$ and OCH$_2$C*H*$_2$, respectively). Our results parallel those of Gibson[11] for closely related (salicylaldiminato)aluminium compounds. As observed for the cationic complex **1a** (vide supra), ethylene does not polymerise appreciably under these conditions; aluminium species **3a** and **5a** are quite stable in CD_2Cl_2 solution.

It is worth noting that in all the examined cases, the broad ^{1}H NMR resonances for *Me*B(C_6F_5)$_3^-$ were observed in the range δ = 0.40−0.48, characteristic of the free anion,[21] thus suggesting that there are no relevant interactions between cation and anion, at least under the conditions used (this remark is further supported by the observed poor solubility of the cationic species in C_6D_6, compared to the high solubility of **1a**, **3a**, and **5a** in dichloromethane).

Preliminary polymerization tests were carried out for all the synthesized Al complexes. Toluene solutions of **3**, **4**, and **5**, when activated with 1 equiv. of B(C_6F_5)$_3$, polymerised ethylene (1 atm) to solid polyethylene with low activity [**3**: 400 g (PE) mol^{-1} h^{-1} atm^{-1}; **4**: 75 g (PE) mol^{-1} h^{-1} atm^{-1}; **5**: 200 g (PE) mol^{-1} h^{-1} atm^{-1}].

Compounds **1** and **2** were considerably less active; some solid polyethylene was obtained only in the presence of some added $AlMe_3$. A more detailed investigation of the polymerization activity of these Al derivatives after activation with different co-catalysts under more severe conditions is in progress.

Experimental Section

General: Manipulations of sensitive materials were carried out under dry nitrogen using Schlenk or glove-box techniques. Toluene, heptane, and THF were dried by reflux over sodium and benzophenone and distilled under nitrogen prior to use. $AlMe_3$ and $AlEt_3$ were purchased from Aldrich and used as received. The 1-(*o*,*o*′-diisopropylphenylamino)-6-(*o*,*o*′-diisopropylphenylimino)-cyclohexene,[12] the imino-phenoxide ligands,[22] and B(C_6F_5)$_3$ [21] were synthesized according to literature procedures. NMR spectra were recorded with a Bruker Advance 400 MHz spectrometer; chemical shifts were referenced to the residual protio impurities of the deuterated solvents. EI MS data were obtained with a Finnigan Thermoquest GCQ Plus 2000 spectrometer, using a direct exposure probe for compound **1** and **2**, and a direct insertion probe for compounds **3**, **4**, and **5**.

Preparation of Complexes

Complex 1: $AlMe_3$ (10.0 mL, 0.62 M in heptane, 6.2 mmol) was slowly added to a solution of 1-(*o*,*o*′-diisopropylphenylamino)-6-(*o*,*o*′-diisopropylphenylimino)cyclohexene (2.5 g, 6.8 mmol) in 20 mL of heptane at 0 °C with stirring. The orange solution was stirred at 0 °C for 1 h, at room temperature for additional 2 h and then was concentrated to 10 mL. Light orange crystals deposited overnight at −20 °C. Further crops were obtained by concentration and cooling of the mother liquor. Overall yield: 2.7 g (90%). Crystals of **1** suitable for an X-ray crystal structure determination were grown from toluene at −20 °C. ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ = −0.37 [s, 6 H, Al(C*H*$_3$)$_2$], 0.96 [d, 6 H, CH(C*H*$_3$)$_3$], 1.27−1.28 [m, 14 H, CH(C*H*$_3$)$_2$ and N=C−CH$_2$C*H*$_2$CH$_2$)], 1.41 [d, 6 H, CH(C*H*$_3$)$_2$], 1.86 (q, 2 H, N=C−CH$_2$CH$_2$C*H*$_2$), 2.00 (t, 2 H, N=C−C*H*$_2$CH$_2$CH$_2$), 3.08 [sept, 2 H, C*H*(CH$_3$)$_2$], 3.68 [sept, 2 H, C*H*(CH$_3$)$_2$], 4.86 (t, 1 H, =C*H*), 7.03−7.28 (m, 6 H, Ar-*H*). ^{13}C NMR (C_6D_6, 293 K): δ = −8.0 [Al(*C*H$_3$)$_2$], 23.9 (N=C−CH$_2$*C*H$_2$CH$_2$), 25.4 (N=C−CH$_2$CH$_2$*C*H$_2$); 24.8, 25.3, 25.4, 26.2 [CH(*C*H$_3$)$_2$], 28.6, 28.8, [*C*H(CH$_3$)$_2$], 30.6 (N=C-*C*H$_2$CH$_2$CH$_2$); 113.8 (*C*H=C−N); 124.7, 125.2, 126.2, 128.4 (*meta* and *para* Ar), 146.8 (CH=*C*−N), 138.0, 141.5, 142.2, 147.6, (*ipso* and *ortho* Ar), 181.1 (*C*=N). Assignments were made using HMQC long-range experiments. EI MS (35 eV): *m*/*z* = 486, 487, 489 [M]$^+$, 471, 472, 473 [M − CH$_3$]$^+$.

Complex 2: $AlEt_3$ (6.0 mL, 1.1 M in heptane, 6.6 mmol) was slowly added to a solution of 1-(*o*,*o*′-diisopropylphenylamino)-6-(*o*,*o*′-diisopropylphenylimino)cyclohexene (2.5 g, 5.8 mmol) in 25 mL of heptane at 0 °C with stirring. The solution was stirred at 0 °C for 1 h and at room temperature for additional 3 h. The solvent was removed in vacuo, and the orange-red oil residue was dissolved in toluene (5 mL). Orange crystals deposited overnight at 0 °C. Yield: 2.4 g (75%). ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ = 0.18 (dq, 2 H, $^3J_{H,H}$ = 8.1 Hz, CH$_3$C*H*$_2$Al), 0.28−0.52 (m, 2 H, CH′$_3$C*H*′$_2$Al),

0.62 (t, 3 H, $CHCH_2CH_3$), 0.90 (t, $^3J_{H,H}$ = 8.1 Hz, 3 H, CH_3CH_2Al), 1.2−1.6 [m, $CH(CH_3)_2$, $CH_2CH_2CH_2CHEt$, $CH_2CH_2CH_2CHEt$, $CHCH_2CH_3$ and $CH'_3CH'_2Al$ overlapping], 1.62−2.02 (m, br, 3 H, CHEt and $CH_2CH_2CH_2CHEt$), 3.27 [sept, 1 H, $CH(CH_3)_2$], 3.74 [sept, 2 H, $CH(CH_3)_2$], 3.96 [sept, 1 H, $CH(CH)_3$], 6.55 (s, 1 H, NH), 7.01−7.29 (m, 6 H, Ar-H). ^{13}C NMR (C_6D_6, 293 K): δ = −0.5 (br, $CH'_3CH'_2Al$ or CH_3CH_2Al), 0.9 (br, CH_3CH_2Al or $CH'_3CH'_2Al$), 9.0 ($CH'_3CH'_2Al$ or CH_3CH_2Al), 9.6 (CH_3CH_2Al or $CH'_3CH'_2Al$), 11.0 ($CHCH_2CH_3$), 18.9 ($CHCH_2CH_3$), 23.2, 24.3, 24.7, 25.0, 25.5, 25.6, 25.7, 26.1, $[CH(CH_3)_2]$, 26.0, 26.1, 26.4, (−CH_2− of cyclohexene), 26.9, 27.1, 27.9, 28.6, $[CH(CH_3)_3]$, 34.5 (CHEt), 108.9 (NC=CNH), 134.6 (NC=CNH), 123.8, 123.86, 123.91, 125.5, 126.0, 126.4 (*meta* and *para* Ar), 140.3, 140.8, 142.9, 147.4, 147.6, 147.8 (*ipso* and *ortho* Ar). Assignments were made using HMQC long-range experiments. EI MS (35 eV): *m*/*z* = 544, 545 $[M]^+$, 543, 544 $[M - H]^+$, 515, 516, 517 $[M - CH_3CH_2]^+$, 514, 515, 516 $[M - CH_3CH_3]^+$.

{[3-*t*Bu-2-(O)C_6H_3]CH=NC_6H_5}$AlMe_2$ (3): $AlMe_3$ solution (15.0 mL, 0.26 M in heptane, 4.0 mmol) was slowly added to a solution of 0.98 g of [3-*t*Bu-2-(OH)C_6H_3]CH=NC_6H_5 (3.9 mmol) in heptane (20 mL) at 0 °C. The reaction was allowed to warm to room temperature and stirred for 1 h. The solution was concentrated and stored at 0 °C, providing **3** as a yellow crystalline solid. Yield: 0. 85 g (71%). ^{1}H NMR (400 MHz, [D_8]toluene, 293 K): δ = −0.30 (s, 6 H, $AlCH_3$), 1.51 [(s, 9 H, $C(CH_3)_3$], 6.58 (t, 1 H, OAr-H), 6.62 (d, 1 H, OAr-H), 6.90−6.98 (m, 5 H, NAr-H), 7.38 (d, 1 H, OAr-H), 7.48 (s, 1 H, CH=N). ^{13}C NMR (C_6D_6, 293 K): δ = −8.4 (br, $AlCH_3$), 29.8 $[C(CH_3)_3]$, 35.7 $[C(CH_3)_3]$, 117.7, 120.4, 122.7, 130.1, 134.5, 135.3, 142.1, 147.4, 165.1, (Ar-C), 170.7 (CH=N). EI MS (35 eV): *m*/*z* = 294, 295 $[M - CH_3]^+$.

{[3-*t*Bu-2-(O)C_6H_3]CH=N(2,6-*i*$Pr_2C_6H_3$)}$AlMe_2$ (4): An $AlMe_3$ solution (10.0 mL, 0.25 M in heptane, 2.5 mmol) was slowly added to a solution of 0.75 g of [3-*t*Bu-2-(OH)C_6H_3]CH=N(2,6-*i*$Pr_2C_6H_3$) (2.2 mmol) in heptane (20 mL) at 0 °C. The reaction was allowed to warm to room temperature and stirred for 2 h. The volatiles were removed in vacuo affording a yellow oil that solidified upon standing one night at room temperature. Yield: 0.78 g (90%). ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ = −0.27 (s, 6 H, $AlCH_3$), 0.81 [d, 6 H, $CH(CH_3)_2$], 1.19 [d, 6 H, $CH(CH_3)_2$], 1.54 [(s, 9 H, $C(CH_3)_3$], 3.13 [(sept, 2 H, $CH(CH_3)_2$], 6.60 (t, 1 H, OAr-H), 6.72 (d, 1 H, OAr-H), 7.00−7.12 (m, 3 H, NAr-H), 7.42 (d, 1 H, OAr-H), 7.82 (s, 1 H, CH=N). ^{13}C NMR (C_6D_6, 293 K): δ = −8.7 (br, $AlCH_3$), 23.0 and 26.2 $[CH(CH_3)_2]$, 28.8 $[CH(CH_3)_2]$, 29.8 $[C(CH_3)_3]$, 35.7 $[C(CH_3)_3]$, 118.1, 119.8, 124.9, 128.8, 134.1, 135.6, 142.4, 142.9, 143.1, 165.3, (Ar-C), 174.5 (CH=N). EI MS (35 eV): *m*/*z* = 393 $[M]^+$, 378, 379 $[M - CH_3]^+$.

{[3-*t*Bu-2-(O)C_6H_3]CH=NC_6F_5}$AlMe_2$ (5): This compound was prepared as above, using an $AlMe_3$ solution (10.0 mL, 0.25 M in heptane, 2.5 mmol) and 0.795 g of [3-*t*Bu-2-(OH)C_6H_3]CH=NC_6F_5 (2.3 mmol) in heptane (20 mL) at 0 °C. Yield: 0.79 g (86%). ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ = −0.27 [t, 6 H, *J*(HF) = 1.4 Hz, $AlCH_3$], 1.46 [(s, 9 H, $C(CH_3)_3$], 6.53 (t, 1 H, OAr-H), 6.64 (d, 1 H, OAr-H), 7.28 (s, 1 H, CH=N), 7.40 (d, 1 H, OAr-H). ^{13}C NMR (C_6D_6, 293 K): δ = −9.74 (br, $AlCH_3$), 29.7 $[C(CH_3)_3]$, 35.7 $[C(CH_3)_3]$, 118.4, 119.7, 135.1, 137.5, 142.8, 166.8 (OAr-C), 177.3 (CH=N). EI MS (35 eV): *m*/*z* = 384 $[M - CH_3]^+$.

Thermolysis of Compound 2: $AlEt_3$ (10 mL, 0.22 M in heptane, 2.2 mmol) was quickly added to a solution of 1-(*o*,*o*′-diisopropylphenylamino)-6-(*o*,*o*′-diisopropylphenylimino)cyclohexene (0.800 g, 1.9 mmol) in 10 mL of toluene at room temperature and then heated under reflux for 2 h. Solvent and volatiles were removed in vacuo, leaving a red oil. ^{1}H NMR (400 MHz, C_6D_6, 293 K): δ = 0.33 (m, 2 H, CH_3CH_2Al), 0.57 (t, 3 H, CH_3CH_2−C), 0.84 (t, 3 H, CH_3CH_2Al), 1.10−1.30 [complex multiplet, $CH(CH_3)_2$ and CH_3CH_2C, overlapping, 26 H], 1.30−1.80 and 1.84−2.01 (three multiplets, CH_2 in the cyclohexene ring), 3.22 [sept, 1 H, $CH(CH_3)_2$], 3.48 [sept, 2 H, $CH(CH_3)_2$], 3.82 [sept, 1 H, $CH(CH_3)_2$], 7.16−7.18 (m, 6 H, Ar-H). ^{13}C NMR (C_6D_6, 293 K), selected resonances: δ = −0.4 (br, CH_3CH_2Al), 8.7 (CH_3CH_2Al), 12.8 ($CHCH_2CH_3$), 19.1 ($CHCH_2CH_3$), 22.7, 23.3, 23.4, 23.8, 25.8, 26.0, 26.9, 27.2 $[CH(CH_3)_2]$, 25.7, 26.4, 26.8 (−CH_2− of cyclohexene), 28.5, 28.8 $[CH(CH_3)_3]$, 34.1 (CHEt), 123.6, 123.9, 126.0, 126.3 (*meta* and *para* Ar), 140.2, 140.9 (NC=CN and NC=CN), 145.9, 146.6, 146.7, 147.2 (*ipso* and *ortho* Ar).

Generation of Cations

Complex 1a: Compound **1** (24 mg, 0.05 mmol) was dissolved in CD_2Cl_2 (0.5 mL). Dry THF (4.0 μL, 0.05 mmol) and $B(C_6F_5)_3$ (26 mg, 0.05 mmol) were sequentially added, and the resulting orange solution was analyzed by NMR spectroscopy at room temperature. ^{1}H NMR (400 MHz, 293 K): δ = −0.41 (s, 3 H, $AlCH_3$), 0.48 (br. s, 3 H, CH_3B), 0.83−1.38 [m, 24 H, $CH(CH_3)_2$], 1.72 −1.98 (m, 2 H, N=C−$CH_2CH_2CH_2$), 2.17 (m, br, 4 H, OCH_2CH_2), 2.50−2.60 [m, 5 H, N=C−$CH_2CH_2CH_2$, N=C−$CH_2CH_2CH_2$, $CH(CH_3)_2$, overlapping], 2.91 [sept, 1 H, $CH(CH_3)_2$], 3.11 [sept, 1 H, $CH(CH_3)_2$], 3.28 [sept, 1 H, $CH(CH_3)_2$], 4.25 (m, br, 4 H, OCH_2CH_2), 5.61 (t, 1 H, =CH), 7.15−7.50 (m, 6 H, Ar-H). ^{13}C NMR (293 K), selected resonances; cation: δ = −13.6 (br, $AlCH_3$), 23.6, 25.7, 30.7 (CH_2 of the cyclohexene ring), 23.7, 24.3, 24.5, 25.5, 25.9, 26.0 $[CH(CH_3)_2]$, 24.9, (OCH_2CH_2), 29.2, 29.6, 30.2 $[CH(CH_3)_2]$, 75.0 (OCH_2), 128.3 (CH=C−N), 123.9, 125.8, 126.0, 126.2, 127.6, 130.3 (*meta* and *para* Ar), 145.0 (CH=C−N), 134.7, 141.6, 142.3, 146.2, 147.0 (*ipso* and *ortho* Ar), 186.8 (C=N); anion: δ = 10.3 (br, BCH_3). Assignments were made using HMQC long-range experiments.

{[3-*t*Bu-2-(O)C_6H_3]CH=NC_6H_5}$AlMe(THF)^+[MeB(C_6F_5)_3]^-$ (3a): This compound was prepared as above by dissolving 15 mg of **5** (0.05 mmol) in CD_2Cl_2 (0.5 mL). Dry THF (4.0 μL, 0.05 mmol) and $B(C_6F_5)_3$ (26 mg, 0.05 mmol) were sequentially added, and the resulting yellow solution was analyzed by NMR spectroscopy at room temperature. ^{1}H NMR (400 MHz, 293 K): δ = −0.15 (s, 3 H, $AlCH_3$), 0.47 (br. s, 3 H, CH_3B), 1.51 [(s, 9 H, $C(CH_3)_3$], 2.14 (m, br, 4 H, OCH_2CH_2), 4.21 (m, br, 4 H, OCH_2CH_2), 7.06 (t, 1 H, OAr-H), 7.28 (d, 2 H, NAr-H), 7.45 (d, 1 H, OAr-H), 7.55−7.61 (m, 3 H, NAr-H), 7.81 (d, 1 H, OAr-H), 8.72 (s, 1 H, CH=N). ^{13}C NMR (293 K); cation: δ = −13.5 (br, $AlCH_3$), 25.9 (OCH_2CH_2), 29.6 $[C(CH_3)_3]$, 35.7 $[C(CH_3)_3]$, 75.8 (OCH_2), 120.0, 121.7, 122.3, 130.5, 131.7, 136.0, 139.1, 142.1, 144.3, 162.6 (all Ar-C), 175.8 (CH=N); anion: δ = 10.8 (br, BCH_3).

{[3-*t*Bu-2-(O)C_6H_3]CH=NC_6F_5}$AlMe(THF)^+[MeB(C_6F_5)_3]^-$ (5a): This compound was prepared as above by dissolving 20 mg of **5** (0.05 mmol) in CD_2Cl_2 (0.5 mL). Dry THF (4.0 μL, 0.05 mmol) and $B(C_6F_5)_3$ (26 mg, 0.05 mmol) were sequentially added, and the resulting yellow solution was analyzed by NMR spectroscopy at room temperature. ^{1}H NMR (400 MHz, 293 K): δ = −0.31 (s, 3 H, $AlCH_3$), 0.40 (br. s, 3 H, CH_3B), 1.45 [(s, 9 H, $C(CH_3)_3$], 2.21 (m, br, 4 H, OCH_2CH_2), 4.28 (m, br, 4 H, OCH_2CH_2), 7.12 (t, 1 H, OAr-H), 7.41 (d, 1 H, OAr-H), 7.93 (d, 1 H, OAr-H), 8.63 (s, 1 H, CH=N). ^{13}C NMR (293 K); cation: δ = −15.5 (br, $AlCH_3$), 25.8 (OCH_2CH_2), 29.7 $[C(CH_3)_3]$, 35.7 $[C(CH_3)_3]$, 76.0 (OCH_2), 118.4, 119.7, 135.1, 137.5, 142.8, 166.8, (OAr-C), 177.3 (CH=N); anion: δ = 10.2 (br, BCH_3).

Polymerization Tests: A typical polymerization test was carried out in a 100-mL glass flask charged under nitrogen with 20 mL of toluene and thermostated at 50 °C. The inert gas was replaced by ethylene at 1 atm, then 0.1 mmol of the proper aluminium complex and 0.1 mmol of $B(C_6F_5)_3$ (each dissolved in 2.0 mL of toluene) were injected into the flask. The flask was fed with constant monomer pressure, and after 15 min the reaction was stopped by injecting methanol. The mixture was poured into acidified methanol, and the polymer was recovered by filtration, washed with fresh methanol, and dried under vacuum.

X-ray Crystallography: Suitable crystals were selected and mounted in Lindemann capillaries under an inert gas. Diffraction data were 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.[23] No absorption correction was applied to the data. The structures were solved by direct methods using the program SIR92[24] and refined by means of full-matrix least squares based on F^2 using the program SHELXL93.[25] For compound **1**, half a molecule of toluene was located on an inversion centre. A rigid-body refinement was performed for the solvent molecule, assuming that two distinct molecules equally share the same site with opposite orientation, methyl group hydrogen atoms were assumed to be disordered over two sites rotated by 60° to each other. All non-hydrogen atoms excluding those belonging to the solvent molecule were refined anisotropically. For the disordered toluene molecule a unique displacement parameter was considered. Hydrogen atoms were positioned geometrically and included in structure factor calculations but not refined. Restraints were applied to the $CH-CH_3$ distance of the isopropyl groups. The presence of the disordered solvent molecule accounts for the low-quality structure refinements. For compound **2** all non-hydrogen atoms were refined anisotropically, hydrogen atoms were positioned geometrically and included in structure factor calculations but not refined. Crystal structures were drawn by means of the program ORTEP32.[26] Crystal data and refinement details for both compounds are reported in Table 2. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-168133 (**1**) and -168132 (**2**). Copies of 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].

Table 2. Crystal data and structure refinement details for compounds **1** and **2**

	1	**2**
Empirical formula	$C_{32}H_{47}N_2Al{\cdot}0.5C_7H_8$	$C_{36}H_{57}N_2Al$
Formula mass	532.76	544.82
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$ (14)	$P2_1/n$ (14)
a [Å]	13.016(6)	9.868(8)
b [Å]	19.889(5)	18.595(8)
c [Å]	13.200(5)	19.365(8)
β [°]	91.20(4)	100.83(5)
V [Å^3]	3416(2)	3489(3)
Z	4	4
D_c [g cm^{-3}]	1.036	1.037
μ(Mo-K_α) [mm^{-1}]	0.08	0.08
F(000)	1164	1200
Indep. refl. measured	4452 (ω/2θ scans)	6134 (ω scans)
Param./restraints	323/7	352/0
$R1$ [$F_o > 4\sigma(F_o)$]	0.0913 [888 refl.]	0.0625 [1904 refl.]
R_w2 (all refl.)	0.3750	0.2513
GooF	1.276	1.073
Δρ(min) [eÅ^{-3}]	−0.33	−0.20
Δρ(max) [e Å^{-3}]	0.52	−0.20

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