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Countercations Direct One- or Two-Electron Oxidation of an Al(III) Complex and Al(III)−Oxo Intermediates Activate C−H Bonds

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Supporting Information

ABSTRACT: Hydrogen abstraction by aluminum(III)−oxo intermediates via reaction pathways reminiscent of late transition metal chemistry has been observed. Oxidation of $M^+[(IP^{2-})_2Al]^-$ (IP = iminopyridine, M = Na, Bu_4N) yielded $[Na(THF)(DME)][(IP^-)(IP^{2-})Al(OH)]$ (**3**) or $[(IP^-)_2Al(OH)]$ (**4**), via O-atom transfer and subsequent C−H activation or proton abstraction, respectively.

The development of routes for selective functionalization of C−H bonds in hydrocarbon feedstocks remains a significant challenge in modern chemistry.[1] For instance, an important subset of possible transformations is controlled oxidation of C−H bonds. The later first row transition-metal ions, such as manganese, iron, and cobalt, can oxidize C−H bonds via high-valent metal−oxo intermediates. In general, the catalytic cycle starts with oxidation of the transition-metal catalyst to form a reactive metal−oxo intermediate, which then abstracts a hydrogen atom from the substrate. Following this C−H activation, the resulting −OH functionality may "rebound" to the organic substrate to yield an oxidized substrate with C−OH functionality. Significantly, this catalytic cycle involves a redox step in which a higher-valent metal−oxo intermediate results from the reaction of an oxidant with a lower-valent transition-metal precursor.

In principle, cheap and abundant main-group elements such as aluminum are appealing for large-scale applications such as catalysis. However, the reliance on redox processes for transformations involving the metal−oxo group may explain in part why similar chemistry for the generally redox-inactive main-group elements remains far less explored. Recent work has shown that redox-active ligands can engender additional redox activity to transition-metal ions.[2] In particular, a zirconium complex that can reductively eliminate biphenyl[3a] and another than can activate O_2[3b] have been reported.

We have previously shown that aluminum(III) complexes with redox-active ligands of the form $(IP^{n-})_2AlX$ [IP = 2,6-bis(1-methylethyl)-*N*-(2-pyridinylmethylene)phenylamine; n = 0, 1, 2; X = monodentate ligand] can be isolated in four oxidation states, including an open-shell triplet.[4] Herein we demonstrate that reactions involving transformations from one redox state of $[(IP^{n-})_2Al]^{m-}$ to another can be effected, that these ligand-based redox processes can be coupled with functionalization of the Al(III) center, and that countercations strongly influence the reactivity. Facile oxidation of $[(IP^{2-})_2Al]^-$ by pyridine-*N*-oxide (pyO) yields proposed Al(III)−oxo intermediates that react with the C−H bonds in the available solvent or countercations to give Al(III)−OH complexes. This reaction pathway is more typical of late-transition-metal complexes (Scheme 1).

Scheme 1

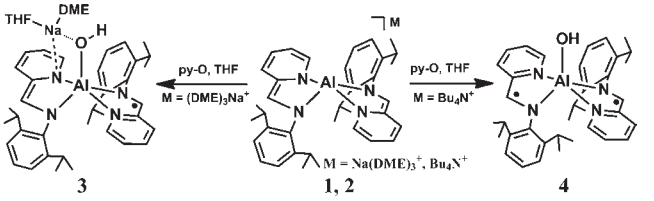

Table 1. Selected Bond Lengths in 3 and 4 (This Work) and in $(IP)AlCl_3$, $(IP^-)_2AlCl$, and $[(IP^{2-})_2Al]^-$ (1) (Prior Work) for Comparison

	$Al-N_{im}$	$Al-N_{py}$	$C_{im}-C_{py}$	$C_{im}-N_{im}$
$(IP)AlCl_3$	2.038(4)	2.084(4)	1.453(7)	1.284(6)
$(IP^-)_2AlCl$	1.915(4)	2.009(15)	1.405(2)	1.354(2)
$[(IP^{2-})_2Al]^-$	1.844(4)	1.873(4)	1.356(6)	1.414(6)
3 (IP^{2-})	1.879(2)	1.956(2)	1.347(3)	1.411(3)
3 (IP^-)	1.948(2)	2.069(2)	1.385(4)	1.349(3)
4 (IP^-)	1.935(3)	2.028(13)	1.396(2)	1.358(2)

A mixture of $[Na(DME)_3][(IP^{2-})_2Al]$ (**1**) (DME = 1,2-dimethoxyethane) with pyO in THF solution was stirred at room temperature for 30 min, during which time the deep-purple color of **1** was replaced by a deep-green color typical of the singly reduced ligand in the $(IP^-)_2AlX$ moiety, which we have previously studied (X = Cl, CF_3SO_3). Single crystals suitable for X-ray diffraction analysis were obtained in 67% yield by cooling a hexane solution of the product at −25 °C for 1 week (Tables S1 and S2 in the Supporting Information). It has been demonstrated that the four bond lengths in Table 1 can aid oxidation state assignments for IP ligands,[4,5] and the solid-state structure in this case revealed a mixed-valent complex with the formulation $[(IP^-)(IP^{2-})Al(OH)]^-$ in which the IP^{2-} ligand and the hydroxo functional group are bridged by the $[Na(DME)(THF)]^+$ countercation (Figure 1). The aluminum center is nearly trigonal-bipyramidal (τ = 0.851).[6] The $C_{py}-N_{py}$ bond length in the IP^{2-} ligand is the only metric that differs from the expected value, and this elongation by 0.04 Å is most likely due to interactions with the Na^+ ion.

The IR spectrum of **3** displays absorption bands assignable to the OH, $C-N_{im}(IP^-)$, and $C-N_{im}(IP^{2-})$, 1.5 functional groups (Table S3 and Figure S1). No absorption band definitively

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attributable to a ligand-to-ligand charge-transfer band was observed in the UV−vis−NIR spectrum (Figure S2). The temperature-independent doublet spin state that was predicted on the basis of the molecular structure of **3** was confirmed by susceptibility measurements between 5 and 300 K; the magnetic moment was measured to be 1.83μ_B. On the basis of the structure and the IR and NIR spectroscopic data, mixed-valent **3** appears to have a fully localized electronic structure (i.e., Robin and Day class I[7]). Cyclic voltammetry (CV) measurements performed on **3** in 0.1 M Bu_4NPF_6 THF solution revealed successive rather than concomitant oxidation and reduction waves for each of the $IP^{2-/-}$ couples (Figure S3). We attribute this observation to the different electronic environment created at each IP ligand by coordination of Na^+ to one of the pyridine rings.[8]

To observe the oxidation chemistry without the influence of the coordinating Na^+ cation, $[Bu_4N][(IP^{2-})_2Al]$ (**2**) was prepared from **1** by salt metathesis with Bu_4NI (Figure S4 and Tables S1 and S2). Reaction of **2** with pyO in THF gave complex **4**, which displayed a sharp band in the IR absorption spectrum at 3713 cm^{-1} indicative of the OH functional group. In addition, absorption bands consistent with the IP^- oxidation state of the ligands are apparent (Table S3 and Figure S1).[9] Single crystals suitable for X-ray diffraction analysis were obtained by cooling a hexane solution of the product at −25 °C for 1 week, and the solid-state structure revealed $(IP^-)_2Al(OH)$ (**4**) (Figure 1). A symmetry plane bisects the aluminum center in **4**, making the IP^- ligands crystallographically equivalent. Metrics for the bond lengths appeared to agree with the IP^- oxidation state assigned by IR spectroscopy and charge balance, but we could not use these bond distances as definitive evidence for the $(IP^-)_2Al(OH)$ formulation. The aluminum center is approximately trigonal-bipyramidal (τ = 0.784). Magnetic susceptibility measurements further supported the formulation of **4** as the triplet biradical $(IP^-)_2Al(OH)$; the magnetic moment of 1.5μ_B at 300 K fell to 0.4μ_B at 20 K (Figure S5). A fit to the experimental data using MAGFIT 3.1[10] and a spin Hamiltonian of the form $\hat{H} = -2J\hat{S}_{L(1)} \cdot \hat{S}_{L(2)}$ with g = 2.0 supported an electronic model in which two IP^--based ligand radicals interact antiferromagnetically at low temperature. The energy of the interaction was fit using J = −370 cm^{-1}. This electronic structure is very similar to the triplet biradical structure of $(IP^-)_2AlCl$ that was previously reported by us, for which J = −230 cm^{-1}.[4]

It is interesting to note that monomeric aluminum−oxo or −hydroxo complexes are rare. A borane-protected monomeric aluminum−oxo complex[11] and a magnesium-capped aluminum−oxo complex[12] have been reported and were obtained by metathesis reactions. Similarly, the hydroxo complexes $LAl(OH)_2$ and $LAlMe(OH)$ [L = $HC\{(CMe)(2,6\text{-}iPrC_6H_3N)\}_2$] were obtained by salt metatheses of $LAlI_2$ and LAlMeCl, respectively, with water/KOH/KH.[13]

It is informative to speculate on the mechanism for the formation of complexes **3** and **4** from **1** and **2**, respectively. When the reaction of **1** with pyO was performed in dry d_8-THF, the OH IR absorption band in the resulting product was split into two bands at 3711 (OH) and 2707 (OD) cm^{-1}, which represent the products **3** and **3D**, respectively. In a subsequent experiment, complex **1** was initially stirred in d_8-THF for 24 h. ^1H NMR spectroscopic analysis confirmed that all of the DME in the $[Na(DME)_3]^+$ countercation of **1** was replaced by d_8-THF. After reaction with pyO, IR spectroscopic investigation of the products revealed close to 100% incorporation of D into the OD functional

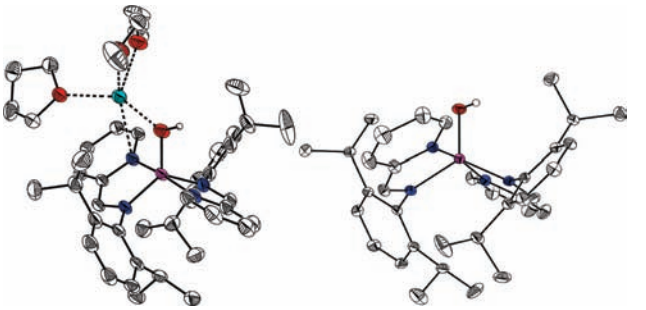

Figure 1. Solid-state structures of $[Na(DME)(THF)][(IP^-)(IP^{2-})Al(OH)]$ (**3**) and $(IP^-)_2Al(OH)$ (**4**).

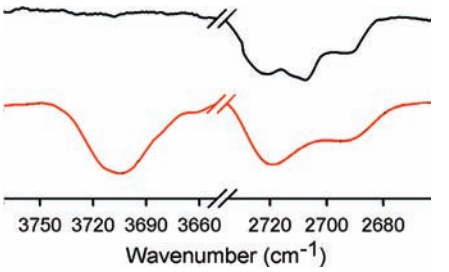

Figure 2. IR absorption spectra for **3** (red) and **3D** (black) in the regions of the OH (3711 cm^{-1}) and OD (2703 cm^{-1}) absorption bands.

group (Figure 2). These observations are consistent with a reaction mechanism in which formation of the Al−O bond and oxidation of **1** are followed by C−H activation of the solvent molecules bound to the Na^+ ion. We observed no evidence for C−H activation of the IP ligand. The reaction of **1** with pyO to form **3** involves only a one-electron oxidation of **1**, although we employed the two-electron oxidant pyO; we postulate that coordination of Na^+ to the py fragment of IP^{2-} stabilizes the $[(IP^{2-})(IP^-)Al(OH)]^-$ moiety toward further oxidation. When the same reaction of **1** with pyO was performed in DME, ether, or dioxane, we again observed formation of the one-electron-oxidized product $[(IP^{2-})(IP^-)Al(OH)]^-$, which was identified by comparison of IR and ^1H NMR spectra with spectra from authentic samples of **3**.

In contrast, the formation of **4** from **2** and pyO involves a two-electron oxidation, and we speculate that in the absence of coordinating Na^+ ion to stabilize IP^{2-}, each of the two IP^{2-} ligands in **2** is oxidized to IP^- as the Al−O bond is formed. Analysis of the reaction mixture by GC−MS and ^1H NMR spectroscopy revealed stoichiometric formation of Bu_3N. This result is consistent with an acid−base process in which proton abstraction from Bu_4N^+ by a putative $[Al\text{−}oxo]^-$ intermediate to give **4** is followed by elimination of butene from $Bu_3(Bu^-)(N^+)$ to give Bu_3N in a Hoffman-type mechanism.

The reaction pathways and resulting products that we have witnessed are reminiscent of redox transformations associated with transition-metal chemistry.[1] Future endeavors will focus on a more detailed understanding of the mechanisms of these reactions and further development and control of the oxidation chemistry and countercation effects, aiming toward chemical transformations.

■ ASSOCIATED CONTENT

Supporting Information. Synthesis and characterization of complexes; X-ray data for **2**−**4**; CIF files; and results of IR,

UV−vis−NIR, magnetic susceptibility, and CV measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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