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Imidazolium formation from the reaction of *N*-heterocyclic carbene stabilised group 13 trihydride complexes with organic acids

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Abstract

The reactions of the *N*-heterocyclic carbene (NHC) stabilised group 13 trihydride complexes [AlH₃(IMeMe)] (1) (IMeMe = 1,3,4,5-tetramethylimidazol-2-ylidene), [AlH₃(IⁱPrMe)] (2) (IⁱPrMe = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) with three molar equivalents of phenol, and [InH₃(IMes)] (3) (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazole-2-ylidene) with one molar equivalent of 1,1,1,5,5,5-hexafluoropentan-2,4-dione (F₆acacH) are presented. These render the imidazolium tetraphenoxya-luminate species; [IMeMe \cdot H][Al(OPh)₄] (4) and [IⁱPrMe \cdot H][Al(OPh)₄] (5), and 1,3-bis(2,4,6-trimethylphenyl)imidazolium 1,1,5,5,5-hexafluoropentan-2,4-dionate; [IMes \cdot H][CH{C(O)CF₃}₂] (6), the latter leading to metallohydride decomposition. The molecular structures of 4 and 6 are described.

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1. Introduction

Recently we have systematically studied the preparation, stability and synthetic utility of *N*-heterocyclic carbene (NHC) adducted group 13 trihydrides [1–7] and trihalides [8–10]. Our success in this area is exemplified by the thermally stable indium trihydride complex [InH3(IMes)] (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazole-2-ylidene), **3** [3], (decomposition in the solid-state 115 °C, cf. [InH3(I⁷PrMe)] decomposition; -5 °C [1], where I⁷PrMe = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) and the thallium trihalide adduct [TlCl3(IMes)] [10], which exhibits a divalent carbon coordinated to a highly oxidative thallium(III) metal centre [11].

Two logical steps in exploring the chemistry of the trihydride derivatives have been their application toward the preparation of group 13–16 [M(ER)3L] species (M = Al, Ga, In; E = group 16 element; L = Lewis base) [2,12], which have potential as set-stoichiometry precursors to III/VI semiconductor materials [13], and the study of their hydrometallation chemistry when treated with unsaturated organic substrates [6,14]. Herein we present two examples of these approaches that, contrary to the anticipated outcomes, yield imidazolium species. These reactions suggest group 13 coordinated *N*-heterocyclic carbenes (NHCs) remain available for secondary acid–base reactions and hence, unlike their amine and phosphine congeners [15,16], may be flawed in terms of their synthetic utility.

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2.1. Reaction of $[AlH_3(NHC)]$ species with phenol

The established preparation of compounds of type $[M(ER_3)L]$ via the reaction of a parent trihydride with 1.5 equivalents of diaryl- or alkyldichalcogenide [2,12], e.g., PhSeSePh, is undesirable for systems where E = oxygen due to the requirement for hazardous organic peroxides. The alternative reaction of NHC stabilised aluminium trihydride species with three equivalents of phenol potentially offers a preferable path to these compounds.

Contrary to the expected [Al(OPh)₃(NHC)] products, low temperature (-50 °C) treatment of tetrahydrofuran solutions of [AlH₃(IMeMe)] (1) (IMeMe = 1,3,4,5-tetramethylimidazol-2-ylidene) or $[AlH_3(I'PrMe)]$ (2) with three equivalents of phenol led to the isolation of colourless solids characterising as the imidazolium tetraphenoxyaluminate salts; [IMeMe · H][Al(OPh)4] (4) and $[I'PrMe \cdot H][Al(OPh)_4]$ (5) (Scheme 1). The ¹H NMR spectra of 4 and 5 (CDCl₃) display the expected methyl and, for the latter, isopropyl resonances in addition to broad singlet resonances integrating for one proton at 8.79 and 8.88 ppm, respectively. These are in the normal region for 1,3-disubstituted imidazolium 2-position protons, those of the related species [IMeMe \cdot H][InBr₄] [9] and [IⁱPrMe · H][InCl₄(IⁱPrMe)] [8] occurring at 8.30 and 9.54 ppm, respectively. The ¹³C NMR spectra of both compounds are as expected with the protonated carbene centres resonating at 134.1 ppm (4) and 132.3 ppm (5). This is considerably upfield from the 2-position carbon resonances of the parent carbenes (212.7 and 205.9, respectively, in C_6D_6 [17], resonances for InX_4 species listed above: 133.4 and 131.8 ppm, respectively) [8,9]. Lastly, the base peaks in the positive ion APCI mass spectra of both compounds correspond to the imidazolium cations (4: 125 m/z, 5: 181 m/z).



Scheme 1. Reagents and conditions: (i) M = AI, 3.0 eq. ethereal phenol, THF, -50 °C, -3/2 H₂(g), -0.25 [AlH₃(NHC)], 4; R¹ = Me, R² = Me, 5; R¹ = ^{*i*}Pr, R² = Me; (ii) M = In, R¹ = 2,4,6-Me₃C₆H₂, R² = H, 1.0 eq. F₆acacH, THF, -50 °C, -3/2 H₂(g), -In(s).

Table 1 Summary of crystal data and refinement parameters for compounds **4** and **6**

| | [IMeMe · H] [Al(OPh) ₄] (4) | [IMes \cdot H] [CH{C(O)CF ₃ } ₂] (6) |
|------------------------------------|--------------------------------------------|------------------------------------------------------------------|
| | | |
| Molecular formula | C31H33N2O4Al | $C_{26}H_{26}F_6N_2O_2$ |
| Molecular weight | 524.57 | 512.49 |
| Temperature (K) | 150(2) | 150(2) |
| Crystal system | triclinic | monoclinic |
| Space group | $P\overline{1}$ | $P2_1/n$ |
| a (Å) | 10.397(8) | 14.801(3) |
| b (Å) | 10.574(9) | 11.687(2) |
| c (Å) | 14.432(11) | 16.161(3) |
| α (°) | 108.43(6) | 90 |
| β (°) | 107.47(6) | 115.78(3) |
| γ (°) | 94.13(5) | 90 |
| Volume (Å ³) | 1411.2(19) | 2517.3(8) |
| Ζ | 2 | 4 |
| $D_{\rm c} ({\rm g}{\rm cm}^{-3})$ | 1.235 | 1.352 |
| $\mu \ (\mathrm{mm}^{-1})$ | 0.934 | 0.116 |
| Reflections collected | 4265 | 4527 |
| Unique reflections | 4265 | 4527 |
| Parameters varied | 347 | 457 |
| R (all data) | 0.1640 | 0.2152 |
| $R(I \ge 2\sigma(I))$ | 0.0606 | 0.0533 |
| wR' (all data) | 0.1799 | 0.1210 |
| $wR'(I \ge 2\sigma(I))$ | 0.1479 | 0.0905 |

Unlike compound 5, which proved insoluble in ethereal solvents, recrystallisation of compound 4 from fresh THF gave yellow prismatic crystals suitable for X-ray structure determination (see Table 1). The molecular structure of 4, which crystallises in the space group $P\overline{1}$ with one ion pair in the asymmetric unit, is depicted in Fig. 1 (see caption for selected bond lengths and angles). Compound 4 contains a rare example of the tetraaryloxyaluminate anion, ² and indeed the first that is devoid of supplementary donors or alkyl groups appended to the aryl ring. Moreover, the configuration of the aryl rings about the "AlO₄" tetrahedral centre of 4 is akin to that of the only structurally characterised $[Al(OAr)_4]^-$ compound (Ar = phenyl ring without supplementary donors); [Li(THF)₄][Al{O(2,4- $Bu^{t}C_{6}H_{3}$]₄[18]. The 1,3,4,5-tetramethylimidazolium cation of 4 has intra-ring parameters consistent with those of the related imidazolium salts; [IMeMe --H][InBr₄] [9] and [I^{*i*}PrMe \cdot H][Br], ³ the N(1)-C(1)-N(2)angle being $107.8(4)^{\circ}$ ([IMeMe \cdot H][InBr₄]; 108.1(8)°, [IⁱPrMe · H][Br]; 109.6(8)). This angle is 'open' relative to that of the parent carbene (IMeMe; 101.5(1)°) [17] indicating a significant enhancement in electronic

² The Cambridge Crystallographic Structural Database (CSD version 2.5 with updates for Jan and Apr 2004) lists 16 examples of an aluminium centre bound by four aryloxides, of which most incorporate either calix-[4]-arene, binaphthol or Schiff base derived phenolates.

³ The single X-ray structure determination of $[I^{i}PrMe \cdot H][Br]$ is included as supplementary material for this article.



Fig. 1. Molecular structure of compound 4 (POV-RAY 40% thermal ellipsoids). All hydrogen atoms except H(1) omitted for clarity. Selected bond lengths (Å) and angles (°): $C(1) \cdots O(1) 3.126(6)$, $H(1) \cdots O(1) 2.22$, N(1)-C(1) 1.315(5), N(2)-C(1) 1.343(5), N(1)-C(2) 1.368(5), N(2)-C(3) 1.364(5), C(2)-C(3) 1.337(6), Al(1)-O(1) 1.730(3), Al(1)-O(2) 1.742(3), Al(1)-O(3) 1.709(3), Al(1)-O(4) 1.736(3), $C(1)-H(1) \cdots O(1) 158.1$, N(1)-C(1)-N(2) 107.8(4), C(1)-N(1)-C(2) 109.7(4), C(1)-N(2)-C(3) 108.0(4), N(1)-C(2)-C(3) 106.5(3), N(2)-C(3)-C(2) 108.1(4), O(1)-Al(1)-O(2) 113.2(2), O(1)-Al(1)-O(3) 109.8(2), O(1)-Al(1)-O(4) 98.5(2), O(2)-Al(1)-O(3) 108.7(1), O(2)-Al(1)-O(4) 113.5(1), O(3)-Al(1)-Al(4) 111.9(2).

delocalisation about the heterocycle. Hydrogen bonding involving the 2-position C-H of imidazolium salts is now well documented [19,20], however, the composition of **4** is novel in that it represents the first structurally characterised imidazolium group 13 'ate' species to display a distinct cation-anion hydrogen bond [8,9,21,22]. This results from the inclusion of oxygen atom hydrogen bond acceptors on the anion, one of which; O(1), accepting donation from the C(1)–H(1) bond (d···A 2.22 Å, D···A 3.126(6) Å, D–H···A 158.1°). ⁴ This renders a hydrogen to oxygen interaction that is extended relative to the only structurally characterised imidazolium phenolate; $[IMes \cdot H][O(2,6^{-t}Bu_2-4-MeC_6H_2)]$ (7)(IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazole-2-ylidene) (d···A 1.87(3) Å, D···A 2.801(4) Å, D-H···A 175(2)°) [23], ⁴ the hydrogen bonding interaction within 7 benefiting from an anionic hydrogen bond acceptor, and distortion of the AlO₄ tetrahedra such that the O(1)-Al(1)-O(4) angle (the O-Al-O 'bite' that is orientated toward the imidazolium) is greater than 10° smaller $(98.5(2)^{\circ})$ than the other O–Al–O angles (108.7(1))– $113.5(1)^{\circ}$). Interestingly, the bonding of 4 is metrically similar to that described by the IMes adduct of diphenylamine, wherein $d \cdots A$ and $D \cdots A^1$ distances of 2.30(1) and 3.196(2) Å are observed [23].

On stoichiometric grounds, the generation of 4 and 5 leaves 0.25 equivalents of 1 and 2 in solution. This was

confirmed by FTIR spectra of the dried reaction mixtures, which both exhibit Al-H stretching modes attributable to the parent trihydride (FTIR Al-H stretch 1; br s 1731 cm⁻¹ [24], **2**; br s 1730 cm⁻¹ [1]). As pronounced steric crowding about the aluminium centre of the intended [Al(OPh)₃(NHC)] product is unlikely, the generation of 4 and 5 suggests both imidazolium cations possess pK_{as} above that of phenol (9.98) [25]. Furthermore, it is noteworthy that there are no Lewis base adducts of triphenoxyalane in the structural database,⁵ the closest example being the tris(trimethylsilyl)silanide salt; 2,2,6,6-tetrapiperidinium triphenoxy-tris(trimethylsilyl)silanidoaluminate [26]. Indeed, protection of the mononuclear neutral tris(aryloxide)aluminium unit with respect to addition of a further aryloxide, and hence aluminate formation, requires steric hindrance at the 2,6phenyl positions of the aryloxide [27–32].

2.2. Reaction of $[InH_3(IMes)]$ with 1,1,1,5,5,5hexafluoroacetylacetone

Since the seminal work of Brown [33], growing interest in group 13 hydrides has seen their synthetic utility extended to organic chemistry [14]. Both boro- and aluminohydrides have an extensive history in this field, however, despite numerous attempts, notably by ourselves [6] and the group of Raston et al. [14], the acquisition of similar applications for gallium and indium trihydride analogues has been hampered by a marked increase in thermal and aerobic instability for these metallohydrides [11]. Accordingly, given our success in the stabilisation of indane (InH_3) species [1,3,4] we sought to elaborate upon the reductive character of these by isolating hydrometallation intermediates that would perhaps shed light on the diastereoselectivity observed for the reduction of di- and hydroxyketones by Lewis base stabilised indane reagents [6]. A report by Raston et al. highlighted 1,1,1,5,5,5-hexafluoropentan-2,4-dione (F₆acacH) as a candidate substrate for this study as intermediates had been isolated by stoichiometric hydrometallation of F₆acacH using alane and gallane reagents [34]. This proceeded before the formation of tris(dionato) compounds, which result from the use of more bulky and/or electron-rich 2,4-pentandiones, e.g., 2,2,6,6-tetramethylheptan-3,5-dione, in place of F₆acacH indicating unconventional group 13 hydride basicity [34]. Accordingly, F₆acacH was treated with our most stable indane; [InH₃(IMes)], 3 [3].

Contrary to analogous reactions with α -diketones or α -hydroxyketones [6], addition of one molar equivalent

⁴ Notation employed for hydrogen bond: D = hydrogen bond donor, A = hydrogen bond acceptor, 'd' used to define hydrogen of hydrogen bond donor in "d···A".

⁵ The Cambridge Crystallographic Structural Database (CSD version 2.5 with updates for Jan and Apr 2004) lists 82 examples of an aluminium bound by at-least three aryloxides (inclusive of those in reference 17). Of these, seven constitute free or Lewis base adducted Al(OAr)₃ compounds, where Ar = a substituted phenyl.

of $F_{6}acacH$ (a β -diketone) to low temperature tetrahydrofuran solutions of **3** (Scheme 1) repeatedly led to immediate decomposition of the indane, as evidenced by the deposition of an indium mirror on reaction vessels. Filtration, followed by removal of all volatiles in vacuo gave a light coloured free flowing powder that characterised as [IMes \cdot H][CH{C(O)CF_3}_2] (**6**). This compound was also prepared from the direct reaction of IMes with $F_{6}acacH$.

As per 4 and 5, the 1 H and 13 C NMR spectra of 6 indicate protonation of the carbenic 2-position (10.39 and 132.8 ppm CD_2Cl_2 , respectively), wherein the ¹³C resonance is considerably shifted from that of the parent carbene (219.7 ppm, d₈-THF) [35]. The FTIR of 6 displays absorbances between 1700 and 1500 cm⁻¹ that are consistent with the inclusion of a symmetrical dionate anion and absence of indium hydride bonds (3; In-H stretch 1650 cm^{-1} [3]). Recrystallisation from diethyl ether gave colourless blocks that characterised as 6. An X-ray structure determination of these was undertaken, for which the molecular structure is depicted in Fig. 2 (see caption for selected bond lengths and angles, Table 1 for a summary of crystal data and refinement parameters). In comparison to 4, and akin to several literature IMes based imidazolium species [19,20,23], compound 6, which crystallises in the space group $P2_1/n$ with one ion pair in the asymmetric unit, exhibits increased $C-H \cdots O$ hydrogen bonding interactions to the counterion. These interactions are bifurcated, as is typical of the hydrogen bond acceptor [36-38], and incorporate both the expected 2-position C-H and one of the unsaturated imidazolium backbone C-H bonds (C(2)-H(2)) thereby generating an unusual 'zig-zag' polymer. Further to an imidazolium N(1)-C(1)-N(2) angle of $108.2(3)^{\circ}$ that is 'open' relative to the $101.4(2)^{\circ}$ of the parent carbene [35] (4; 107.8(4)°, 7; 107.3(2)° [23], [IⁱPr-Me \cdot H][Br]; 109.6(6)°), ³ the interconnection of the IMes \cdot H units of 6 with proximal F₆acac counterions provides the following contact parameters: H(1); $d \cdots O(1)$ 2.38(3) Å, D-H···O(1) 121(2)°, $d \cdots O(2)$ 2.29(3) Å, D-H···O(2) 154(3)°, H(2); d···O(1)# 2.83(4) Å, D-H···O(1)# 138(2)°, d···O(2) 2.23(4)# Å, D-H···O(2)# 151(3)°. ⁴ With the exception of the H(2)-O(1)# contact, these are within the combined van der Waals radii contact of hydrogen and oxygen (2.40 A) despite bifurcation [39]. Furthermore, the solid-state 'binding' of the F_{6} acac anion of **6** appears to be augmented by C-H···aryl contact between the C(3)-H(3) bond and C(6)# (see Fig. 2 for atom locations; $d \cdots A 2.72(4)^\circ$, D-H···A 175(3)°), this type of contact has precedent most notably in the C–H $\cdots\pi$ contacts displayed by 7 [23], wherein one mesityl ring participates as a hydrogen bond acceptor to an imidazolium 'alkenyl' C-H (d···A 2.30°, D-H···A 149°, where A = mesityl centroid), and the species derived from the treatment of unsaturated cyclic hydrocarbons with

C(13) 0(2)Fig. 2. Molecular structure of compound 6 (POV-RAY 40% thermal ellipsoids). All hydrogen atoms except those of the imidazolium cations omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)-H(1) 0.96(3), $C(1) \cdots O(1)$ 2.995(5), $C(1) \cdots O(2)$ 3.182(5), $H(1) \cdots O(1)$ 2.38(3), H(1)···O(2) 2.29(3), C(2)-H(2) 0.95(4), C(2)···O(1)#1 3.586(5), C(2)···O(2)#1 3.099(5), H(2)···O(1)#1 2.83(4), H(2)···O(2)#1 2.23(4), N(1)-C(1) 1.327(4), N(2)-C(1) 1.331(4), N(1)-C(2) 1.380(4), N(2)-C(3) 1.389(4), C(2)-C(3) 1.340(5), O(1)-C(22) 1.243(4), O(2)-C(24) 1.248(4), C(22)–C(23) 1.396(5), C(23)–C(24) 1.373(5), C(1)–H(1)···O(1) 121(2), $C(1)-H(1)\cdots O(2)$ 154(3), $C(2)-H(2)\cdots O(1)#1$ 138(3), C(2)- $H(2) \cdots O(2)$ #1 151(3), N(1)-C(1)-N(2) 108.2(3), C(1)-N(1)-C(2) 108.8(3), C(1)-N(2)-C(3) 108.8(3), N(1)-C(2)-C(3) 107.6(4), N(2)-C(3)-C(2) 106.6(4), N(1)-C(1)-H(1) 130(2), N(2)-C(1)-H(1) 122(2), N(1)-C(2)-H(2) 120(2), C(3)-C(2)-H(2) 132(2), $O(1)\cdots H(1)\cdots O(2)$ 78(1), O(1)···H(2)#2···O(2) 70(1), O(1)-C(22)-C(23) 128.9(4), C(22)-C(23)-C(24) 124.1(4), O(2)-C(24)-C(23) 130.3(4), plane to plane angle of C(4) aryl ring:imidazol-2-ylidyl ring 88.5(1), C(13) aryl ring:imidazol-2-ylidyl ring 72.6(2), C(4) aryl ring:C(13) aryl ring 34.6(1). Symmetry operations used to define # atoms: #1 1/2 - x, 1/2 + y, 3/2 - z; #2 1/ 2 - x, y - 1/2, 3/2 - z.

NHCs recently studied by Cowley (e.g., [IMeMe \cdot H][Fluorenide]; d \cdots A 2.26(2) Å, where A = C₅ centroid) [40].

The structure of compound **6** makes a novel contribution to the growing catalogue of IMes derived imidazolium salts that exhibit significant hydrogen bond donation from the 2-, 4- and 5-imidazolium C–H bonds [19,20,23,40,41]. To this end, IMes appears unique in its ability to participate simultaneously in numerous contacts; however, this may simply reflect the prevalence of IMes relative to other NHCs. ⁶



⁶ Of the 426 structures deposited in 'The Cambridge Crystallographic Structural Database' (CSD version 2.5 with updates for Jan and Apr 2004) that contain an imidazol-2-ylidene or 4,5-dihydroimidazol-2-ylidene coordinated to a metal via the 2-position carbon (348 and 78 examples, respectively), 47 employ the NHC IMes.

The immediate metal deposition observed upon F_{6} acacH reaction with **3** (as is consistent with the destabilisation of an indium trihydride fragment) indicates "acid–base" reaction of the highly nucleophilic NHC ligand prior to β -diketone hydrometallation by the indane. As noted, this is contrary to previous surveys using alane and gallane [34] and controverts studies of the reducing agent nature of **3** undertaken with α -diketones or α -hydroxyketones [6]. These provide reasonable yields of the hydrometallation product albeit with reduced yields compared to tricyclohexyl-phosphine stabilised indane [2]. This lessened activity has been attributed to the increased steric bulky of IMes relative to P(*c*-C₆H₁₁)₃, which may impede hydride delivery.

The composition of species **4–6** highlights the availability of NHCs toward undesirable acid–base secondary reactions with organic substrates despite coordination to an aluminium or indium metal centre. This further emphasises the potential of NHCs to promote unusual solid-state interactions.

3. Experimental

3.1. General

The group 13 trihydride compounds 1 [1] and 3 [3] were prepared using literature procedures. Compound 2 was prepared using a modification of the literature method for compound 1 [1,24]. Phenol was purchased from Aldrich and used as received. 1,1,1,5,5,5-Hexafluoropentan-2,4-dione and CDCl₃ were purchased from Aldrich, dried over molecular sieves (3 Å) and freeze-thaw degassed prior to use. Tetrahydrofuran (THF), diethyl ether and hexane were dried over sodium, freshly distilled from sodium benzophenone ketyl and freeze-thaw degassed prior to use. Deutero dichloromethane was stored over CaH₂ under argon and freeze-thaw degassed prior to use. All manipulations were performed using conventional Schlenk or glovebox techniques under an atmosphere of high purity argon in flame-dried glassware. Infrared spectra were recorded as Nujol mulls using sodium chloride plates on a Nicolet Nexus FTIR spectrophotometer. ¹H NMR spectra were recorded at 400 MHz and ¹³C NMR spectra were recorded at 100 MHz using a Bruker DPX 400 spectrometer at ambient temperature, and chemical shifts were referenced to the ¹³C or residual ¹H resonances of the *deutero* chloroform or dichloromethane solvent employed. Mass Spectra were recorded using a VG Fisons Platform II instrument under APCI conditions. Melting points were determined in sealed glass capillaries under argon and are uncorrected.

3.2. Synthetic procedure for compounds 4 and 5

Phenol (1.81 g, 19.23 mmol) in Et₂O (20 cm³) was added dropwise to either [AlH₃(IMeMe)] (1.00 g, 6.49 mmol) or [AlH₃(I[']PrMe)] (1.35 g, 6.42 mmol) (for **4** and **5** respectively) in THF (50 cm³) at low temperature (-50 °C). Effervescence was observed, and the solution was warmed to ambient temperature and stirred for a further 2 hours. Removal of volatiles in vacuo rendered compounds **4** and **5** as a light yellow solid and pale brown oil, respectively. These worked up as follows.

3.3. $[IMeMe \cdot H][Al(OPh)_4]$ (4)

Extraction of the light yellow solid into fresh THF (20 cm³) followed by placement at -35 °C overnight yielded yellow prismatic crystals of **4** (1.18 g, 47 %), m.p. 123 °C. ¹H NMR (CDCl₃): δ 2.02 (s, 6H, C₂(CH₃)₂), 3.49 (s, 6H, N(CH₃)), 6.60–7.00 (m, 20H, Ar–H), 8.79 (br s, 1H, NC(H)N). ¹³C NMR (CDCl₃): δ 9.6 (s, C₂(CH₃)₂), 32.3 (s, N(CH₃)), 116.4, 118.9 (s, Ar–C), 126.3 (s, C₂(CH₃)₂), 129.9 (s, Ar–C), 134.1 (s, NC(H)N), 152.4 (s, CO). FTIR (nujol) v/cm⁻¹: 1592 (m), 1285 (m), 1163 (m), 877 (m), 695 (m). MS APCI: *m*/z (%) 125 [(IMeMe · H)⁺, 100].

3.4. $[I^{i}PrMe \cdot H][Al(OPh)_{4}]$ (5)

Repeated washing of the pale brown oil with hexane $(3 \times 5 \text{ cm}^3)$ and Et₂O $(2 \times 5 \text{ cm}^3)$ provided **5** as a pale brown solid that proved insoluble in ethereal solvents (0.87 g, 31%), m.p. 67 °C. ¹H NMR (CDCl₃): δ 1.28 (s, 6H, C₂(CH₃)₂), 1.94 (br s, 12H, CH(CH₃)₂), 4.11 (septet, 2H, CH(CH₃)₂, ³J_{HH} 7.0 Hz), 6.60–7.70 (m, 20H, Ar–H), 8.88 (br s, 1H, NC(H)N). ¹³C NMR (CDCl₃): δ 8.4 (s, C₂(CH₃)₂), 22.0 (s, CH(CH₃)₂), 51.0 (s, CH(CH₃)₂), 117.1, 119.8 (s, Ar–C), 124.9 (s, C₂(CH₃)₂), 126.4 (s, Ar–C), 132.3 (s, NC(H)N), 150.4 (s, CO). FTIR (nujol) ν/cm^{-1} : 1550 (m). MS APCI: m/z (%) 181 [(IⁱPrMe · H)⁺, 100].

3.5. $[IMes \cdot H][CH\{C(O)CF_3\}_2]$ (6)

Method (i): $F_{6}acacH$ (155 µl, 1.10 mmol) was added dropwise to a solution of **3** (0.23 g, 0.54 mmol) in THF (20 cm³) at -50 °C. The clear colourless solution immediately deposited a metallic mirror onto the surface of the reaction vessel and was warmed to room temperature and stirred for 2 h. Removal of volatiles under reduced pressure rendered the title compound as a free flowing lightly coloured powder. Extraction into fresh Et₂O (ca. 10 cm³) followed by concentration to the point of crystallisation and placement at -35 °C yielded **6** as small colourless blocks (0.21 g, 76%), m.p. 158 °C.

Method (ii): $F_{6}acacH$ (237 µl, 1.67 mmol) was added dropwise to a solution of IMes (0.51 g, 1.68

mmol) in THF (35 cm³) at -30 °C. The resulting clear yellow solution was warmed to room temperature and stirred for 2 h. Concentration in vacuo followed by placement at -35 °C overnight gave 6 as colourless blocks. These were isolated by filtration and washed with cold (0 °C) hexane $(2 \times 3 \text{ cm}^3)$ (0.71 g, 83%), m.p. 162 °C. ¹H NMR (CD₂Cl₂): δ 2.14 (s, 12H, o- CH_3), 2.35 (s, 6H, *p*- CH_3), 5.09 (s, 1H, $CH\{C(O)CF_3\}_2$, 7.00 (s, 4H, *m*-H), 7.42 (s, 2H, C_2H_2), 10.39 (s, 1H, N₂CH). ¹³C NMR (CD₂Cl₂): δ 17.9 (s, o-CH₃), 21.6 (s, p-CH₃), 84.1 (s, CH{C(O)CF₃}₂), 124.3 (s, C₂H₄), 130.4 (s, m-CH), 131.6 (s, p-CCH₃), 132.8 (s, NC(H)N), 135.1 (s, o-CCH₃), 142.1 (s, *ipso-C*), carbonyl carbon signals not observed. FTIR (nujol) v/cm^{-1} : 1669 (sh s), 1544 (sh s), 1527 (sh s), 1237 (m), 1177 (m), 1126 (br m), 851 (m). MS APCI: m/z (%) 305 [{M - F₆acac}⁺, 100].

3.6. X-ray crystal structure determination

Crystals of 4 and 6 suitable for X-ray structure determination were mounted on glass fibres, in viscous hydrocarbon oil at -123 °C (150 K). Crystal data were obtained using an Enraf-Nonius CAD4 diffractometer. X-ray data were solved by direct methods and refined on F^2 by full matrix least squares (SHELX-97) [42] using all unique data. For both 4 and 6, all non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were placed in calculated positions for compound 4 (riding model). For compound 6 the positions and isotropic displacement parameters of all hydrogen atoms were refined. Empirical absorption corrections were carried out by the DIFABS method [43]. For compound 6 the three fluorine atoms (F(1)-F(3)) of one CF₃ group were disordered over two sites of partial occupancy. These were modelled satisfactorily with occupancies of 60:40. Crystal data and refinement parameters for both compounds are compiled in Table 1.

Crystallographic data (excluding structure factors) for the two compounds reported in this paper and the related imidazolium salt $[I^{i}PrMe \cdot H][Br]^{3}$ (deposited as supplementary material with this journal) have been deposited with the Cambridge Crystallographic Data Centre as supplementary numbers 241096–241098. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 (0) 1223 336033; E-mail: deposit@ccdc.cam.ac.uk).

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2004.07.036.

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