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Catalysis

Hydrogenation of Arenes by Dual Activation: Reduction of Substrates Ranging from Benzene to C_{60} Fullerene under Ambient Conditions**

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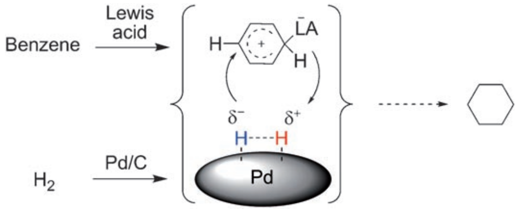
Catalytic hydrogenation of aromatic compounds is an important reaction which is useful for making key intermediates in organic chemistry and for the production of aromatic-content-free fuels. More recently, there has been much interest in the potential for storage of molecular hydrogen, as an energy source, by catalytic hydrogenation of carboneous materials (e.g., fullerene and carbon nanotubes).[1,2] Although the science of metal and metal-oxide-catalyzed arene hydrogenations have been significantly advanced since the original findings of Sabatier and Senderens,[3] harsh conditions (high temperatures or pressures) are still required for the catalytic hydrogenation of aromatic compounds. The reduction of benzene requires harsher conditions compared to that of most other aromatic compounds because of its high stabilization energy resulting from aromaticity. The catalytic activity of heterogeneous noble metal catalysts for the hydrogenation of benzene decreases in the order of Rh > Ru > Pt > Ni > Pd.[4] At low temperature palladium usually does not reduce a benzene ring, and palladium nanoparticles[5] have been shown to be nearly inactive for the hydrogenation of benzene. It is well known that Lewis acids can activate aromatic compounds[6] and that Pd/C can be used to activate molecular hydrogen. We wondered if these two types of activation could work cooperatively for the hydrogenation of arenes by the novel ionic mechanism depicted in Scheme 1. Herein we report the highly efficient catalytic hydrogenation of benzene and other hydrocarbon-based aromatic compounds, including C_{60} fullerene, under ambient conditions (1 bar of H_2 and RT) by simultaneous activation of molecular hydrogen and the aromatic substrate with Pd/C and a Lewis acidic ionic liquid [bmim]Cl-$AlCl_3$ (**1**, bmim = 1-butyl-3-methylimidazolium; x of $AlCl_3 = 0.67$ where x is the mole fraction of $AlCl_3$), respectively.



Scheme 1. Concept for a new cooperative catalytic system for the double activation of an arene and molecular hydrogen.

Table 1: Catalytic hydrogenation of benzene to cyclohexane.[a]

Entry	Metal cat. (equiv)	Lewis acid (equiv)	H_2 [bar]	Time [h]	Conversion [%][b]
1	Pd/C (0.02)	–	3	6	n.r.
2	Pd_{NP}[c] (0.02)	–	3	6	n.r.
3[d]	Pd_{NP}/SiO_2	–	30	2	4
4	–	**1** (0.5)	3	6	n.r.
5	Pd/C (0.02)	$AlCl_3$ (0.5)	3	6	n.r.
6	Pd/C (0.02)	**1** (0.5)	3	6	> 99
7	Pd/C (0.1)	**1** (1)	1	24	> 99

[a] Reaction conditions: Unless otherwise indicated, reactions were carried out with benzene (1 mmol), Pd/C (2 mol%) in the presence or absence of a Lewis acid in 1,2-dichloroethane (2 mL) at room temperature. [b] Conversions were determined by GC methods. [c] Pd_{NP} = Pd nanoparticles; Pd_{NP} was prepared from $[Pd(acac)_2]$ according to a literature procedure.[10] [d] Data from reference [5]. n.r. = no reaction; acac = acetylacetonate.

We initially examined the hydrogenation of benzene to cyclohexane in the presence of Lewis acids and palladium (Table 1). Pd/C (Table 1, entry 1) and palladium nanoparticles (Table 1, entries 2 and 3) were ineffective as catalysts for the hydrogenation reaction. Lewis acidic ionic liquid **1** was also ineffective for the hydrogenation reaction (Table 1, entry 4).[7] However, when Lewis acidic ionic liquid **1** and Pd/C (0.5 and 0.02 equiv, respectively) were combined, the hydrogenation reaction went to completion (Table 1, entry 6). When the amounts of **1** and Pd/C were increased to 1 and 0.1 equivalents, respectively, benzene was hydrogenated at 1 bar of H_2 (Table 1, entry 7). When **1** was replaced by $AlCl_3$ (Table 1, entry 5), a mixture of unidentified condensation products were formed by the Scholl reaction.[8,9]

Subsequent to our encouraging results, we focused on the hydrogenation of bicyclic and polycyclic aromatic compounds (Table 2). These aromatic substrates are more reactive to hydrogenation than benzene, therefore all of the compounds were smoothly hydrogenated to completion under ambient conditions when both **1** and Pd/C were used in combination (Table 2, entries 3, 4, 7, 10, and 12). Here again, the hydrogenation reactions were ineffective in the absence of **1**, even under higher pressures of H_2 (Table 2, entries 1, 5, 8, and 11). When **1** was replaced with $AlCl_3$, various inseparable condensation products (> 99 %) were formed by the Scholl

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Table 2: Palladium-catalyzed hydrogenation of various aromatics.[a]

Entry	Arene	Additive (equiv)	H_2 [bar]	Time [h]	Conversion [%][b,c]
1	biphenyl	none	3	6	<1
2		$AlCl_3$(0.5)	3	6	<1
3		**1** (0.5)	3	6	>99
4		**1** (1)	1	24	>99
5	naphthalene	none	10	16	<1
6		$AlCl_3$(0.5)	10	16	trace
7		**1** (0.5)	1	24	>99[d]
8	anthracene	none	1	16	<6[d]
9		$AlCl_3$(0.5)	1	16	trace
10		**1** (0.5)	1	16	97[d]
11	naphthacene	none	1	16	11[d]
12		**1** (0.25)	1	16	>99[d]

[a] Reactions were carried out with arenes (0.5 mmol) and Pd/C (2 mol%) in the presence or absence of an additive in 1,2-dichloroethane (2 mL) at room temperature. [b] Conversions were determined by GC-MS methods. [c] Yields of isolated products after chromatography: 84% (entry 3), 80% (entry 4), 81% (entry 7), 85% (entry 10), and 94% (entry 12). [d] For the structures and ratios of the hydrogenated products, see the Supporting Information.

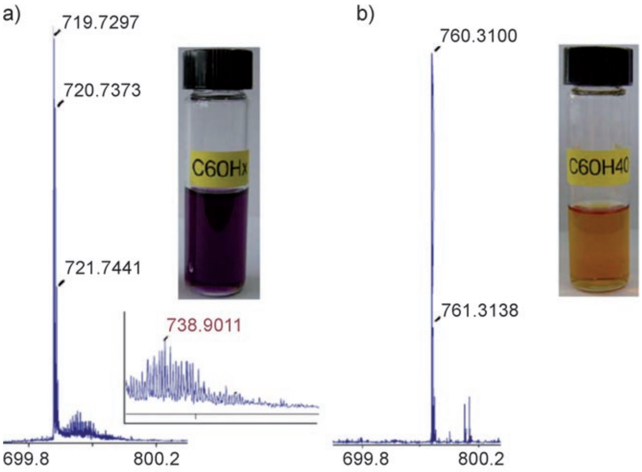
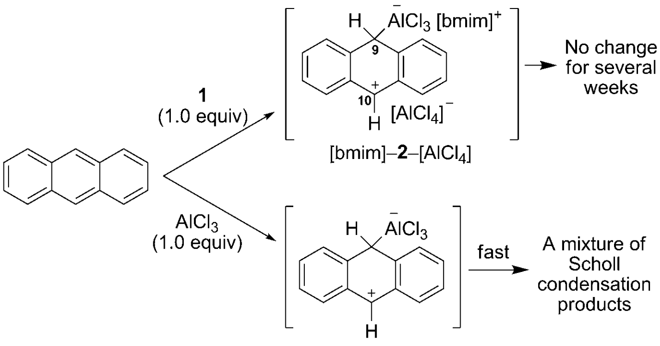


Figure 1. MALDI TOF mass spectra of the hydrogenation products of C_{60}: a) 1 equiv of **1** and 0.1 equiv of Pd/C per C_6 unit (5 bar H_2, RT, 24 h); b) 10 equiv of **1** and 1 equiv of Pd/C per C_6 unit (1 bar H_2, RT, 48 h).



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Scheme 2. Two different anthracenium intermediates, [bmim]–**2**–[$AlCl_4$] and **2**, generated by mixing anthracene with **1** or $AlCl_3$, respectively.

reaction as detected by GC-MS methods (Table 2, entries 2, 6, and 9; see the Supporting Information).

There has been much interest in hydrogenation of C_{60} fullerene, and this reaction generally requires extremely harsh conditions (e.g., 120 bar of H_2 at 400 °C).[1] However, by employing our cooperative catalytic system [Pd/C (0.1 equiv per C_6 unit) and **1** (1 equiv per C_6 unit)], C_{60} fullerene can be hydrogenated under very mild reaction conditions (5 bar H_2 at RT for 24 h). After the reduction, a dark brown powder (violet solution in 1,2-dichloroethane) was separated by column chromatography to give a 95% yield. MALDI TOF mass spectrometry detected ions predominantly in the range from m/z 720 to 760, having a maximum at m/z 738. This peak corresponds to $C_{60}H_{18}$ (Figure 1 a). When the amounts of **1** and Pd/C are increased ten-fold [Pd/C (1 equiv per C_6 unit) and **1** (10 equiv per C_6 unit], the C_{60} fullerene can be hydrogenated under ambient conditions (1 bar of H_2 at RT for 48 h). A faintly yellow colored oil (yellow solution in 1,2-dichloroethane) was isolated from the reaction mixture after column chromatography.[11] The MALDI TOF mass spectrum of this product shows a prominent peak at m/z 760 which corresponds to $C_{60}H_{40}$ (Figure 1 b). To our knowledge, this represents the first hydrogenation of C_{60} fullerene under ambient conditions.

On the basis of our experimental results, it is clear that Lewis acidic ionic liquid **1** works cooperatively with Pd/C. To compare the difference in the effects of a Lewis acid ($AlCl_3$) versus the Lewis acidic ionic liquid (**1**) with aromatic compunds, we treated anthracene with a stoichiometric amount of $AlCl_3$ or **1** in [D_4]1,2-dichloroethane at room temperature (Scheme 2). The reaction mixture was stirred for 30 minutes, after which it was subjected to NMR analysis. Interestingly, the reaction of anthracene with **1** gave what appears to be a single, stable compound that we assign to anthracenium salt [bmim]–**2**–[$AlCl_4$] (Scheme 2 and Figure 2).[12,13] The anthracenium salt with a carbocation center at C10 and an sp^3 center at C9 is expected to give characteristic ^1H and ^{13}C NMR chemical shifts. We propose that the downfield shifted ^1H NMR signal at $\delta = 9.95$ results from H10 and the upfield shifted signal at $\delta = 4.9$ results from H9. The four aromatic signals [$\delta = 8.5$ (d, $J = 6$ Hz, 2H), 8.4 (t, $J = 6$ Hz, 2H), 8.1 (t, $J = 6$ Hz, 2H), and 8.0 (d, $J = 6$ Hz, 2H)] can also be easily assigned. Similarly, we assign the ^{13}C NMR signals at $\delta = 182.3$ and $\delta = 39.8$ to C10 and C9, respectively. Moreover, the proton-coupled ^{13}C NMR spectrum shows the typical coupling constants of sp^2 (164 Hz) and sp^3 carbon centers (128 Hz) for C10 and C9, respectively (Figure 2 b). The ionic intermediate, [bmim]–**2**–[$AlCl_4$], is so stable that the NMR signals did not change appreciably for several weeks at 25 °C.[14] In contrast, mixing anthracene and a stoichiometric amount of $AlCl_3$ in [D_4]1,2-dichloroethane resulted in rapid oligomerization of the arene without showing the characteristic NMR signals for anthracenium intermediate **2** (Scheme 2 and Figure 2 a).

The dramatic stabilization of arenium intermediate [bmim]–**2**–[$AlCl_4$] is also supported by ab initio calculations (see the Supporting Information for the computational details). The enthalpy ($\Delta H_3 = \Delta H_1 + \Delta H_2$) of the complex formation between **2** and [bmim][$AlCl_4$] was calculated to be

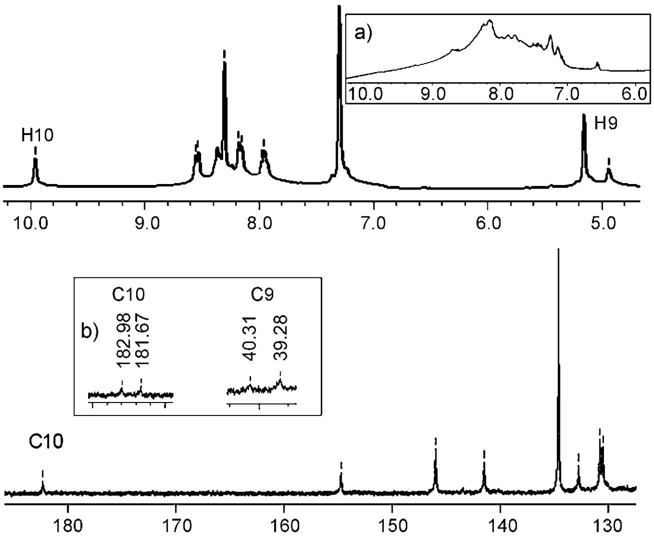


Figure 2. ^{1}H and ^{13}C NMR spectra (top and bottom) of the mixture of anthracene and **1**. a) ^{1}H NMR spectrum of a mixture of anthracene and $AlCl_3$; b) section of a proton coupled ^{13}C NMR spectra for the mixture of anthracene and **1**.

$-10.4\ \text{kcal mol}^{-1}$ (Scheme 3).[15] Furthermore, as shown in Figure 3, the reactive sites of arenium intermediate [bmim]–**2**–[$AlCl_4$] are protected by the bulky ions of the ionic liquid, [bmim][$AlCl_4$]. The exothermicity and the remarkable kinetic stabilility of [bmim]–**2**–[$AlCl_4$] prevent potential side reactions.

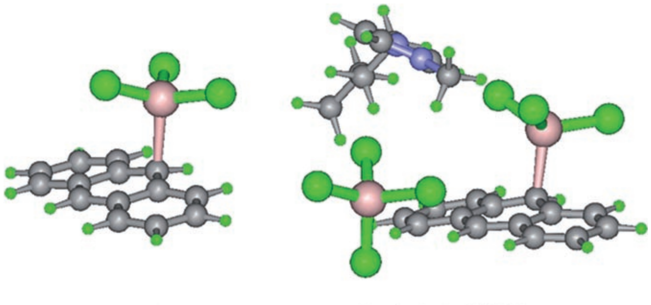
In conclusion, a highly efficient catalytic hydrogenation of benzene and other hydrocarbon-based aromatic substrates, including C_{60} fullerene, have been accomplished under ambient conditions (1 bar H_2 and RT) by cooperative interaction of Lewis acidic ionic liquid **1** and Pd/C. A new ionic hydrogenation mechanism has been proposed for our catalytic process. To support the proposed mechanism, a key intermediate ([bmim]–**2**–[$AlCl_4$]) has been generated and characterized by ^{1}H and ^{13}C NMR spectroscopy at ambient temperature. The calculations indicate that the role of the ionic liquid is to provide both kinetic and thermodynamic stabilization for the arenium intermediate. The stabilization of the arenium intermediate by the cation and the anion of [bmim][$AlCl_4$] not only allows its detailed characterization, but also results in increasing the rate of the hydrogenation reaction. Furthermore, protection of the arenium intermediate with the bulky ions of the ionic liquid, [bmim][$AlCl_4$], prevents side reactions.

$$[\text{bmim}][\text{AlCl}_4] \longrightarrow [\text{bmim}]^+ + [\text{AlCl}_4]^- \qquad \Delta H_1 = 67.3\ \text{kcal mol}^{-1}$$

$$\mathbf{2} + [\text{bmim}]^+ + [\text{AlCl}_4]^- \longrightarrow [\text{bmim}]\text{–}\mathbf{2}\text{–}[\text{AlCl}_4] \qquad \Delta H_2 = -77.7\ \text{kcal mol}^{-1}$$

$$\mathbf{2} + [\text{bmim}][\text{AlCl}_4] \longrightarrow [\text{bmim}]\text{–}\mathbf{2}\text{–}[\text{AlCl}_4] \qquad \Delta H_3 = -10.4\ \text{kcal mol}^{-1}$$

Scheme 3. The enthalpy of the complex formation between **2** and [bmim][$AlCl_4$].



2 [bmim]–**2**–[$AlCl_4$]

Figure 3. Computed structures of **2** and [bmim]–**2**–[$AlCl_4$].

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[12] In 1980 Buchanan et al. reported that the stable anthracenium salt, [anthracenium]$AlCl_4$ can be generated by mixing anthracene and a Brønsted superacidic melt, HCl/$SbCl_3$/$AlCl_3$; A. C. Buchanan III, A. S. Dworkin, G. P. Smith, *J. Am. Chem. Soc.* **1980**, *102*, 5262–5265.

[13] The stable anthracenium salt can also be obtained by mixing anthracene with other quaternary ammonium analogues of **1**, such as [NMe_4]Cl-$AlCl_3$ (x of $AlCl_3 = 0.67$); see the Supporting Information, Figure S1).

[14] An additional hydrogenation experiment was conducted with the anthracenium salt, [bmim]–**2**–[$AlCl_4$], under the same conditions used for entry 10 in Table 2. As anticipated, the same reduced products were obtained with those formed from entry 10 in Table 2.

[15] In the case of benzene, the enthalpy of the complex formation between benzene–$AlCl_3$ and [bmim][$AlCl_4$] is $-9.3\ \text{kcal mol}^{-1}$. For details, see the Supporting Information.