DALTON
FULL PAPER

Synthesis and characterisation of neutral and cationic alkyl aluminium complexes bearing *N*,*O*-Schiff base chelates with pendant donor arms

Paul A. Cameron, Vernon C. Gibson,* Carl Redshaw, John A. Segal, Andrew J. P. White and David J. Williams

Department of Chemistry, Imperial College, South Kensington, London, UK SW7 2AY

Received 10th July 2001, Accepted 14th November 2001
First published as an Advance Article on the web 8th January 2002

The Schiff base ligands [3,5-Bu^t_2-2-$(OH)C_6H_2CH{=}NL$] [L = $CH_2CH_2NMe_2$ (**1a**), 2-$(PhO)C_6H_4$ (**1b**), 2-$CH_2C_5H_3N$ (**1c**), 8-C_9H_6N (quinoline) (**1d**) and 2-$(PPh_2)C_6H_4$ (**1e**)] are accessed in good yields (>85%) *via* standard imine condensation reactions. Reaction of **1a**–**e** with Me_3Al at room temperature affords the corresponding complexes [(3,5-Bu^t_2-2-$(O)C_6H_2CH{=}NL)AlMe_2$] (**2a**–**e**); in the case of L = 8-quinoline, the same reaction conducted in refluxing toluene affords binuclear {[3,5-Bu^t_2-2-$(O)C_6H_2CHMeN$-8-$C_9H_6N]AlMe\}_2$ (**3**) by methyl migration from metal to ligand. Further reaction of the dimethyl compounds with $B(C_6F_5)_3$ in CD_2Cl_2 or C_6D_6 affords the cationic systems [(3,5-Bu^t_2-2-$(O)C_6H_2CH{=}NL)AlMe]^+$ (**4a**–**e**). The crystal structures of **2a**, **2c**, **2e** and **3** have been determined. In **2a** and **2c** the respective ligands bind to the metal centre *via* all three heteroatoms, the aluminium having a trigonal bipyramidal geometry, whereas in **2e** coordination is *via* nitrogen and oxygen only, and the aluminium is tetrahedral. Complex **3** has a dimeric structure with the ligand adopting both tridentate and binucleating roles; the aluminium centres are trigonal bipyramidal.

Introduction

In recent years there has been considerable and growing interest in the coordination chemistry of bulky bi- and tridentate ligands, in part because these ligands can be used to provide protective shields for catalytically active metal centres. This protection strategy is one which we and others have recently employed in late transition metal systems.[1] In other studies, we have demonstrated[2] the use of *tridentate N,N,N*-bis(imino)-pyridines, bearing bulky substituents, in the formation of new [ligand]aluminium dialkyl complexes, from which cationic monoalkyl aluminium species can be readily generated by reaction with $B(C_6F_5)_3$. These cationic complexes were shown to be active ethylene polymerisation catalysts.[2] Coles and Jordan reported[3] a similar use of *bidentate* ligands, *i.e.* bulky *N,N*-dialkylamidinates, in the formation of aluminium dialkyls which could also be converted to polymerisation-active cationic aluminium alkyls. In seeking to extend these studies to *N,O* chelates, we developed the synthesis of novel Schiff base dialkylaluminium compounds derived from salicylaldimines bearing bulky groups.[4] However, our initial findings showed[4] that these bidentate *N,O*-salicylaldiminato complexes could not be converted to stable alkylaluminium cations in the absence of another donor ligand. We reasoned that the targeted monoalkylaluminium cation, presumed to be formed as an intermediate, would be a highly reactive and coordinatively unsaturated 3-coordinate system which would be likely to abstract an anion either from the boron counter ion or from the solvent. It was thus anticipated that the provision of one additional donor ligand would lead to a much more stable 4-coordinate methylaluminium cation, and to this purpose we synthesised a series of potentially *tridentate* salicylaldimine ligands each bearing a pendant *O*, *N*, or *P* donor arm attached to the imine nitrogen. These ligands were then employed in the synthesis of [*N,O*-salicylaldiminato]aluminium dialkyl complexes which have, accordingly, the additional weakly bonding *N*- or *O*-donor, or non-bonding *P*-donor, pendant arms. As expected, reactions of these compounds with $B(C_6F_5)_3$ lead to the formation of stable alkylaluminium cations. In each case, the weakly bonding or non-bonding donor arm in the neutral precursor becomes a normal ligand occupying the fourth coordination position in the cation, thereby stabilising the electropositive aluminium centre. These cations were found to be active in the catalysis of ethylene polymerisation and this work has been the subject of a preliminary communication.[5]

Here we report the synthesis and characterisation of the series of new potentially tridentate Schiff-base ligands [3,5-Bu^t_2-2-$(OH)C_6H_2CH{=}NL$] [L = $CH_2CH_2NMe_2$ (**1a**), 2-$(PhO)C_6H_4$ (**1b**), 2-$CH_2C_5H_3N$ (**1c**), 8-C_9H_6N (quinoline) (**1d**) and 2-$(PPh_2)C_6H_4$ (**1e**)], the corresponding dimethylaluminium complexes [(3,5-Bu^t_2-2-$(O)C_6H_2CH{=}NL)AlMe_2$] (**2a**–**e**), and the cations [(3,5-Bu^t_2-2-$(O)C_6H_2CH{=}NL)AlMe]^+$ (**4a**–**e**). A dimeric complex **3**, resulting from methyl migration from the metal to the ligand when L = 8-quinoline, is also described.

Results and discussion

Ligands of the form 3,5-Bu^t_2-2-$(OH)C_6H_2CH{=}NL$

The ligands **1a**–**e** (Fig. 1) were prepared *via* the condensation

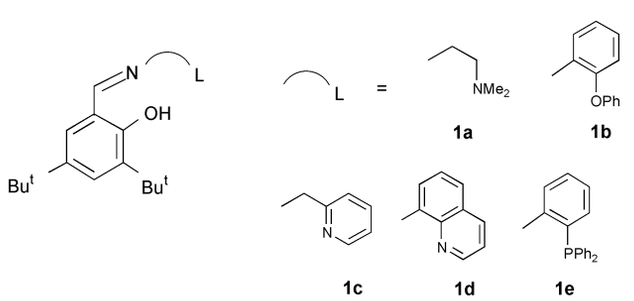
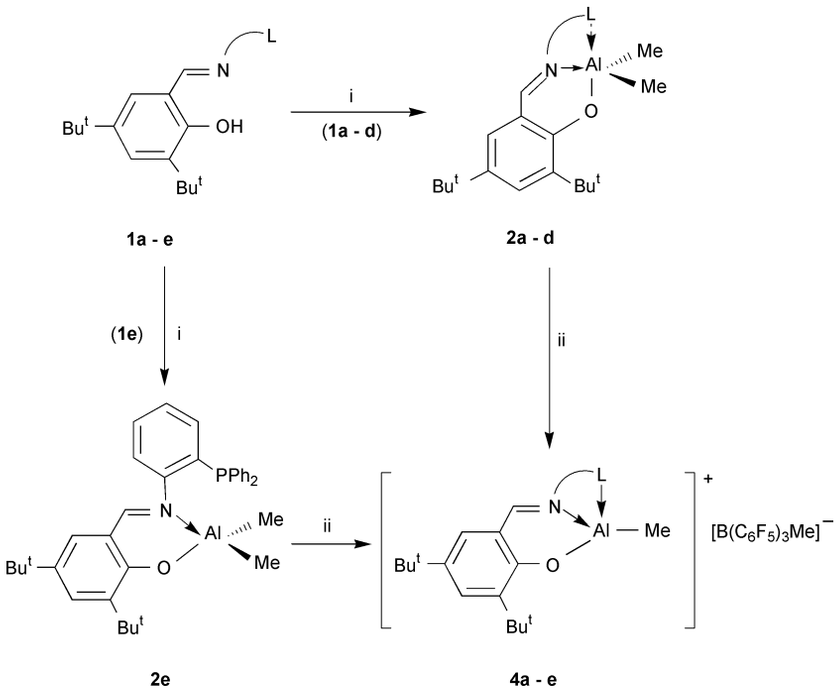


Fig. 1 Ligands **1a**–**e**.

reaction between 3,5-di-*tert*-butylsalicylaldehyde and the relevant amine, and obtained as yellow to orange solids in good yield (>85% isolated yield). The ^1H NMR spectra of these ligands exhibit resonances in the region δ 7.84–8.63 for the CH



Scheme 1 Formation of aluminium complexes **2a**–**e** and corresponding cations **4a**–**e**. *Reagents:* i. $AlMe_3$, toluene; ii. $B(C_6F_5)_3$, C_6D_6 or CD_2Cl_2.

imine protons, with the corresponding ^{13}C NMR resonances occurring in the range δ 164.9–168.4. The phenolic resonances appear at characteristically low field (δ 13–15). The infrared absorption bands of the imine C=N stretch occur in the region 1615–1634 cm^{-1}. In all cases the parent ion is observed by electron ionisation mass spectrometry, and all the compounds gave satisfactory microanalyses.

Complexes of the form (3,5-Bu^t_2-2-(O)C_6H_2CH=NL)$AlMe_2$

Treatment of **1a**–**e** with trimethylaluminium in toluene at room temperature caused the evolution of methane and afforded (see Scheme 1) the corresponding dimethyl complexes [3,5-Bu^t_2-2-(O)C_6H_2CH=N$CH_2CH_2NMe_2$]$AlMe_2$ (**2a**–**e**). Compounds **2a**, **2c** and **2e** were obtained in good yields as yellow or pale orange crystalline solids from hot saturated MeCN solutions on cooling. Complexes **2b** and **2d**, however, were obtained as orange oily solids from MeCN at −30 °C. Drying of the oils *in vacuo* yielded **2b** and **2d** as glassy solids (>95% pure by ^1H NMR spectroscopy). Satisfactory microanalyses were obtained on all the compounds except **2d** (see Experimental section). In general, the ^1H NMR spectra of compounds **2a**–**e** exhibit resonances in the region δ 7.40–8.11 for the imine CH protons, with corresponding signals in the ^{13}C NMR spectrum in the range δ 169.1–172.8. The resonances attributable to the aluminium-bound methyl groups occur at δ −0.05 to −0.29, with corresponding ^{13}C NMR resonances at δ −4.0 to −9.0. A representative ^1H NMR spectrum (compound **2c**, C_6D_6, 298 K) is illustrated in Fig. 2. Two doublets (δ 7.70 and 6.83, ^4J (HH) *ca.* 2.5 Hz) are present for the salicylaldehyde derived aromatic signals. The imine CH=N group is seen as a singlet at δ 7.42, and there are several multiplets between δ 8.3 and δ 6.2, which are due to the pyridyl protons. The backbone NCH_2 group gives rise to a singlet at δ 3.86. The *tert*-butyl groups afford two singlets at δ 1.76 and 1.37 and the methyls attached to aluminium occur at high field (δ −0.19). The characteristic infrared absorption band for the imine C=N stretch in **2a**–**e** occurs in the region 1614–1623 cm^{-1}. In all cases the envelope corresponding to $m/z = [M - CH_3]^+$ is observed by electron ionisation mass spectrometry; for **2d** the parent ion, and for **2e** the parent + H^+ is also observed. In many cases the $[M - CH_3]^+$ lines are very intense, *e.g.* for **2e** they are the strongest in the mass spectrum, indicating the relative

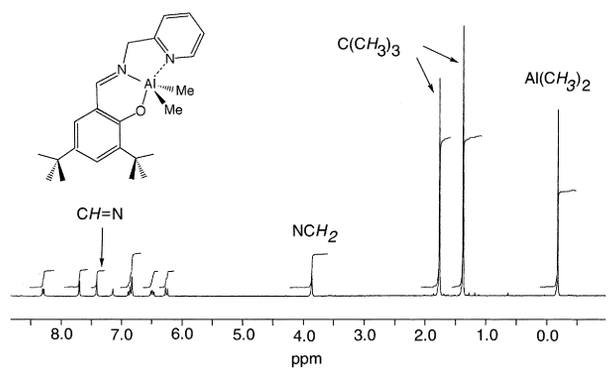


Fig. 2 ^1H NMR spectrum (250 MHz) of **2c** in C_6D_6.

stability of these cations which have also been formed chemically (*vide infra*). The X-ray structural data which follow show that in compounds **2a** and **2c** the pendant arm donor groups behave as weakly bound fifth ligands, and we infer that this weak bonding will also pertain to the *O* and *N* donor arms in compounds **2b** and **2d**. However, the pendant PPh_2 group in **2e** is found to be non-bonding in the solid state.

The molecular structure of **2a** is shown in Fig. 3, and selected

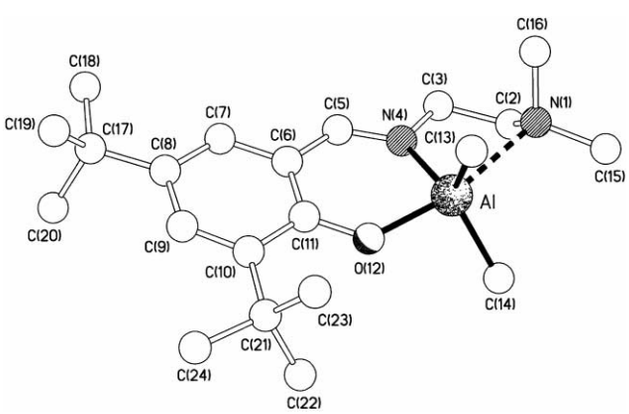


Fig. 3 The molecular structure of **2a**, showing the trigonal bipyramidal geometry at aluminium and the very long Al–N(amino) linkage.

Table 1 Selected bond lengths (Å) and angles (°) for **2a**

Al–N(1)	2.413(5)	Al–N(4)	1.998(4)
Al–O(12)	1.854(4)	Al–C(13)	1.978(6)
Al–C(14)	1.976(5)	N(4)–C(5)	1.294(6)
O(12)–Al–C(14)	96.6(2)	O(12)–Al–C(13)	98.3(2)
C(14)–Al–C(13)	123.7(3)	O(12)–Al–N(4)	88.2(2)
C(14)–Al–N(4)	116.0(2)	C(13)–Al–N(4)	118.4(2)
O(12)–Al–N(1)	163.0(2)	C(14)–Al–N(1)	91.4(2)
C(13)–Al–N(1)	89.5(2)	N(4)–Al–N(1)	74.9(2)

Table 2 Selected bond lengths (Å) and angles (°) for **2c**

Al–N(1)	2.254(2)	Al–N(8)	1.999(2)
Al–O(16)	1.854(2)	Al–C(17)	1.982(3)
Al–C(18)	1.975(2)	N(8)–C(9)	1.295(3)
O(16)–Al–C(18)	98.97(10)	O(16)–Al–C(17)	98.61(11)
C(18)–Al–C(17)	123.69(12)	O(16)–Al–N(8)	88.11(7)
C(18)–Al–N(8)	118.18(10)	C(17)–Al–N(8)	115.47(10)
O(16)–Al–N(1)	162.52(8)	C(18)–Al–N(1)	89.78(10)
C(17)–Al–N(1)	88.87(11)	N(8)–Al–N(1)	74.41(8)

bond lengths and angles are given in Table 1. The geometry at aluminium is best described as trigonal bipyramidal, with N(4), C(13) and C(14) occupying the equatorial sites, the aluminium atom lying 0.16 Å out of the equatorial plane in the direction of O(12). Importantly, the relatively weak interaction of the NMe_2 pendant group with the aluminium centre is apparent from the long Al–N(1) bond length of 2.413(5) Å. Within the six-membered chelate ring the binding to aluminium is unsymmetrical, with the bond to the oxygen atom being typical of an alkoxide [1.854(4) Å], whilst that to the imino nitrogen atom is, as expected, appreciably longer at 1.998(4) Å. Both these distances, however, are statistically significantly longer than their counterparts in simple chelate analogues,[4] *e.g.* [3,5-Bu^t_2-2-(O)C_6H_2CH=N(2,6-$Me_2C_6H_3$)]$AlMe_2$, reflecting the presence of the additional donor in **2a** with subsequent competition for electron density. This effect is more pronounced in the alkoxide case [Al–O: 1.854(4) Å *cf.* 1.773(3) Å for the above simple chelate], due to this ligand being *trans* to the NMe_2 group. As in the simple chelates, the chelate C=N bond retains its double bond character, being 1.294(6) Å. The six-membered metallacycle has a half-boat conformation, the aluminium lying 0.50 Å out of the plane of the other five atoms, these being coplanar to within 0.03 Å. The five-membered chelate ring has an envelope conformation, the NCH_2CH_2N portion of the ligand adopting a *gauche* geometry. There are no intermolecular packing interactions of note.

The structure of **2c** (Fig. 4, Table 2) is very similar to that of

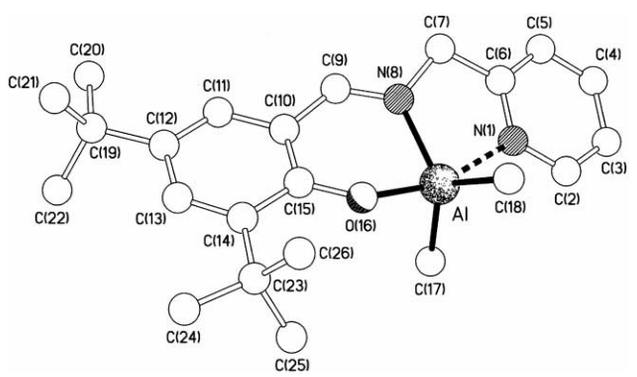


Fig. 4 The molecular structure of **2c**.

2a, retaining a distorted trigonal bipyramidal geometry at aluminium with N(1) and O(16) occupying the axial positions. The only major difference is a significant shortening of the bond from the pendant arm heteroatom N(1) to the aluminium centre, Al–N(1) 2.254(2) Å, *cf.* 2.413(5) Å in **2a**. In

Table 3 Selected bond lengths (Å) and angles (°) for **2e**

Al–N	1.973(4)	Al–O	1.754(3)
Al–C(1)	1.949(6)	Al–C(2)	1.942(6)
N–C(9)	1.300(5)		
O–Al–C(2)	114.5(3)	O–Al–C(1)	108.9(3)
C(2)–Al–C(1)	116.9(3)	O–Al–N	94.57(14)
C(2)–Al–N	106.5(3)	C(1)–Al–N	113.4(2)

the six-membered chelate ring the aluminium lies 0.58 Å out of the plane of other five atoms which are co-planar to within 0.05 Å. The only intermolecular interactions of note are a pair of short C–H · · · π contacts between one of the C(7) methylene hydrogen atoms in one molecule and the 3,5-di-*tert*-butylphenyl ring of its centrosymmetrically related neighbour and *vice versa* (H · · · π 2.56 Å, C–H · · · π 174°). The shortest "equivalent" interaction in **2a** is from C(2)–H, but with a much longer H · · · π separation of 2.99 Å and with a C–H · · · π angle of 139°.

The X-ray analysis of **2e** (Fig. 5, Table 3) shows the ligand

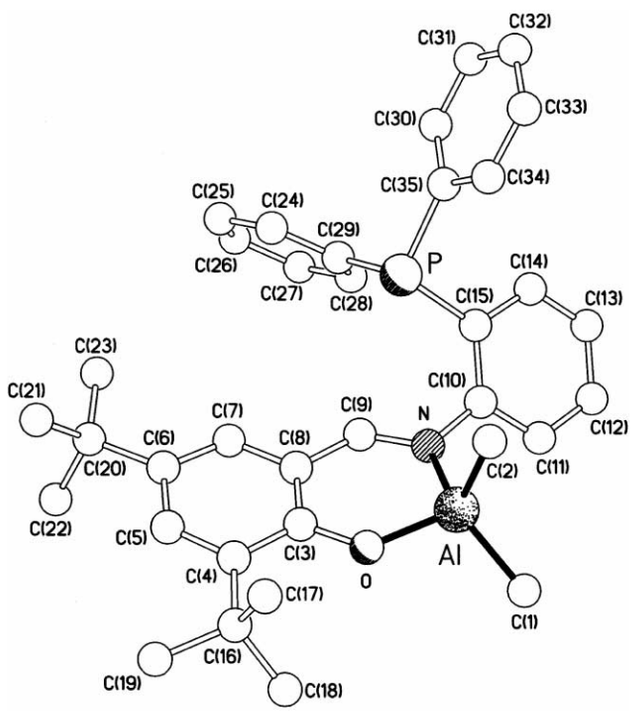


Fig. 5 The molecular structure of **2e** showing the tetrahedral geometry at aluminium and the non-coordination of the phosphorus centre.

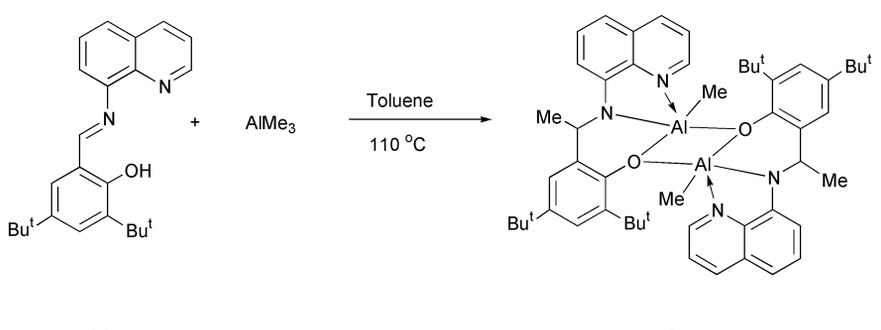
coordination to be *via* only the oxygen and nitrogen atoms, the phosphorus being remote (4.56 Å) from the aluminium centre, its lone pair being directed over the N=C(9) bond. The geometry at aluminium is distorted tetrahedral with angles ranging between 94.57(14) and 116.9(3)°, the most "acute" angle being associated with the bite angle of the chelating ligand. As in **2a**, the metal–donor bonds within the six-membered chelate ring are unsymmetrical [Al–O 1.754(3), Al–N 1.973(4) Å], these distances being in close accord with those of the similar *bidentate* ligand complexes[4] referred to above. The ring has a slightly folded conformation with the aluminium lying 0.28 Å out of the plane of the other five atoms which are co-planar to within 0.02 Å; the chelate C=N bond retains its double bond character [1.300(5) Å]. There are no noteworthy intermolecular interactions.

The dimeric complex {[3,5-Bu^t_2-2-(O)C_6H_2CHMeN-8-C_9H_6N]-$AlMe$}$_2$ (3)

In refluxing toluene, the interaction of $AlMe_3$ with the

Table 4 Selected bond lengths (Å) and angles (°) for the two crystallographically independent dimers (**A** and **B**) present in the structure of **3**

	A	B		A	B
Al(1)–O(1)	1.944(3)	1.964(3)	Al(1)–N(1)	1.882(4)	1.879(3)
Al(1)–C(1)	1.968(5)	1.955(5)	Al(1)–O(2)	1.866(3)	1.856(3)
Al(1)–N(2)	2.064(4)	2.089(4)	Al(2)–O(1)	1.881(3)	1.870(3)
Al(2)–O(2)	1.918(3)	1.951(3)	Al(2)–C(2)	1.967(6)	1.963(5)
Al(2)–N(3)	1.880(5)	1.871(4)	Al(2)–N(4)	2.077(4)	2.067(4)
O(2)–Al(1)–N(1)	123.4(2)	124.7(2)	O(2)–Al(1)–O(1)	75.32(14)	75.85(13)
N(1)–Al(1)–O(1)	89.9(2)	89.37(14)	O(2)–Al(1)–C(1)	123.6(2)	120.9(2)
N(1)–Al(1)–C(1)	113.0(2)	114.2(2)	O(1)–Al(1)–C(1)	104.2(2)	101.6(2)
O(2)–Al(1)–N(2)	94.3(2)	94.4(2)	N(1)–Al(1)–N(2)	81.7(2)	80.7(2)
O(1)–Al(1)–N(2)	160.2(2)	158.7(2)	C(1)–Al(1)–N(2)	95.6(2)	99.6(2)
N(3)–Al(2)–O(1)	125.3(2)	123.3(2)	N(3)–Al(2)–O(2)	89.9(2)	89.8(2)
O(1)–Al(2)–O(2)	75.61(14)	75.88(13)	N(3)–Al(2)–C(2)	112.4(3)	113.7(2)
O(1)–Al(2)–C(2)	122.3(3)	122.8(2)	O(2)–Al(2)–C(2)	103.5(2)	101.2(2)
N(3)–Al(2)–N(4)	82.0(2)	81.3(2)	O(1)–Al(2)–N(4)	94.3(2)	94.7(2)
O(2)–Al(2)–N(4)	160.0(2)	160.7(2)	C(2)–Al(2)–N(4)	96.5(2)	98.1(2)
Al(1)–O(1)–Al(2)	99.6(2)	99.92(14)	Al(1)–O(2)–Al(2)	101.1(2)	100.89(14)



1d **3**

Scheme 2 The preparation of **3**.

quinoline ligand **1d** did not follow the room temperature reaction above (to yield the dimethylaluminium complex **2d**), but instead afforded the dimeric complex $\{[3,5\text{-}Bu^t_2\text{-}2\text{-}(O)C_6H_2\text{-}CHMeN\text{-}8\text{-}C_9H_6N]AlMe\}_2$ (**3**). This product is the result of a methyl migration from the aluminium centre to the parent ligand backbone, see Scheme 2; such migrations have been noted previously.[2,6–8] A dimeric structure is indicated by electron ionisation MS, which displays the envelope corresponding to the parent ion ($m/z = 832$). The methyl migration to the imine carbon is revealed by the absence of a signal in the infrared or ^{13}C NMR spectrum for this group. Also, the ^1H NMR spectrum of **3**, shows signals corresponding to a $CH(CH_3)$ group, *i.e.* a quartet [^3J(HH) 6.8Hz] at δ 4.77 and a corresponding doublet [^3J(HH) 6.8Hz] at δ 0.79.

Crystals of **3** suitable for an X-ray structure determination were grown from a saturated acetonitrile solution at room temperature. The X-ray analysis (Fig. 6, Table 4) reveals a dimeric complex to have been formed where the Schiff base ligands adopt both tridentate and binucleating roles. The asymmetric unit contains two independent, but geometrically very similar, dimers each of which exhibits approximate molecular C_2 symmetry. The phenolic oxygens are seen to bridge adjacent aluminium centres to form a slightly folded (*ca.* 27° about the non-bonded O ··· O vector) Al_2O_2 ring. The Al–O–Al bridges are slightly asymmetric, the Al–O distances falling into two distinct groupings, averaging 1.868(3) and 1.944(3) Å. The non-bonded Al ··· Al separations in the two independent molecules are 2.922(2) and 2.936(2) Å, respectively. The geometries at the aluminium centres are distorted trigonal bipyramidal, with the phenolic oxygen and the quinoline nitrogen occupying the axial positions. The equatorial Al–N(amido) bonds [av. 1.878(4) Å] are, as expected, significantly shorter than those to the axial quinoline nitrogens [av. 2.074(4) Å]. The aluminium atoms do not deviate significantly out of the plane of their three equatorial substituents. The six-membered chelate rings again adopt

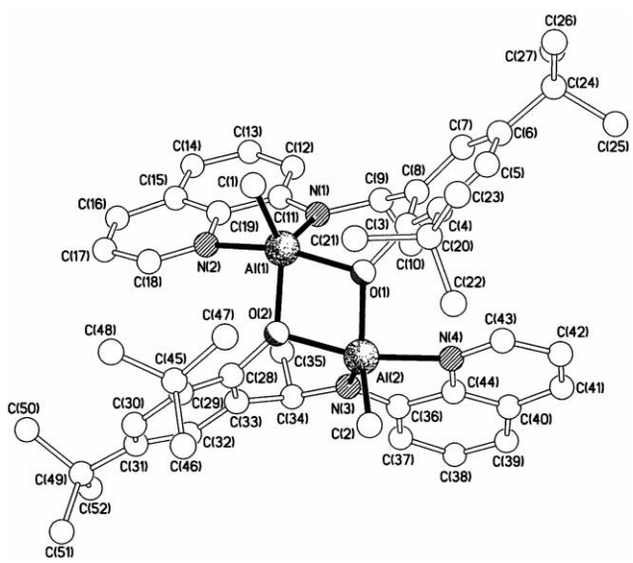


Fig. 6 One of the two independent dimeric molecules present in the structure of **3**.

half-boat conformations, but with their phenolic oxygen atoms (rather than the metal centres) lying out of the ring plane by *ca.* 0.76 Å. An interesting feature of the methyl migration and the consequent loss of the imino function is the retention within each molecule of a common chirality at each of these stereogenic centres, *i.e.* in the crystal we have only the *RR* and *SS* diastereomers and not the *meso*-*SR* or *RS* species. Inspection of molecular models reveals that a simple inversion at each of these centres would result in a severely sterically congested geometry with overlap of the methyl and quinoline hydrogen atoms. The only intermolecular interaction of note is a partial stacking of the quinoline ring systems.

Cations of the form [(3,5-Bu$^t_2$-2-(O)C$_6$H$_2$CH=NL)AlMe]$^+$

The reaction of the dimethyl complexes **2a**–**e** with a molar equivalent of B(C$_6$F$_5$)$_3$, in CD_2Cl_2 or C_6D_6, resulted in the formation of the cations [(3,5-Bu$^t_2$-2-(O)C$_6$H$_2$CH=NL)AlMe]$^+$ (**4a**–**e**). Whereas the reaction of **2a** with B(C$_6$F$_5$)$_3$ could be carried out successfully in CD_2Cl_2 and gave the cation **4a** in high purity, this was not the case for the formation of the remaining cations **4b**–**e**. In CD_2Cl_2 slightly impure products were obtained, and it was generally found best to conduct the reaction with B(C$_6$F$_5$)$_3$ in C_6D_6. Using this solvent the cations formed lower oily layers which were separated and pumped to dryness. The cations **4a**–**e** were thus formed in high purity, as demonstrated by their ^{1}H, ^{13}C, and ^{19}F NMR spectra recorded in CD_2Cl_2. Crystalline materials could not however be obtained. The ^{1}H NMR spectra of this series of cations have the imine resonance appearing in the range δ 8.16 to 8.67 and the resonance of the remaining aluminium methyl in the range δ −0.12 to −0.47; the corresponding ^{13}C NMR signals lie between δ 166.1 and 176.5 and between δ −9.4 and −14.8 respectively. The ^{1}H NMR resonance of the methyl group in the [CH$_3$B(C$_6$F$_5$)$_3$]$^-$ counter ions, which is broadened by the boron quadrupole, is seen in the range δ 0.38 to 0.48, with the similarly broadened carbon resonance at *ca* δ 10.5 throughout the series. The ^{19}F NMR spectra show a single set of three signals in a 2 : 1 : 2 ratio (at δ −135, −167, and −170 respectively) as anticipated for a C$_6$F$_5$ group. These data for the [CH$_3$B(C$_6$F$_5$)$_3$]$^-$ groups are consistent[9] with their formulation, and therefore the formulation of the aluminium cations, as separated ions. The observation for cation **4e** of ^{31}P coupling from the ligand PPh$_2$ group to the methyl bound to the aluminium centre in both the ^{1}H and ^{13}C NMR spectra [*J*(PH) 1.9 Hz, *J*(PC) 35.3 Hz respectively] indicates that a bond exists between the metal and the phosphorus atom. By contrast, no similar coupling is seen for the dimethylaluminium precursor compound **2e** where the PPh$_2$ group is not bonded to the aluminium centre. This evidence confirms our description of the cations **4a**–**e** as the formally coordinatively saturated 4-coordinate species shown in Scheme 1.

Concluding remarks

This work demonstrates that the provision of a pendant donor group significantly alters the course of the reaction of the aluminium dimethyl compounds with B(C$_6$F$_5$)$_3$, allowing the cationic aluminium monomethyl systems to be isolated. Corresponding cations could not be formed in the absence of these additional donors. The donor arms which, in the dimethyl aluminium systems, are weakly bonding (**2a**–**d**) or non-bonding (**2e**) become normal donor groups in the cations **4a**–**e** and thereby stabilise these species.

Experimental

General

All manipulations were carried out under an atmosphere of dry nitrogen either using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glove-box. Solvents were refluxed over an appropriate drying agent, and distilled and degassed prior to use. Elemental analyses were performed by the microanalytical services of the Department of Chemistry at Imperial College or by Medac Ltd. ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded in C_6D_6 for the ligands and neutral compounds, and in CD_2Cl_2 for the cationic complexes, on Bruker AM500, DRX400 or AC250 machines at ambient temperature. ^{1}H and ^{13}C chemical shifts were referenced *via* the solvent signals to TMS, and ^{19}F and ^{31}P shifts were referenced to external standards ($CFCl_3$ and H_3PO_4). ^{13}C chemical shift assignments were based on DEPT experiments. IR spectra (nujol mulls, KBr or CsI windows) were run on Perkin-Elmer 577 and 457 grating spectrophotometers and mass spectra were measured on either a VG Autospec or a VG Platform II spectrometer. The reagent 1,2-(NH$_2$)(PPh$_2$)C$_6$H$_4$ was prepared by a previously described procedure.[10] All other chemicals were obtained commercially and used as received unless stated otherwise.

Preparation of ligands

3,5-Bu$^t_2$-2-(OH)C$_6$H$_2$CH=NCH$_2$CH$_2$NMe$_2$(1a). To a stirred solution of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (5.00 g, 21.3 mmol) in methanol (100 cm^3) was added *N*,*N*-dimethylethylenediamine (2.34 cm^3, 21.3 mmol). The solution was heated at reflux for 12 h, and was then dried over MgSO$_4$ and filtered. Removal of the volatile components *in vacuo* yielded a yellow oil. Repeated washing of the oil with pentane (5 × 5 cm^3) at −78 °C afforded **1a** as a yellow solid. Yield 6.1 g, 94%. Found C, 75.1; H, 10.7; N, 8.9. C$_{19}$H$_{32}$N$_2$O requires C, 75.0; H, 10.6; N, 9.2%. IR: 1732 (w), 1694 (w), 1634 (m, C=N stretch), 1362 (s), 1275 (s), 1253 (s), 1203 (s), 1173 (s), 1133 (w), 1041 (m), 969 (w), 933 (w), 877 (m), 828 (m), 773 (m), 730 (m), 645 (m). MS (EI): *m*/*z* 304 [M]$^+$, 289 [M − CH$_3$]$^+$, 260 [M − NMe$_2$]. ^{1}H NMR: δ 14.26 (s, 1H, O*H*), 7.84 (s, 1H, C*H*=N), 7.56 [d, 1H, ^{4}*J*(HH) 2.4 Hz, C$_6$*H*$_2$], 6.98 [d, 1H, ^{4}*J*(HH) 2.4 Hz, C$_6$*H*$_2$], 3.31 [t, 2H, ^{3}*J*(HH) 6.8 Hz, C*H*$_2$CH$_2$], 2.28 [t, 2H, ^{3}*J*(HH) 6.8 Hz, CH$_2$C*H*$_2$], 2.02 (s, 6H, N(C*H*$_3$)$_2$), 1.65 (s, 9H, C(C*H*$_3$)$_3$), 1.32 (s, 9H, C(C*H*$_3$)$_3$). ^{13}C NMR: δ 166.8 (*C*H=N), 158.9, 140.0, 137.1, 126.7, 126.3, 118.7 (4 quaternary + 2 CH resonances, *C*$_6$H$_2$), 60.1 (*C*H$_2$), 57.8 (*C*H$_2$), 45.7 [N(*C*H$_3$)$_2$], 35.4 (*C*Me$_3$), 34.3 (*C*Me$_3$), 31.7 [C(*C*H$_3$)$_3$], 29.8 [C(*C*H$_3$)$_3$].

3,5-Bu$^t_2$-2-(OH)C$_6$H$_2$CH=N-2-OPhC$_6$H$_4$ (1b). As for **1a** but with 2-phenoxyaniline (3.95 g, 21.3 mmol) in place of the ethylenediamine and using formic acid (2 drops) as catalyst. Slow concentration of the resulting dried methanolic solution led to crystallisation of the product. **1b** was obtained as a yellow solid by filtration. Yield 7.25 g, 85%. Found C, 80.7; H, 7.8; N, 3.3. C$_{27}$H$_{31}$NO$_2$ requires C, 80.8; H, 7.6; N, 3.5%. IR: 1620 (s, C=N stretch), 1582 (m), 1378 (s), 1363 (m), 1276 (m), 1243 (s), 1216 (m), 1202 (m), 1168 (s), 1102 (m), 1075 (w), 1035 (w), 981 (w), 940 (w), 887 (m), 853 (m), 824 (w), 797 (w), 777 (w), 761 (s), 749 (s), 688 (m). MS (EI): *m*/*z* 401 [M]$^+$, 386 [M − CH$_3$]$^+$, 344 [M − C(CH$_3$)$_3$]$^+$. ^{1}H NMR: δ 13.83 (s, 1H, O*H*), 8.18 (s, 1H, C*H*=N), 7.56 [d, 1H, ^{4}*J*(HH) 2.4 Hz, C$_6$*H*$_2$], 7.05–6.79 (m, 10H, Ar-*H*), 1.56 (s, 9H, C(C*H*$_3$)$_3$), 1.29 (s, 9H, C(C*H*$_3$)$_3$). ^{13}C NMR: δ 164.9 (CH=N), 164.6, 163.8, 159.2, 158.2, 150.0, 141.2, 140.3, 137.5, 129.9, 127.3, 124.7, 123.0, 121.3, 121.0, 119.0, 118.0 (7 quaternary + 9 CH resonances, *C*$_6$H$_2$ + *C*$_6$H$_4$ + *C*$_6$H$_5$), 35.4 (*C*Me$_3$), 34.2 (*C*Me$_3$), 31.6 [C(*C*H$_3$)$_3$], 29.7 [C(*C*H$_3$)$_3$].

3,5-Bu$^t_2$-2-(OH)C$_6$H$_2$CH=N-2-CH$_2$C$_5$H$_4$N (1c). As for **1a** but using 2-(methylamino)pyridine (2.12 cm^3, 21.3 mmol) in place of the diamine and with methanol (50 cm^3). After the reflux, the volatile components were removed *in vacuo* affording a yellow oily solid. Washing with pentane (5 × 5 cm^3) at −78 °C afforded **1c** as a yellow solid. Yield 6.0 g, 87%. Found C, 77.9; H, 8.5; N, 8.6. C$_{21}$H$_{28}$N$_2$O requires C, 77.7; H, 8.7; N, 8.6%. IR: 1631 (s, C=N stretch), 1591 (s), 1571 (m), 1378 (s), 1362 (s), 1342 (m), 1314 (w), 1297 (w), 1271 (m), 1252 (s), 1203 (m), 1174 (m), 1148 (m), 1133 (w), 1098 (w), 1058 (m), 1048 (m), 1005 (m), 993 (w), 963 (w), 928 (w), 883 (m), 853 (m), 827 (m), 802 (w), 769 (s), 750 (m), 729 (m), 705 (w), 645 (w). M.S. (EI): *m*/*z* 324 [M]$^+$, 309 [M − CH$_3$]$^+$, 267 [M − C(CH$_3$)$_3$]$^+$, 232 [M − CH$_2$C$_5$H$_4$N]$^+$. ^{1}H NMR: δ 14.12 (s, 1H, O*H*), 8.44–8.41 (m, 1H, C$_5$*H*$_4$N), 7.86 (s, 1H, C*H*=N), 7.57 [d, ^{4}*J*(HH) 2.5 Hz, C$_6$*H*$_2$], 7.01–6.98 (m, 2H, C$_5$*H*$_4$N), 6.93 [d, ^{4}*J*(HH) 2.5 Hz, C$_6$*H*$_2$], 6.61–6.56 (m, 1H, C$_5$*H*$_4$N), 4.63 (s, 2H, C*H*$_2$), 1.63 [s, 9H, C(C*H*$_3$)$_3$], 1.32 [s, 9H, C(C*H*$_3$)$_3$]. ^{13}C NMR: δ 168.4 (*C*H=N), 163.7, 158.9, 149.6, 140.3, 137.1, 136.3, 127.1, 126.8, 122.0, 121.6, 118.7

(5 quaternary + 6 CH resonances, C_6H_2 + C_5H_4N), 65.2 (CH_2), 35.4 (CMe_3), 34.3 (CMe_3), 31.7 [$C(CH_3)_3$], 29.8 [$C(CH_3)_3$].

3,5-Bu$^t_2$-2-(OH)C_6H_2CH-N-8-C_9H_6N (1d). As for **1c** but using 8-aminoquinoline (3.07 g, 21.3 mmol) in place of the pyridine and with formic acid (2 drops). After the reflux, the resulting rust-coloured precipitate was filtered off and was washed with methanol (10 cm^3) to provide **1d** as an orange powder. Yield 6.9 g, 90%. Found C, 79.7; H, 8.0; N, 7.6. $C_{24}H_{28}N_2O$ requires C, 80.0; H, 7.8; N, 7.8%. IR: 1615 (s, C=N stretch), 1563 (m), 1498 (m), 1378 (s), 1367 (s), 1325 (m), 1312 (m), 1274 (m), 1250 (s), 1201 (m), 1179 (m), 1163 (m), 1088 (m), 1055 (m), 1026 (w), 980 (w), 930 (w), 906 (w), 885 (w), 826 (m), 805 (w), 791 (s), 774 (m), 756 (m), 728 (w). MS (EI): *m*/*z* (EI, *m*/*z*) 360 $[M]^+$, 345 $[M - CH_3]^+$, 303 $[M - C(CH_3)_3]^+$. ^{1}H NMR: δ 14.82 (s, 1H, O*H*), 8.68–8.65 (m, 1H, C_9H_6N), 8.63 (s, 1H, C*H*=N), 7.65 [d, ^4J(HH) 2.4 Hz, C_6H_2], 7.53–7.48 (m, 1H, C_9H_6N), 7.25–7.02 (m, 3H, C_9H_6N), 7.15 [d, ^4J(HH) 2.4 Hz, C_6H_2], 6.75–6.70 (m, 1H, C_9H_6N), 1.69 (s, 9H, $C(CH_3)_3$), 1.32 (s, 9H, $C(CH_3)_3$). ^{13}C NMR: δ 166.8 (*C*H=N), 163.3, 159.5, 150.1, 146.0, 142.6, 140.0, 139.6, 137.3, 135.3, 129.1, 126.3, 125.4, 121.3, 119.7, 119.1 (7 quaternary + 8 CH resonances, C_6H_2 + C_9H_6N), 35.3 (CMe_3), 34.0 (CMe_3), 31.4 [$C(CH_3)_3$], 29.6 [$C(CH_3)_3$].

3,5-Bu$^t_2$-2-(OH)C_6H_2CH=N-2-PPh$_2$$C_6H_4$ (1e). As for **1b** but with 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (3.00 g, 12.8 mmol) and 2-diphenylphosphinoaniline (3.55 g, 12.8 mmol) in ethanol (100 ml). Slow concentration of the dried ethanolic solution resulted in crystallisation of the product. **1b** was obtained by filtration as a yellow crystalline solid. Yield 5.5 g, 87%. Found C, 79.7; H, 7.3; N, 2.8. $C_{33}H_{36}NPO$ requires C, 80.3; H, 7.4; N, 2.8%. IR: 1616 (s, C=N stretch), 1595m, 1595m, 1311w, 1283m, 1248m, 1199w, 1163m, 1135w, 1092w, 1023w, 979w, 936w, 887w, 802w, 760s, 739s, 689s, 668w. MS (EI): *m*/*z* 493 $[M]^+$. ^{1}H NMR: δ 13.46 (s, 1H, O*H*), 7.97 (s, 1H, C*H*=N), 7.54 [d, ^4J(HH) 2.4 Hz, C_6H_2] 7.55–6.65 (several m, 14H, C_6H_4 + C_6H_5), 6.88 [d, ^4J(HH) 2.4 Hz, C_6H_2] 1.61 [s, 9H, $C(CH_3)_3$], 1.27 [s, 9H, $C(CH_3)_3$]. ^{13}C NMR: δ 163.81 (H*C*=N), 158.89, 140.18, 137.29, 118.80 (4 quaternaries of C_6H_2), 152.14 [d, *J*(PC) 19.1 Hz, PAr–*C*N], 136.90 [d, *J*(PC) 11.9 Hz, P(C_6H_5) quaternary), 134.50 [d, *J*(PC) 13.9 Hz, PC_6H_4 quaternary], 134.68 [d, *J*(PC) 20.6 Hz], 133.35, 129.88, 128.90 [d, *J*(PC) 12.2 Hz], 128.71, 128.22 [d, *J*(PC) 16.7 Hz], 127.38, 126.77, 118.00 (9 *C*H resonances, C_6H_2 + C_6H_4 + C_6H_5), 35.39 (CMe_3), 34.16 (CMe_3), 31.58 [$C(CH_3)$], 29.65 [$C(CH_3)$]. ^{31}P NMR δ 13.53 (s).

Preparation of complexes

AlMe$_2$[3,5-Bu$^t_2$-2-(O)C_6H_2CH=NCH$_2$CH$_2$NMe$_2$] (2a). Trimethylaluminium in toluene (2.0 M, 1.81 cm^3, 3.61 mmol) was added dropwise to a solution of **1a** (1.00 g, 3.28 mmol) in toluene (30 cm^3). The reaction was stirred at room temperature for 12 h, then the volatiles removed *in vacuo*. The product was extracted into hot MeCN (30 cm^3). Filtration and cooling to room temperature afforded **2a** as large yellow platy needles. Yield 0.83 g. 70%. Found C, 69.8; H, 10.3; N, 7.8. $C_{21}H_{37}AlN_2O$ requires C, 69.6; H, 10.3; N, 7.4%. IR: 1623 (s, C=N stretch), 1607 (m), 1555 (m), 1540 (m), 1422 (m), 1360 (m), 1347 (m), 1335 (m), 1279 (w), 1260 (s), 1239 (m), 1202 (m), 1178 (s), 1135 (w), 1098 (w), 1082 (m), 1066 (w), 1045 (w), 1027 (m), 995 (w), 982 (w), 948 (w), 929 (w), 896 (m), 880 (w), 847 (m), 814 (w), 791 (m), 751 (w), 690 (s), 667 (s), 639 (s). MS (EI): *m*/*z* 345 $[M - CH_3]^+$. ^{1}H NMR: δ 7.66 [d, 1H, ^4J(HH) 2.4 Hz, C_6H_2], 7.39 (s, 1H, C*H*=N), 6.80 [d, 1H, ^4J(HH) 2.6 Hz, C_6H_2], 2.86 [t, 2H, ^3J(HH) 6.8 Hz, CH_2CH_2], 2.08 [t, 2H, ^3J(HH) 6.2 Hz, CH_2CH_2], 1.85 [s, 6H, N(CH_3)$_2$], 1.63 [s, 9H, $C(CH_3)_3$], 1.30 [s, 9H, $C(CH_3)_3$], −0.26 (s, 6H, AlCH_3). ^{13}C NMR: δ 172.8 (*C*H=N), 163.3, 140.9, 137.9, 131.4, 118.5 (5 Ar-*C* resonances, 6th obscured by solvent, C_6H_2), 57.8 (CH_2), 54.1 (CH_2), 45.2 [N(CH_3)$_2$], 35.4 (CMe_3), 34.1 (CMe_3), 31.6 [$C(CH_3)_3$], 29.6 [$C(CH_3)_3$], −8.3 (br, AlCH_3). *Crystal data* for **2a**: $C_{21}H_{37}N_2OAl$, M = 360.5, monoclinic, $P2_1/c$ (no. 14), a = 10.332(2), b = 24.982(4), c = 9.729(2) Å, β = 115.98(1)°, V = 2257.4(7) Å^3, Z = 4, D_c = 1.061 g cm^{-3}, μ(Mo-Kα) = 1.00 cm^{-1}, T = 293 K, yellow platy needles; 2934 independent measured reflections, F^2 refinement, R_1 = 0.067, wR_2 = 0.156, 1646 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 45°$], 226 parameters.

CCDC reference number 134423.

AlMe$_2$[3,5-Bu$^t_2$-2-(O)C_6H_2CH=N-2-OPhC_6H_4] (2b). Trimethylaluminium in toluene (2.0 M, 1.37 cm^3, 2.74 mmol) was added dropwise to a solution of **1b** (1.00 g, 2.49 mmol) in toluene (30 cm^3). After refluxing for 12 h, the volatiles were removed *in vacuo*, and the product extracted into MeCN (10 cm^3). Cooling to −30 °C resulted in the formation of an orange oil. On drying the oil under reduced pressure, a bright yellow glassy solid, **2b**, was formed. Yield 0.72 g, 63%. Found: C, 75.8; H, 7.9; N, 3.4. $C_{29}H_{36}AlNO_2$ requires C, 76.1; H, 7.9; N, 3.1%. (satisfactory analysis not obtained; ascribed to oily nature of product). IR: 1622 (s, C=N stretch), 1575 (w), 1555 (w), 1538 (m), 1504 (w), 1488 (w), 1424 (s), 1363 (m), 1353 (m), 1336 (m), 1286 (m), 1257 (m), 1237 (m), 1225 (m), 1200 (m), 1174 (s), 1070 (m), 1050 (m), 1019 (w), 1007 (w), 917 (w), 881 (w), 846 (w), 792 (w), 763 (m), 752 (w), 727 (m), 660 (s), 639 (s). MS (EI): *m*/*z* 442 $[M - CH_3]^+$. ^{1}H NMR: δ 7.73 (s, 1H, C*H*=N), 7.70 [d, ^4J(HH) 2.6 Hz, C_6H_2], 6.97–6.61 (m, 10H, C_6H_2 + C_6H_4 + C_6H_5), 1.58 [s, 9H, $C(CH_3)_3$], 1.27 [s, 9H, $C(CH_3)_3$], −0.19 (s, 6H, AlCH_3). ^{13}C NMR: δ 172.7 (*C*H=N), 163.8 (Ar–*C*), 155.7 (Ar–*C*), 151.1 (Ar–*C*), 141.3 (Ar–*C*), 139.0 (Ar–*C*), 137.8 (Ar–*C*), 133.0 (Ar–*C*), 130.3 (Ar–*C*), 130.2 (Ar–*C*), 129.6 (Ar–*C*), 126.7 (Ar–*C*), 124.6 (Ar–*C*), 123.8 (Ar–*C*), 123.4 (Ar–*C*), 120.4 (Ar–*C*), 119.5 (Ar–*C*), 117.9 (Ar–*C*), 35.6 (CMe_3), 34.1 (CMe_3), 31.4 [$C(CH_3)_3$], 29.6 [$C(CH_3)_3$], −9.0 (br, AlCH_3).

AlMe$_2$[3,5-Bu$^t_2$-2-(O)C_6H_2CH=N-2-CH$_2$$C_5H_4$N] (2c). As for **2a** but with trimethylaluminium (2.0 M, 1.69 cm^3, 3.39 mmol) and **1c** (1.00 g, 3.08 mmol). The product was extracted into hot MeCN and filtered. Concentration of this solution to 15 cm^3 and cooling to −30 °C resulted in the formation of **2c** as pale orange crystals. Yield 0.74 g, 63%. Found: C, 72.2; H, 8.7; N, 6.9. $C_{23}H_{33}AlN_2O$ requires C, 72.6; H, 8.7; N, 7.4%. (%C consistently low. Sample pure spectroscopically). IR: 1615 (s, C=N stretch), 1587 (s), 1556 (m), 1540 (s), 1490 (s), 1438 (s), 1410 (m), 1363 (m), 1324 (m), 1278 (m), 1252 (s), 1200 (s), 1175 (s), 1136 (w), 1111 (m), 1072 (w), 1025 (w), 987 (w), 930 (w), 894 (w), 876 (w), 857 (m), 787 (m), 761 (m), 750 (m), 687 (s). MS (EI): *m*/*z* 365 $[M - CH_3]^+$. ^{1}H NMR: δ 8.31–8.28 (m, 1H, C_5H_4N), 7.72 [d, 1H, ^4J(HH) 2.6, C_6H_2], 7.38 [t, 1H, ^4J(HH) 1.3, C*H*=N), 6.83 [d, 1H, ^4J(HH) 2.5, C_6H_2], 6.80 [dt, 1H, ^3J(HH) 7.7, ^4J(HH) 1.7, C_5H_4N], 6.50–6.39 (m, 1H, C_5H_4N), 6.22–6.14 (m, 1H, C_5H_4N), 3.81 (br. s, 2H, CH_2), 1.76 (s, 9H, $C(CH_3)_3$), 1.38 (s, 9H, $C(CH_3)_3$), −0.15 (s, 6H, AlCH_3). ^{13}C NMR: δ 172.5 (*C*H=N), 166.1, 153.8, 146.6, 141.3, 137.5, 136.5, 131.5, 123.0, 120.5, 118.1 (10 Ar–C*C* resonances, 11th obscured by solvent, C_6H_2 + C_5H_4N), 59.3 (CH_2), 35.7 (CMe_3), 34.1 (CMe_3), 31.6 [$C(CH_3)_3$], 29.8 [$C(CH_3)_3$], −5.1 (br, AlCH_3). *Crystal data for* **2c**: $C_{23}H_{33}N_2OAl$, M = 380.5, monoclinic, $P2_1/c$ (no. 14), a = 15.009(2), b = 12.207(2), c = 14.129(1) Å, β = 116.36(1)°, V = 2319.5(4) Å^3, Z = 4, D_c = 1.090 g cm^{-3}, μ(Mo-Kα) = 1.01 cm^{-1}, T = 293 K, yellow prisms; 5299 independent measured reflections, F^2 refinement, R_1 = 0.054, wR_2 = 0.136, 3526 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 55°$], 245 parameters.

CCDC reference number 134424.

AlMe$_2$[3,5-Bu$^t_2$-2-(O)C_6H_2CH=N-9-C_9H_6N] (2d). As for **2a** but with trimethylaluminium in toluene (2.0 M, 0.76 cm^3, 1.53

mmol) and **1d** (0.50 g, 1.39 mmol) in toluene (15 cm^3). The resulting solution was evaporated to dryness *in vacuo* affording **2d** as a dark red glassy solid. Approx. yield 0.39 g, 67%. Found: C, 71.9; H, 7.7; N, 6.2. $C_{26}H_{33}AlN_2O$ requires C, 75.0; H, 8.0; N, 6.7%. (satisfactory analysis not obtained; ascribed to oily nature of product). IR: 1618 (s, C=N stretch) 1600 (m), 1587 (s), 1537 (s), 1505 (s), 1439 (s), 1412 (s), 1363 (m), 1339 (m), 1319 (w), 1253 (m), 1234 (m), 1202 (m), 1182 (m), 1169 (m), 1132 (w), 1088 (m), 1069 (w), 1027 (w), 980 (w), 921 (w), 875 (w), 846 (w), 831 (w), 794 (m), 756 (w), 730 (w), 766 (m). MS (EI): *m*/*z* 416 $[M]^+$, 401 $[M - CH_3]^+$. ^{1}H NMR: δ 8.48–8.45 (m, 1H, C_9H_6N), 8.11 (s, 1H, C*H*=N), 7.77 [d, 1H, ^4J(HH) 2.6 Hz, C_6H_2], 7.32–7.28 (m, 1H, C_9H_6N), 7.06–6.96 (m, 2H, C_9H_6N), 6.94 [d, 1H, ^4J(HH) 2.6 Hz, C_6H_2], 6.66–6.58 (m, 2H, C_9H_6N), 1.79 [s, 9H, $C(CH_3)_3$], 1.39 [s, 9H, $C(CH_3)_3$], −0.05 (s, 6H, $AlCH_3$). ^{13}C NMR: δ 169.1 (H*C*=N), 165.9, 146.5, 142.4, 142.0, 139.7, 137.2, 136.7, 133.2, 129.3, 128.7, 127.8, 124.2, 122.6, 118.7, 114.9 (7 quaternary + 8 CH resonances, C_6H_2 + C_9H_6N), 35.7 (CMe_3), 34.2 (CMe_3), 31.5 [$C(CH_3)_3$], 29.8 [$C(CH_3)_3$], −4.0 ($AlCH_3$).

$AlMe_2$[3,5-Bu^t_2-2-(O)C_6H_2CH=N-2-$PPh_2C_6H_4$] (2e). As for **2b** but with trimethylaluminium in toluene (2.0 M, 1.12 cm^3, 2.24 mmol) and (**1e**) (1.00 g, 2.03 mmol). After removal of the volatiles *in vacuo* the product was extracted into MeCN (10 cm^3). Cooling and prolonged standing (1–2 days) at ambient temperature resulted in the formation of yellow crystalline **2e**. Yield 0.79 g, 71%. Found: C, 76.4; H, 7.3; N, 3.1. $C_{35}H_{41}$AlNPO requires C, 76.5; H, 7.5; N, 2.6%. IR: 1614 (s, C=N stretch) 1598 (m), 1584 (s), 1559 (s), 1543 (s), 1461 (s), 1437 (s), 1407 (w), 1388 (s), 1362 (m), 1320 (m), 1279 (w), 1256 (s), 1241 (m), 1178 (s), 1137 (w), 1126 (w), 1092 (w), 1068 (w), 1027 (w), 998 (w), 952 (w), 929 (w), 885 (m), 869 (w), 852 (s), 812 (w), 786 (w), 766 (s), 746 (s), 698 (s), 680 (s), 664 (m). MS (EI): *m*/*z* 550 $[M + H]^+$, 534 $[M - CH_3]^+$. ^{1}H NMR: δ 7.69 [d, 1H, ^4J(HH) 2.6 Hz, C_6H_2], 7.35 [d, 1H, J(PH) 3.4 Hz, C*H*=N], 7.38–7.29 (m, 1H, PC_6H_4), 7.22–7.16 (complex m, 5H, PAr-*H*), 7.03–6.90 (complex m, 7H, PAr-*H*), 6.82 [dt, 1H, J(HH) 7.5 Hz, J(PH) 1.4 Hz, PAr-*H*], 6.19 [d, 1H, ^4J(HH) 2.6 Hz, C_6H_2], 1.58 [s, 9H, $C(CH_3)_3$], 1.23 [s, 9H, $C(CH_3)_3$], −0.04 (s, 6H, Al-CH_3). ^{13}C NMR: δ 173.87 [d, J(PC) 5.7 Hz, H*C*=N], 163.26, 151.66 [d, J(PC) 24.4 Hz], 141.09, 138.86, 136.96 [d, J(PC) 11.30 Hz], 132.76 [d, J(PC) 18.8 Hz], 118.17 (7 quaternary aryl resonances), 136.50, 134.33 [d, J(PC) 20.4 Hz], 133.00, 130.15. 129.74, 128.98 [d, J(PC) 11.0 Hz], 128.89, 127.55, 124.68 (9 aryl *C*H resonances from C_6H_2, PC_6H_4 and $P(C_6H_5)_2$), 35.59 (CMe_3), 34.03 (CMe_3), 31.42 [$C(CH_3)_3$], 29.58 [$C(CH_3)_3$], −8.57 ($AlCH_3$). ^{31}P NMR: δ −18.14 (s). *Crystal data for* **2e**: $C_{35}H_{41}$NOPAl · 0.5MeCN, M = 570.2, monoclinic, $P2_1/n$ (no. 14), a = 15.329(1), b = 13.366(1), c = 17.575(1) Å, β = 108.81(1)°, V = 3408.5(4) $Å^3$, Z = 4, D_c = 1.111 g cm^{-3}, μ(Cu-Kα) = 11.7 cm^{-1}, T = 293 K, yellow prisms; 5019 independent measured reflections, F^2 refinement, R_1 = 0.069, wR_2 = 0.167, 3187 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 120°$], 359 parameters.

CCDC reference number 171206.

{AlMe[3,5-Bu^t_2-2-(O)C_6H_2CHMe-N-8-C_9H_6N]}$_2$ (3). Trimethylaluminium in toluene (2.0 M, 1.53 cm^3, 3.05 mmol) was added dropwise to a solution of **1d** (1.00 g, 2.77 mmol) in toluene (20 cm^3). After refluxing for 12 h, the volatiles were removed *in vacuo*, and the product extracted into MeCN (20 cm^3). Cooling to ambient temperature afforded an orange crystalline product consisting of ~81% **3** and ~19% **2d**. Pure **3** was obtained as orange crystals at room temperature after a recrystallisation from hot MeCN (50 cm^3). Overall yield 0.42 g, 36%. Found: C, 74.8; H, 8.1; N, 6.7. $C_{52}H_{66}Al_2N_4O_2$ requires C, 75.0; H, 8.0; N, 6.7%. IR: 1598 (m), 1575 (s), 1505 (s), 1429 (m), 1338 (s), 1287 (w), 1273 (w), 1261 (w), 1235 (m), 1220 (m), 1199 (m), 1174 (m), 1148 (m), 1129 (m), 1104 (m), 1081 (w), 1069 (w), 1057 (m), 977 (w), 957 (w), 938 (w), 918 (w), 904 (w), 879 (w), 830 (m), 817 (s), 805 (m), 785 (s), 777 (m), 744 (m), 738 (m), 674 (m), 621 (s). MS (EI): *m*/*z* 832 $[M]^+$, 817 $[M - CH_3]^+$, 416 [1/2 $M]^+$, 401 [1/2 M − $CH_3]^+$. ^{1}H NMR (integrals as for monomeric unit): δ 8.03–8.00 (m, 2H, C_9H_6N), 7.58 [d, 2H, ^4J(HH) 2.6 Hz, C_6H_2], 7.36–7.24 (m, 4H, C_9H_6N), 6.79 [d, 2H, ^4J(HH) 2.6 Hz, C_6H_2], 6.55–6.38 (m, 6H, C_9H_6N), 4.77 [q, 2H, ^3J(HH) 6.8 Hz, $CH(CH_3)$], 2.00 [s, 18H, $C(CH_3)_3$], 1.26 [s, 18H, $C(CH_3)_3$], 0.79 [d, 6H, ^3J(HH) 6.8 Hz, $CH(CH_3)$], −0.19 (s, 3H, $AlCH_3$). ^{13}C NMR: δ 149.6 (Ar–*C*), 149.1 (Ar–*C*), 144.4 (Ar–*C*), 143.5 (Ar–*C*), 140.2 (Ar–*C*), 139.1 (Ar–*C*), 138.8 (Ar–*C*), 137.6 (Ar–*C*), 140.2 (Ar–*C*), 139.1 (Ar–*C*), 138.8 (Ar–*C*), 137.6 (Ar–*C*), 130.8 (Ar–*C*), 129.6 (Ar–*C*), 119.9 (Ar–*C*), 108.6 (Ar–*C*), 106.2 (Ar–*C*), 57.1 (*C*HMe) 37.1 (CMe_3), 34.5 (CMe_3), 34.2 [$C(CH_3)_3$], 31.6 [$C(CH_3)_3$], 20.6 [CH-(CH_3)]. $AlCH_3$ not observed. *Crystal data for* **3**: $C_{52}H_{66}$-$N_4O_2Al_2$, M = 833.1, triclinic, $P\bar{1}$ (no. 2), a = 13.617(1), b = 18.114(2), c = 22.065(1) Å, α = 113.61(1), β = 96.62(1), γ = 95.98(1)°, V = 4885.5(7) $Å^3$, Z = 4 (2 independent molecules), D_c = 1.133 g cm^{-3}, μ(Cu-Kα) = 8.56 cm^{-1}, T = 293 K, orange blocky needles; 13981 independent measured reflections, F^2 refinement, R_1 = 0.071, wR_2 = 0.181, 9453 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 120°$], 1170 parameters.

CCDC reference number 171205.

See http://www.rsc.org/suppdata/dt/b1/b106131n/ for crystallographic data in CIF or other electronic format.

Preparation of cations

{AlMe[3,5-Bu^t_2-2-(O)C_6H_2CH=N$CH_2CH_2NMe_2$]}{MeB-(C_6F_5)$_3$} (4a). A solution of $B(C_6F_5)_3$ (25.6 mg, 0.05 mmol) in CD_2Cl_2 (0.20 ml) was added dropwise to a vigorously shaken solution of **3a** (18.0 mg, 0.05 mmol) in CD_2Cl_2 (0.30 ml) resulting in an essentially NMR-pure yellow–green solution of the product. ^{1}H NMR: δ 8.55 (s, 1H, C*H*=N), 7.76 [d, 1H, ^4J(HH) 2.6 Hz, C_6H_2], 7.27 [d, 1H, ^4J(HH) 2.6 Hz, C_6H_2], 4.0 (br.s, CH_2CH_2), 3.0 (br.s, CH_2CH_2), 2.77 (br.s, 6H, $N(CH_3)_2$), 1.41 (s, 9H, $C(CH_3)_3$), 1.31 (s, 9H, $C(CH_3)_3$), 0.47 (s, 3H, BCH_3), −0.31 (s, 3H, $AlCH_3$). ^{13}C NMR: δ (cation part only) 175.83 (H*C*=N), 158.88, 143.78, 141.65, 120.00 (4 quaternaries, C_6H_2), 135.44, 129.33 (2 *C*H resonances, C_6H_2), 58.42 (CH_2), 48.86 (CH_2), 46.23 [br, $N(CH_3)_2$], 35.79 (CMe_3), 34.60 (CMe_3), 31.10 [$C(CH_3)_3$], 29.45 [$C(CH_3)_3$], −14.78 (br, $AlCH_3$), also CH_3B of anion seen as broad resonance at δ 10.4. ^{19}F NMR: δ −135.4 (6F), −167.3 (3F), −170.0 (6F).

{AlMe[3,5-Bu^t_2-2-(O)C_6H_2CH=N-2-OPhC_6H_4]}{MeB(C_6F_5)$_3$} (4b). A solution of $B(C_6F_5)_3$ (51.2 mg, 0.10 mmol) in C_6D_6 (0.50 ml) was added dropwise to a vigorously shaken solution of **2b** (45.8 mg, 0.10 mmol) in C_6D_6 (0.40 ml). During the addition the solution became cloudy and an oil began to separate. C_6D_6 (0.20 ml) was used to wash the residual $B(C_6F_5)_3$ into the shaken reaction mixture. After standing for 0.5 h the supernatant C_6D_6 solution was decanted and the residual oil was evacuated to yield a foamed solid which was dissolved in CD_2Cl_2. ^{1}H NMR: δ8.58 (s, 1H, C*H*=N), 8.16 [d, 1H, ^4J(HH) 2.5, C_6H_2], 7.71 [d, 1H, ^4J(HH) 2.5, C_6H_2], 7.6–6.9 (several m, 9H, C_6H_4 + C_6H_5), 1.46 (s, 9H, $C(CH_3)_3$), 1.26 (s, 9H, $C(CH_3)_3$), 0.43 (br s, 3H, BCH_3), −0.35 (s, 3H, $AlCH_3$). ^{13}C NMR: δ (cation part only) 167.23 (H*C*=N), 152.08, 150.04, 149.74, 149.01, 143.65, 128.59, 123.56 (7 quaternaries, C_6H_2 + C_6H_4 + C_6H_5), 139.85, 134.24, 133.42, 132.92, 131.04, 130.59, 127.53, 123.17, 117.59, (9 CH resonances, C_6H_2 + C_6H_4 + C_6H_5), 36.54 (CMe_3), 35.45 (CMe_3), 31.79 [$C(CH_3)_3$], 31.01 [$C(CH_3)_3$], −10.67 ($AlCH_3$), also CH_3B of anion seen as broad resonance at δ 10.5. ^{19}F NMR: δ −135.4 (6F), −167.3 (3F), −170.0 (6F).

{AlMe[3,5-Bu^t_2-2-(O)C_6H_2CH=N-2-$CH_2C_5H_4$N]}{MeB-(C_6F_5)$_3$} (4c). As for **4b**, but using **2c** (38.0 mg, 0.10 mmol). ^{1}H NMR: δ 8.46 (s, 1H, C*H*=N), 8.05 [dt, 1H, ^3J(HH) 7.9, ^4J(HH)

1.5, C_5H_4N], 8.00 [d, 1H, ^4J(HH) 2.5, C_6H_2], 7.82 [d, 1H, ^3J(HH) 5.3, C_5H_4N], 7.51 [d, 1H, ^3J(HH) 8.0, C_5H_4N], 7.20 [m, 1H, C_5H_4N], 7.20 [dt, 1H, ^3J(HH) 6.3, ^4J(HH) 1.1, C_5H_4N], 7.07 [d, 1H, ^4J(HH) 2.5, C_6H_2], 5.15 [AB q, 2H, ^3J(HH) 1.5, CH_2CH_2], 4.98 [AB q, 2H, ^3J(HH) 1.5, CH_2CH_2], 1.75 (s, 9H, $C(CH_3)_3$), 1.26 (s, 9H, $C(CH_3)_3$), 0.48 (br s, 3H, BCH_3), −0.47 (s, 3H, $AlCH_3$). ^{13}C NMR: δ (cation part only) 176.45 (H*C*=N), 151.78, 150.25, 149.84, 145.20, 143.77, 142.74, 138.49, 132.95, 125.74, 123.89, 122.98 (6 *C*H and 5 quaternary resonances, C_6H_2 + C_5H_4N), 56.06 (CH_2), 37.11 (CMe_3), 34.95 (CMe_3), 32.95 [$C(CH_3)_3$], 30.94 [$C(CH_3)_3$], −9.45 ($AlCH_3$), also CH_3B of anion seen as broad resonance at δ 10.5. ^{19}F NMR: δ −135.4 (6F), −167.1 (3F), −169.8 (6F).

{AlMe[3,5-Bu$^t_2$-2-(O)C$_6$H$_2$CH=N-8-C$_9$H$_6$N]}{MeB(C$_6$F$_5$)$_3$} (4d). As for **4b**, but using $B(C_6F_5)_3$ (30.7 mg, 0.60 mmol) and **2d** (25.0 mg, 0.60 mmol). ^{1}H NMR: δ 8.67 [dd, 1H, J(HH) 8.4 Hz, J(HH) 1.3 Hz, C_9H_6N], 8.26–8.16 9 (m, 2H, C_9H_6N), 8.08 [d, 1H, ^4J(HH) 2.5 Hz, C_6H_2], 8.02 (s, 1H, *H*C=N), 7.91 (t, 1H, J(HH) 8.0, C_9H_6N), 7.48 [dd, J(HH) 8.4 Hz, J(HH) 8.4 Hz, C_9H_6N], 7.33 [d, 1H, J(HH) 7.6, C_9H_6N], 6.94 [d, ^4J(HH) 2.5 Hz, C_6H_2], 1.83 [s, 9H, $C(CH_3)_3$], 1.25 [s, 9H, $C(CH_3)_3$], 0.38 (br s, 3H, BCH_3), −0.35 (s, 3H, $AlCH_3$). ^{13}C NMR: δ (cation part only) 166.10 (H*C*=N), 150.57, 150.49, 142.93, 137.59, 134.52, 129.04, 123.08 (7 quaternaries, C_6H_2 + C_9H_6N), 148.36, 143.34, 131.12, 129.73, 123.93, 117.94 (6 *C*H resonances of C_9H_6N), 139.09, 133.30 (2 *C*H resonances of C_6H_2), 37.02 (CMe_3), 34.98 (CMe_3), 32.75 [$C(CH_3)_3$], 30.86 [$C(CH_3)_3$], −9.82 ($AlCH_3$), also CH_3B of anion seen as broad resonance at δ 10.5. ^{19}F NMR: δ −135.4 (6F), −167.1 (3F), −169.8 (6F).

{AlMe[3,5-Bu$^t_2$-2-(O)C$_6$H$_2$CH=N-2-PPh$_2$C$_6$H$_4$]}{MeB(C$_6$F$_5$)$_3$} (4e). As for **4b**, but using $B(C_6F_5)_3$ (41.0 mg, 0.80 mmol) in C_6D_6 (0.5 ml) and **2e** (44.0 mg, 0.80 mmol) in C_6D_6 (0.5 ml). ^{1}H NMR: δ 8.59 [d, J(PH) 2.0 Hz, *H*C=N), 7.95–7.85 (m, 1H, PC_6H_4), 7.79 [d, 1H, ^4J(HH) 2.6 Hz, C_6H_2], 7.75–7.30 (complex m′s, 13H, Ar − *H*), 7.26 [d, 1H, ^4J(HH) 2.6 Hz, C_6H_2], 1.49 (s, 9H, $C(CH_3)_3$), 1.29 (s, 9H, $C(CH_3)_3$), 0.46 (br.s, 3H, BCH_3), −0.12 [d, 3H, J(PH) 1.9 Hz, $AlCH_3$]. ^{13}C NMR: δ (cation part only) 172.59 (H*C*=N), 160.27, 148.11 [d, J(PC) 12.6 Hz], 143.97, 141.74, 120.73 [d, J(PC) 40.2 Hz], 119.46 (6 aryl quaternaries, 7th is obscured), 136.79, 136.59, 134.66, 134.11, 133.54, 131.47 [d, (J(PC) 6.3 Hz], 130.85, 130.75, 119.89 [d, J(PC) 3.5 Hz] (9 aryl *C*H resonances C_6H_2, C_6H_4 and C_6H_5), 35.71 (CMe_3), 34.58 (CMe_3), 31.02 [$C(CH_3)$], 29.41 [$C(CH_3)$], −11.00 [d, J(PC) 35.3 Hz, $AlCH_3$], also CH_3B of anion seen as broad resonance at δ 10.4. ^{19}F NMR: δ −135.5 (6F), −167.5 (3F), −170.1 (6F).

Acknowledgements

BP-Amoco Chemicals and ICI Acrylics are thanked for financial support and the Royal Society & Leverhulme Trust for Fellowships (J. A. S. & C. R., respectively).

References

1 See S. D. Ittel, L. K. Johnson and M. Brookhart, *Chem. Rev.*, 2000, **100**, 1203 and references therein; also see *e.g.* (*a*) B. L. Small and M. Brookhart, *J. Am. Chem. Soc.*, 1998, **120**, 7143; (*b*) B. L. Small, M. Brookhart and A. M. A. Bennett, *J. Am. Chem. Soc*, 1998, **120**, 4049; (*c*) G. J. P. Britovsek, V. C. Gibson, B. S. Kimberley, P. J. Maddox, S. J. McTavish, G. A. Solan, A. J. P. White and D. J. Williams, *Chem. Commun.*, 1998, 849; (*d*) C. Wang, S. Friedrich, T. R. Younkin, R. T. Li, R. H. Grubbs, D. A. Bansleben and M. W. Day, *Organometallics*, 1998, **17**, 3149; (*e*) T. R. Younkin, E. F. Conner, J. I. Henderson, S. K. Friedrich, R. H. Grubbs and D. A. Bansleben, *Science*, 2000, **287**, 460; (*f*) L. K. Johnson, C. M. Killian and M. Brookhart, *J. Am. Chem. Soc.*, 1995, **117**, 6414; (*g*) L. K. Johnson, S. Mecking and M. Brookhart, *J. Am. Chem. Soc.*, 1996, **118**, 267.
2 M. Bruce, V. C. Gibson, C. Redshaw, G. A. Solan, A. J. P. White and D. J. Williams, *Chem. Commun.*, 1998, 2523.
3 M. P. Coles and R. F. Jordan, *J. Am. Chem. Soc.*, 1997, **119**, 8125.
4 P. A. Cameron, V. C. Gibson, C. Redshaw, J. A. Segal, G. A. Solan, A. J. P. White and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 2001, 1472.
5 P. A. Cameron, V. C. Gibson, C. Redshaw, J. A. Segal, M. Bruce, A. J. P. White and D. J. Williams, *Chem. Commun.*, 1999, 1883.
6 V. C. Gibson, C. Redshaw, A. J. P. White and D. J. Williams, *J. Organomet. Chem.*, 1998, **550**, 453.
7 J. M. Klerks, D. J. Stufkens, G. van Koten and K. Vrieze, *J. Organomet. Chem.*, 1979, **181**, 271.
8 G. van Koten and K. Vrieze, *Adv. Organomet. Chem.*, 1982, **21**, 151.
9 X. Yang, C. L. Stern and T. J. Marks, *J. Am. Chem. Soc.*, 1994, **116**, 10015.
10 M. K. Cooper, J. M. Downes, P. A. Duckworth, M. C. Kerby, R. J. Powell and M. D. Soucek, *Inorg Synth.*, 1989, **25**, 129.