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On the Alcoholysis of Alkyl-Aluminum(III) Alkoxy-NHC Derivatives: Reactivity of the Al-Carbene Lewis Pair *versus* Al-Alkyl

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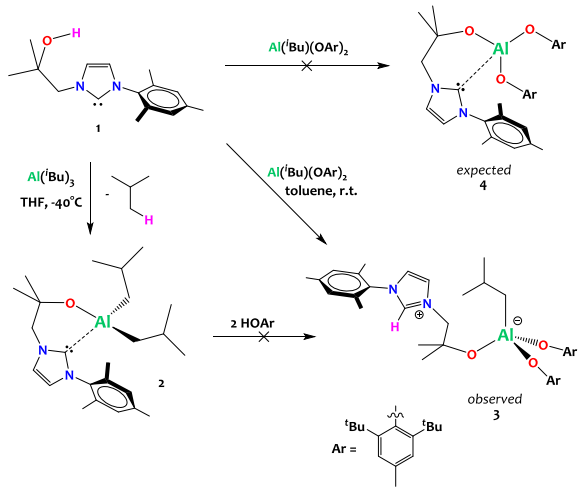
Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Abstract. The reaction of a bifunctional hydroxy N-heterocyclic carbene (NHC-OH) ligand with alkyl-aluminum(III) derivatives appears to be dependent of the precursor used. The expected alkoxy-NHC metallated product is indeed obtained with Al(^{i}Bu)$_3$. In contrast, the sterically hindered [Al(^{i}Bu)(OAr)$_2$] (OAr = 2,6-di-*tert*butyl-4-methylphenoxy) displays reactivity at the carbene and affords an imidazolium-aluminate zwitterion. The non-innocence of the Al-NHC motif is further highlighted by the heterolytic cleavage of the phenol O-H bond across the Al-C$_{NHC}$ bond from Al(O-NHC)X$_2$ derivatives (X = ^{i}Bu, OAr).

In recent years, metal-ligand cooperation - *i.e.* systems where both the metal and the ligand are directly involved in bond activation processes - has attracted increasing interest in organometallic catalysis.[1–4] Metal-ligand synergistic effects are particularly attractive to promote the heterolytic cleavage of strong sigma bonds and have significantly expanded the scope of reactivity promoted by organometallic complexes. N-heterocyclic carbenes (NHCs) are excellent nucleophiles that have found a large breath of applications as ligands in homogeneous catalysis. These ligands are classically regarded as spectators since they form strong bonds with a large variety of metal ions. Still, rare examples of substrate activations across metal-NHC bonds have been reported.[5–16] In particular, P. Arnold and coworkers have described unique addition/elimination reactions of polar substrates across the metal-carbene bond in a variety of rare-earth and actinide NHC complexes.[11–13] In these reactions, the Lewis acidity of the metal and the Lewis basicity of the NHC ligand are not mutually neutralized by the formation of a Lewis acid-base adduct. This mechanism of action involving two Lewis partners, is, to some extent, reminiscent of the chemistry of "frustrated" Lewis pairs (FLPs), a notion which is more and more recognized to extend beyond systems featuring sterically segregated donor and acceptor sites.[17–19] Quite appealingly, NHC/Al(C$_6$F$_5$)$_3$ pairs have been found to effectively polymerize vinyl monomers *via* the formation of imidazolium aluminate active species.[20,21] Most notably, the concerted action of the Lewis partners is not quenched by the formation of Lewis-pair adducts in these systems as well. Yet the combination of NHCs with Lewis acidic group 13 elements to promote FLP chemistry[22–24] is still largely unexplored compared to other Lewis-bases. We recently reported the straightforward synthesis of a new hydroxyl-tethered NHC ligand, **1**, and the versatility of this bifunctional motif for the generation of well-defined monometallic and heterobimetallic tantalum and rhodium species.[25] Herein we explore the reactivity of this ligand platform towards isobutyl-aluminum(III) derivatives and report the non-innocence of the Al-NHC interaction.



Scheme 1. Expected *vs.* observed reaction between the hydroxyl-tethered NHC ligand **1** and Al(^{i}Bu)$_3$ or Al(^{i}Bu)(OAr)$_2$ (Ar = 2,6-^{t}Bu-4-Me-C$_6$H$_2$).

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Electronic Supplementary Information (ESI) available: [Experimental details, NMR spectra, X-ray crystallographic data and files in .cif format]. See DOI: 10.1039/x0xx00000x

Alkyl aluminum reagents classically react with alcohols or phenols by liberating alkanes and generating aluminum alkoxides or phenoxides. For instance, [Al(*i*Bu)(OAr)$_2$] (OAr = 2,6-di-*tert*butyl-4-methylphenoxy) is prepared from the reaction between Al(*i*Bu)$_3$ and HOAr.[26] Accordingly, treatment of the hydroxyl-tethered NHC pro-ligand **1** with Al(*i*Bu)$_3$ yields the alkoxy bis-alkyl Al(III) NHC adduct Al(L)(*i*Bu)$_2$, **2**, in good isolated yield (Scheme 1). The ^{1}H and ^{13}C NMR data for **2** in solution are in agreement with the proposed formula, with a $^{13}C_{NHC}$ resonance at δ = 173.5 ppm (^{13}C-labelling of the NHC carbon was performed to enhance this signal – see Fig. S3) typical for an Al-bound carbene moiety.[27–29] The ^{27}Al NMR spectrum for **2** displays a broad signal centered around δ = 72 ppm, which is in agreement with a four-coordinate Al(III) species.[30,31] Complex **2** can be recrystallized from saturated pentane solutions at -40°C allowing characterization *via* X-ray crystallography. The solid-state structure for **2**, shown on Figure 1-top, confirms the effective bidentate coordination of the alkoxy-NHC ligand to Al, with the formation of an Al-C_{NHC} bond exhibiting a distance in the expected range (2.069(5) Å).[27–29] The Al-C_{iBu} bond lengths are slightly shorter, averaging 1.978(17) Å. Note that the ligand C1-Al1-O1 bite angle of 95.2(6)° enforces a distortion of the tetrahedral coordination geometry around Al, and imposes a slightly bent Al-NHC interaction, as shown by the deviations of the N-C1-Al1 angles (118.8(4)° and 136.7(1)°) from 120°.

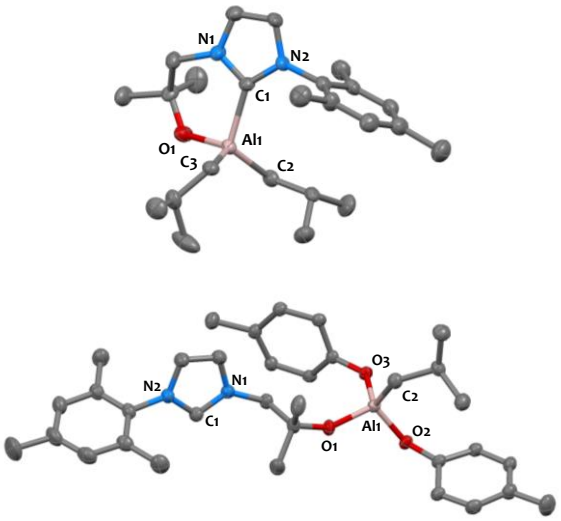
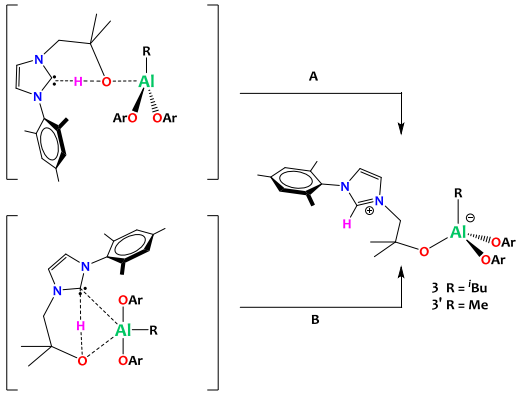


Figure 1. Solid-state molecular structures of **2** (top) and **3** (bottom) (50% probability ellipsoids). Hydrogen atoms and ^{t}Bu aryl substituents have been omitted for clarity. Selected bond distances [Å] and angles [°] (averaged parameters for both components found in the asymmetric unit) for **2**: Al1-C1 2.069(5); Al1-C_{iBu} 1.978(17); Al1-O1 1.770(4); C1-N_{imid} 1.354(8); N1-C1-N2 104.5(4); C1-Al1-O1 95.2(6); Al1-C1-N1 118.8(4); Al1-C1-N2 136.7(1) for **3**: Al1-O1 1.731(6); Al1-O_{Ar} 1.787(6); Al1-C2 1.986(8); C1-N_{imid} 1.328(11); N1-C1-N2 108.6(1).

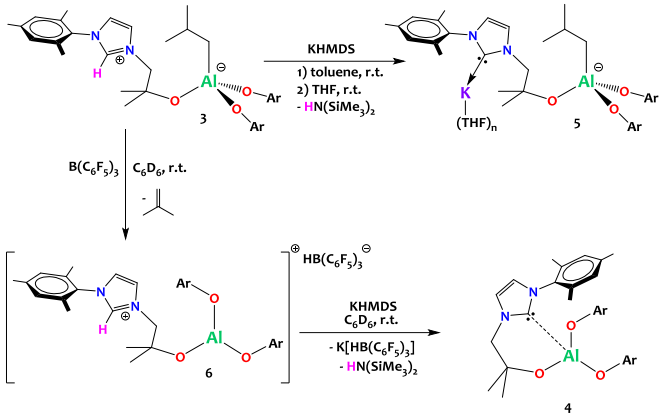
Surprisingly, complex **2** does not react with HOAr in C_6D_6 or in THF even after prolonged heating at 60°C. We attribute this phenomenon to the high steric hindrance imposed by the HOAr ring substituents, since **2** reacts with HOPh (see below). Note that it was previously observed that Al(*i*Bu)(OAr)$_2$ does not react further with HOAr for similar reasons.[26] We thus attempted the preparation of the bis-phenolate alkoxy-NHC aluminum derivative **4** from the reaction of **1** with Al(*i*Bu)(OAr)$_2$. However, this turned instead to the quantitative formation of the imidazolium-aluminate zwitterion [HL][Al(*i*Bu)(OAr)$_2$], **3** (Scheme 2), isolated in excellent yield. Compound **3** is stable at 110°C in toluene solution for several hours, and no evidence of deprotonation of the imidazolium moiety by the remaining alkyl group on aluminum was observed. The characterization of **3** by NMR spectroscopy is unambiguous, with notably three ^{1}H imidazolium signals at δ = 7.51, 6.27 and 5.48 ppm appearing as triplets and a ^{13}C resonance found at δ = 135.6 ppm corresponding to the protonated carbene (signal enhanced on the ^{13}C-labelled compound, Fig. S7). X-ray diffraction structural analysis (Fig. 1-bottom) confirms that the product contains a 4-coordinate aluminate center with a pendant imidazolium group. The protonation of the carbene to imidazolium is confirmed by the analysis of the metrical parameters, with a characteristic shortening of the C1-N_{imid} bond lengths (1.328(11) Å in **3** *vs* 1.354(8) Å in **2**) and a relaxation of the internal NCN ring angle (108.6(1)° in **3** *vs* 104.5(4)° in **2**).[25,32,33] Note that the analogous imidazolium-aluminate zwitterion [HL][AlMe(OAr)$_2$], **3'** is obtained from AlMe(OAr)$_2$.



Scheme 2. Proposed FLP (**A**) or bond metathesis (**B**) mechanisms for the formation of **3**.

The contrasting outcomes of these reactions illustrate the drastic impact of aluminum substituents on the reactivity of the Al-*i*Bu motif. While classical protonolysis reaction leading to the anticipated metallated product **2**, with release of isobutane, is observed upon treatment of **1** with Al(*i*Bu)$_3$, the reactivity of **1** with Al(*i*Bu)(OAr)$_2$ or AlMe(OAr)$_2$ occurs at the NHC and leads to the zwitterions. Such difference in reactivity is likely driven by the increased steric hindrance around the Al center imparted by the bulky aryloxide substituents. Such sterically-driven behavior is reminiscent of a two-partners heterolytic cleavage of a polar O-H bond by FLPs (Scheme 2-A).[23,34,35] Alternatively, the transfer of proton from OH to carbene may occur only after initial carbene coordination to aluminum in a sigma-bond metathesis type mechanism (Scheme 2-B). While NHC coordination to Al(III) centers generally produces robust aluminum reagents featuring inert NHC-Al bonds,[27] the non-innocence of the Al-NHC interaction has been reported in a few occurences.[14–16,24,29,36,37] In particular, S. Dagorne and coworkers recently showed that the bulky NHC adduct (I^{t}Bu)AlMe$_3$ deprotonates Al$_2$Me$_6$ to yield the quantitative formation of the imidazolium salt of an unusual AlMe$_3$-stabilized Al-CH_2^- anion, a reaction which does not

proceed with less sterically hindered NHCs.[16] The present study shows that steric congestion around the Al(III) center is equally important and can be used as an additional tool to tune the reactivity of Al-NHC motifs.



Scheme 3. Deprotonation and alkyl-abstraction of the imidazolium-aluminate zwitterion **3**.

Since the putative species **4** could neither be synthesized from the direct reaction between Al(*i*Bu)(OAr)$_2$ and HL nor the reaction between Al(L)(*i*Bu)$_2$ and HOAr (Scheme 1), we attempted generating it through an alternative two-step procedure involving (i) alkyl abstraction from the Al(III) center in **3** to restore the Lewis-acidic site and (ii) deprotonation of the imidazolium moiety (Scheme 3).

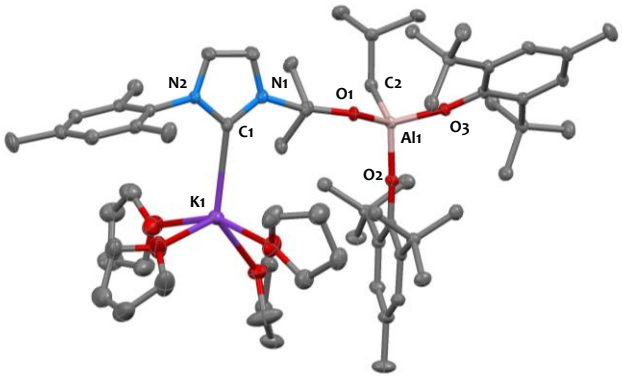
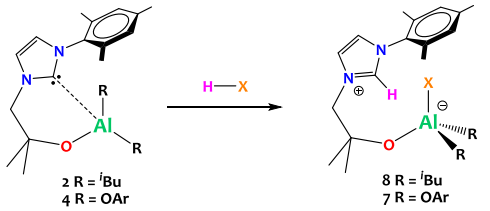


Figure 2. Solid-state molecular structures of **5** (50% probability ellipsoids). Hydrogen atoms have been omitted for clarity. Selected bond distances [Å] and angles [°]: Al1-O1 1.7447(18) Al1-O2 1.7647(18); Al1-O3 1.7711(18); Al1-C2 2.003(2); N1-C1 1.365(3); N2-C1 1.379(3); C1-K1 2.921(3); N1-C1-N2 101.8(2).

The NHC moiety can be restored upon treatment of **3** with strong bases such as KHMDS (HMDS = hexamethyldisilylamide) or benzyl potassium, leading to the formation of [K(THF)$_n$L][Al(*i*Bu)(OAr)$_2$], **5** (Scheme 3). Complex **5** crystallizes from THF solutions as a tetra-THF adduct (n = 4) but loses two THF molecules upon drying *in vacuo* and is isolated in high yields as a bis-THF adduct (n = 2), as confirmed by ^{1}H NMR and elemental analyses. The ^{13}C NMR carbenic carbon resonance for **5** (δ = 211.1 ppm in THF-d_8; δ = 204.8 ppm in C_6D_6) is drastically shifted compared to the corresponding signal in the imidazolium complex **3** (δ = 135.6 ppm) and that for the Al-bound NHC in **2** (δ = 173.5 ppm), and is diagnostic of a K-bound NHC carbene.[38] The solid-state structure for **5**, shown on Figure 2, is as expected, with a N1-C1-N2 ring angle of 101.8(2)°, average N-C$_{carbene}$ bond lengths of 1.372(7) Å and a K1-C1 distance of 2.921(3) Å, which fall in the typical range.[25,32,33,38]

Alkyl abstraction from the aluminum center is achieved upon treatment of the zwitterion **3** with B(C$_6$F$_5$)$_3$. Reaction monitoring by ^{1}H, ^{11}B, ^{19}F, and ^{13}C-NMR in C_6D_6 solution shows the quantitative formation of the tris-(alkoxy/aryloxy)Al(III) imidazolium borohydride complex [(HL)Al(OAr)$_2$][HB(C$_6$F$_5$)$_3$], **6** (Scheme 3). B(C$_6$F$_5$)$_3$ is known to perform alkyl abstraction from a variety of metal derivatives, including aluminum, releasing typically alkylborate anions [RB(C$_6$F$_5$)$_3$]$^-$.[39–47] The presence of a signal at δ = - 24.5 ppm in the ^{11}B NMR spectrum is consistent with the formation of a 4-coordinate borate centre. Yet this resonance is shifted compared to that of alkylborates [RB(C$_6$F$_5$)$_3$]$^-$ (typical range: -10 to -14 ppm)[48] and appears as a doublet ($^1J_{B-H}$ = 79 Hz). Therefore it is instead assigned to the borohydride anion [HB(C$_6$F$_5$)$_3$]$^-$.[42,48–51] The characteristic upfield shift of the resonances observed in the ^{19}F NMR spectrum (δ = -134.7, -161.0 and -165.1 ppm for [HB(C$_6$F$_5$)$_3$]$^-$ vs δ = -128.7, -141.6 and -159.9 ppm for B(C$_5$F$_6$)$_3$) are also consistent with literature data for [HB(C$_6$F$_5$)$_3$]$^-$.[42,48–50,52] [HB(C$_6$F$_5$)$_3$]$^-$ is most likely formed via *β*-hydride elimination from the isobutyl group with loss of isobutene which was identified in the ^{1}H NMR spectrum as a septuplet at δ = 4.75 ppm and a triplet at δ = 1.60 ppm.[53] Similar phenomenon has been reported before in some occurences.[42,46–48,54,55]

Gratifyingly, combining alkyl abstraction with B(C$_6$F$_5$)$_3$ and subsequent imidazolium deprotonation with KHMDS yields **4** quantitatively (Scheme 3), as monitored by ^{1}H and ^{13}C NMR spectroscopy. The ^{13}C resonance for the carbene carbon in **4** appears as a broad signal at δ = 167.7 ppm. This value lies between the chemical shift of K-bound carbenes, as found in **5** (δ = 211.1 ppm), and imidazolium salts as in **3** (δ = 135.6 ppm) or **6** (δ = 136.1 ppm), and falls in the lower range of NMR resonances for NHC-supported alkylaluminum species (165-206 ppm ; 173.5 ppm in **2**),[27] indicating an Al-C$_{carbene}$ ligation in solution. This is confirmed by the solid-state structure for **4**, reported in SI, featuring similar structural features than **2**.



Scheme 4. Activation of H-X bonds (X = OPh) across the NHC-Al motif.

Preliminary reactivity studies indicate that compounds **2** and **4** promote selective activation of the O-H bond of phenol (Scheme 4), as evidenced from ^{13}C NMR studies which show quantitative formation of imidazolium species (Figs. S18 and

S19). Similarly, **2** reacts with $HOSi(O^tBu)_3$ and 2-naphtalenethiol to yield imidazolium species (Figs. S20 and S21). Therefore, such aluminum-NHC cooperative reactivity seems to be a general trend for these systems since 1,2 X-H addition preferentially occurs across the Al-C_{NHC} bond *versus* Al-C_{iBu} bonds in **2**, leading to imidazolium elimination rather than alkane elimination, which is striking and unexpected. Importantly, this demonstrates that coordination of the NHC moiety to Al(III) does not quench the reactivity which can be considered at the borderline of FLP chemistry in which the Lewis adduct is formally formed, but might be hemilabile and can react with small molecules. These results showcase the potential of these aluminum-NHC species to promote the heterolytic cleavage of polar H-X bonds across non-innocent Al-C_{NHC} bonds. Studies regarding the synthetic utility of these aluminum derivatives are currently ongoing in our group. The authors would like to thank the "Programme Avenir Lyon Saint-Etienne de l'Université de Lyon", as part of the "Investissements d'Avenir" program (ANR-11-IDEX-0007) and the CNRS-MOMENTUM program for supporting our work in this area.

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