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# Electrocatalytic Hydrogen Production by an Aluminum(III) Complex: Ligand-Based Proton and Electron Transfer

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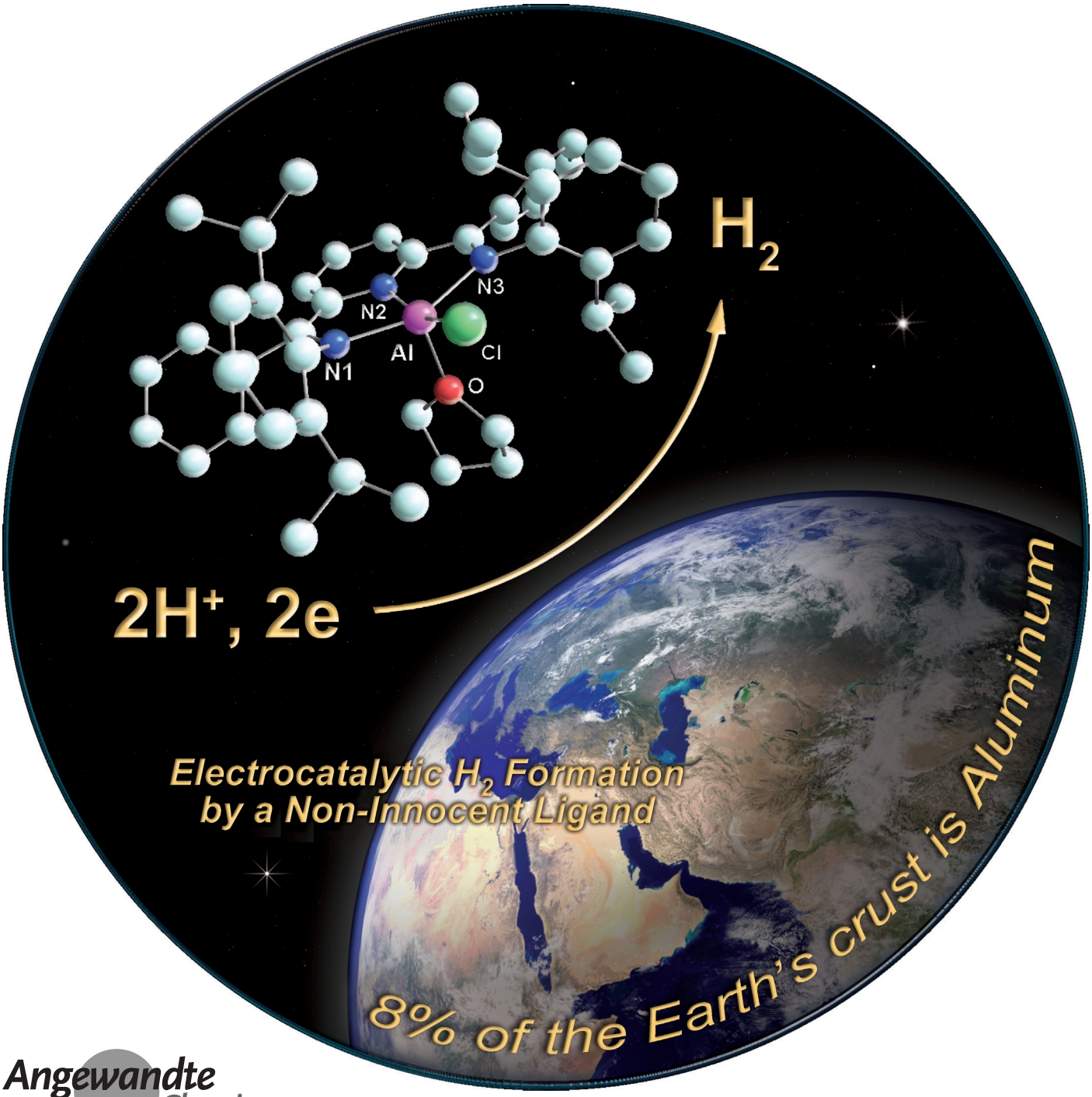


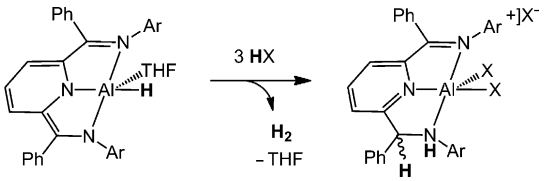
***Abstract:*** *Environmentally sustainable hydrogen-evolving electrocatalysts are key in a renewable fuel economy, and ligand-based proton and electron transfer could circumvent the need for precious metal ions in electrocatalytic $H_2$ production. Herein, we show that electrocatalytic generation of $H_2$ by a redox-active ligand complex of $Al^{3+}$ occurs at −1.16 V vs. SCE (500 mV overpotential).*

A key area of research into fuel-producing electrocatalysts is in the development of effective homogeneous and heterogeneous materials that comprise earth-abundant elements.[1–3] Work in this area encompasses earth-abundant transition metals such as iron, cobalt, or copper,[4] organic mediators,[5] and metal-free graphitic materials.[6] Redox-active ligands are also organic molecules that have been used in a variety of supporting roles for transition-metal electrocatalysts.[7] For example, ligand models of NADH have been employed to shuttle hydrides to Ru and Re catalysts.[8] Ligands with a proton shuttle increase the rates of reaction, and lower the overpotentials, for proton reduction by various Ni, Fe, and Co catalysts.[9] Ligand-mediated electron transfer that augments electron transfer and catalysis at a redox-active metal center has also been employed, in particular by using Co and Ni.[10] In all of these examples, the metal ion performs the electron transfer to the substrate, and interacts with the substrate during bond-forming and breaking events.

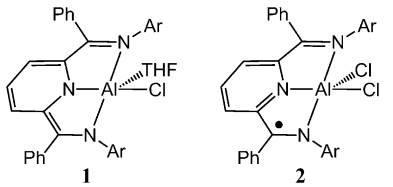
As an alternative approach, a ligand that mediates proton and electron transfer could be coordinated to a positively charged metal center as a route to anodically shifted redox potentials of an organic molecule. Stoichiometric proton–electron transfer reactions at transition-metal complexes have been demonstrated with ligand-based pathways.[11] Herein, we describe electrocatalytic $H_2$ evolution at −1.16 V versus SCE, catalyzed with 500 mV of overpotential, by a redox-active ligand complex of $Al^{3+}$. The role of $Al^{3+}$ is to tune the reduction potential of the ligand to an accessible range for low-overpotential proton reduction. We have previously described that the Al hydride complex [($^{Ph}I_2P^{2-}$)Al(THF)H] (where $^{Ph}I_2P^{2-}$ is a phenyl-substituted bis(imino)pyridine ligand) can be protonated three times. One of these protons reacts with the Al hydride to afford $H_2$, and the other two protons react with the ligand (Scheme 1).[12]

We now focus on ligand reactivity only, and report herein that the analogous aluminum chloride complex [($^{Ph}I_2P^{2-}$)Al(THF)Cl] (**1**, Scheme 2)[13] promotes $H_2$ production from protons in the presence of an applied reducing potential. We also discuss [($^{Ph}I_2P^{1-}$)$AlCl_2$] (**2**),[14] where the $^{Ph}I_2P$ ligand is reduced by only one electron.

Cyclic voltammograms (CVs) of **1** recorded in a 0.3 M solution of $Bu_4NPF_6$ in THF show the [($^{Ph}I_2P^{2-/3-}$)Al(THF)Cl] (**1**$^{0/1-}$) couple at −1.55 V versus SCE (Figure 1a), and a similar experiment performed on **2** shows the $^{Ph}I_2P^{1-/2-}$ and $^{Ph}I_2P^{2-/3-}$ couples at −0.9 and −1.15 V, respectively (Figure 1b). Comparison of the data for **1** and **2** shows that the $^{Ph}I_2P^{2-/3-}$ couples are quite different: −1.55 V for **1** and −1.15 V for **2**, and we attribute this to the additional chloro ligand bound to the Al center in **2**.




***Scheme 1.*** Protonation of ($^{Ph}I_2P^{2-}$)Al(THF)H.[12] Ar = diisopropylphenyl.




***Scheme 2.*** ($^{Ph}I_2P^{2-}$)Al(THF)Cl (**1**),[13] and ($^{Ph}I_2P^{1-}$)$AlCl_2$ (**2**).[14] Ar = 2,6-diisopropylphenyl.

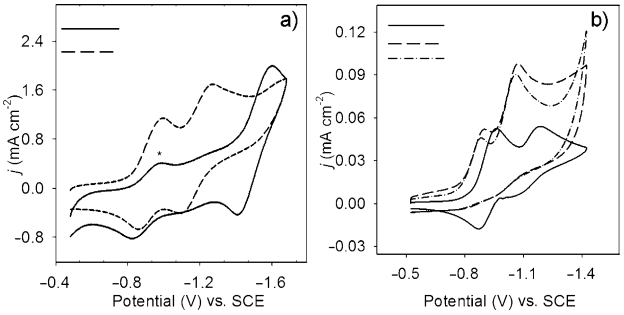



***Figure 1.*** Experiments recorded in 0.3 M solution of $Bu_4NPF_6$ in THF. Scan rate = 100 mV s$^{-1}$, glassy carbon working electrode. a) CVs of **1** (solid line) and $H_2$**1**$^{2+}$ (dashed line). Trace water protonates **1** and some $H_2$**1**$^{2+}$ are indicated with *. b) CVs of 0.5 mM **2** (solid line), and with aliquots of [DMAPH]$BF_4$ (dashed line: 2.0 mM, dot/dashed line: 5.0 mM).

After addition of two equivalents of 2,6-lutidinium acid (lutH$^+$) to a solution of **1**, two reduction events were observed, namely at −0.95 V and −1.20 V, and the anodic shift of these events compared with reduction of **1** (−1.55 V) is consistent with the additional positive charge on the complex resulting from protonation of the ligand (Figure 1a). With excess lutH$^+$, the current density increased to $j_c/j_p = 10$; this result suggested that a catalytic event had occurred (Figure 2a).[15] Controlled potential electrolysis (CPE) experiments performed with 0.3 mM **1** and 20 equivalents of acid at −1.16 V over 1.5 h (Table 1 and Figure S1 in the Supporting Information) indicated that $H_2$ was produced with 70 or 85% Faradaic efficiency (FE) using lutH$^+$ or 4-dimethylaminopyridinium (DMAPH$^+$), respectively. Quantification of $H_2$ was performed by using gas chromatography with a thermal conductivity detector (GC-TCD) on samples taken from the headspace of the CPE experiment. To

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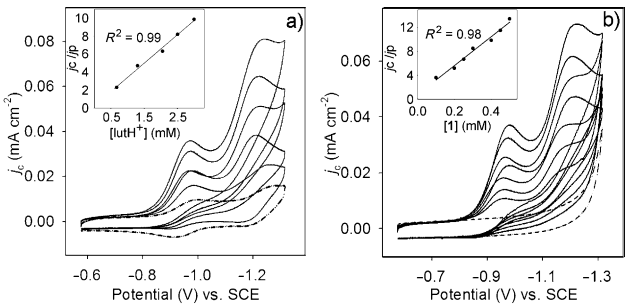



***Figure 2.*** a) CVs of 0.033 mM $[(H_2I_2P)AlCl(lut)_2]^{2+}$ (dashed line), and with aliquots of $[lutH]BF_4$ (solid lines). Inset: $j_c/j_p$ vs. $[H^+]$. b) CVs of 4.0 mM $lutH^+$ (dashed line), and with aliquots of **1** (solid lines). Inset: $j_c/j_p$ vs. [**1**]. Scan rate = 100 mV s$^{-1}$, glassy carbon working electrode. Both $j_c/j_p$ plots use data read at −1.19 V vs. SCE.

***Table 1:*** CPE experiments with **1** and **2** over 1.5 h.[a]

| | Acid | $E_{1/2}$ ($H^+/^1/_2H_2$) [V][b,c] | $\eta$[d] [mV] | $\eta$[e] [mV] | TOF [TON/h] | Farad. yield [%] |
|---|---|---|---|---|---|---|
| **1** | $lutH^+$ | −0.42 | 780 | 740 | 3.3 | 70 ± 7 |
| **1** | $DMAPH^+$ | −0.66 | 540 | 500 | 0.38 | 85 ± 4 |
| **2** | $DMAPH^+$ | −0.66 | 520 | 560 | 0.03 | 15 ± 9 |

[a] Average of at least three experiments. [b] Values reported vs. SCE. [c] Thermodynamic potential for $H^+$ reduction calculated from $pK_a$ in THF (see the Supporting Information for details).[15–17] [d] With respect to $E_{cat/2}$ for reduction of the catalyst.[18] [e] With respect to applied potential of the CPE experiment: −1.16 V for **1** and −1.22 V for **2**.

maintain a similar overpotential for proton reduction to $H_2$, $DMAPH^+$ was used to study proton reduction with **2**. Upon addition of excess $DMAPH^+$ to a solution of **2**, an increase in the current density was observed ($j_c/j_p = 4$) (Figure 1b). CPE experiments showed that the FE for $H_2$ production by **2** is only 15% when using $DMAPH^+$ (Table 1).

To further probe the disparate reactivity of **1** and **2** in the presence of protons and an applied potential, we turned first to the CPE experiments. Addition of two equivalents of $DMAPH^+$ to **1** produced a product identified as $[(^{Ph}H_2I_2P)Al(DMAP)_2Cl]^{2+}$ ($H_2\mathbf{1}^{2+}$) by using proton NMR spectroscopy, and comparison with previous reports of protonated $I_2P^{2-}$ ligands (Figure S2).[12,19] A CPE experiment with **1** and $DMAPH^+$ (1:20) was next investigated by using proton NMR spectroscopy to characterize a sample taken from the CPE cell following the experiment. The major species in solution was identified as $H_2\mathbf{1}^{2+}$ (Figure 3). Addition of two equivalents of $DMAPH^+$ to paramagnetic **2** resulted in a product that appeared diamagnetic by proton NMR spectroscopy (Figure S3), the spectrum obtained closely resembled that of the reaction product of $I_2P^-$ with $DMAPH^+$. These experiments suggest that protonation of **2** results in loss of $I_2P^-$ from the Al coordination sphere, which is consistent with the low stability of **2** in CPE experiments (Table 1).

Further mechanistic insight into $H_2$ evolution by **1** was obtained from CV experiments where successive aliquots of $lutH^+$ were added to a solution of **1**, and, separately, where additions of **1** were added to a solution of $lutH^+$ (Figure 2). Plots of $j_c/j_p$ versus $[lutH^+]$ and $j_c/j_p$ versus [**1**] were obtained,

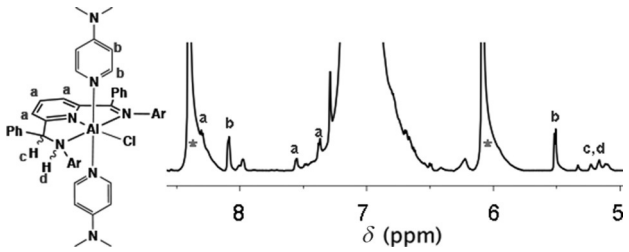



***Figure 3.*** $^1H$ NMR spectrum of the CPE experiment with **1** after 1.5 h at −1.16 V. The solvent was removed and the residue dissolved in $C_6D_6$. The signals for $DMAPH^+$ are at 8.40 and 6.08 (*, see Figure S4 for the spectrum of $DMAPH^+$ in $C_6D_6$). The region upfield from 5 ppm is not shown because of interference from the $Bu_4N^+$ electrolyte salt.

and showed that the electrocatalytic reaction is pseudo-first-order with respect to acid and first order with respect to **1**, as determined using the relationship described in Equation (1).[9a,10b,20,21] Similar results were obtained from the analogous experiments performed with $DMAPH^+$ (Figures S5, S6). In Equation (1), $k_{cat}$ is the observed rate constant, $v$ is scan rate, $R$ is the ideal gas constant, $T$ is temperature, $F$ is Faraday's constant, and $[H^+]$ is acid concentration.

$$\frac{j_c}{j_p} = \frac{n}{0.446}\sqrt{\frac{RTk_{cat}[H^+]^2}{Fv}} = 0.72\sqrt{\frac{k_{cat}[H^+]^2}{v}} \quad (1)$$

We further analyzed the reaction pathway for $H_2$ evolution by **1** by using stoichiometric experiments. Addition of two equivalents of the reductant sodium anthracenide to $H_2\mathbf{1}^{2+}$ produced $H_2$ in 90% yield, as measured by GC-TCD. If just one equivalent of reductant was added to $H_2\mathbf{1}^{2+}$, no $H_2$ was evolved. We further analyzed the resulting paramagnetic product $H_2\mathbf{1}^+$ by using electron paramagnetic resonance (EPR) spectroscopy (Figure 4). The EPR measurements performed at room temperature showed a single signal at $g = 2.0058$ which is consistent with formation of a ligand-based radical. Hyperfine coupling in the spectrum was partially resolved and was best modeled by coupling of the unpaired electron to two nitrogen atoms. The addition of a third nitrogen atom to the simulation did not improve the fit and this result supports a model for $H_2\mathbf{1}^+$ where a ligand-based radical is delocalized over the pyridyl and imino functional groups (Scheme 3). Our previous reports on the

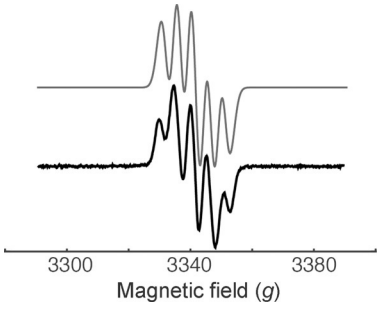
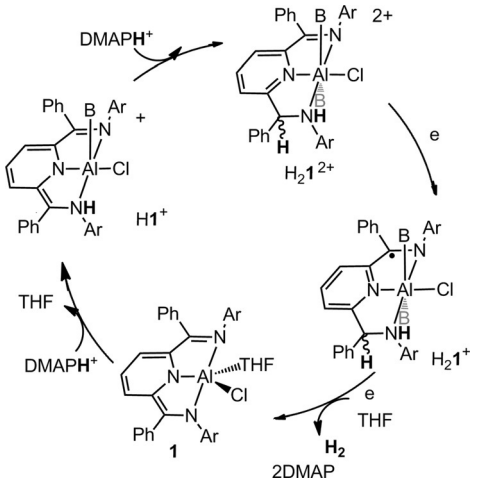



***Figure 4.*** EPR spectrum of $H_2\mathbf{1}^+$ (below) and simulation (above). Fit parameters: $g = 2.0058$, $A^{N1} = 14.1407$, $A^{N2} = 11.7566$.




***Scheme 3.*** Proposed mechanism for $H^+$ reduction (B = DMAP).

electronic structure of Al complexes of iminopyridine ligands have also implicated the presence of ligand-based radicals.[22]

In conclusion, a mechanism for the reduction of protons to $H_2$ by **1** likely involves two protonation events at the ligand in **1**, followed by a two-electron reduction of the protonated ligand to liberate $H_2$ (Scheme 2). Thus, we have shown that ligand-based proton and electron transfer can mediate efficient proton reduction, and this work defines a new reaction pathway for electrocatalytic reduction chemistry that may be extended to a range of substrates such as $CO_2$ or $N_2$. Future work will address the design of new catalysts, and the reduction of other small molecule substrates using the principles of ligand-based proton and electron transfer that we have presented here.

## Acknowledgements

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