

## Metal-Mediated C–C Bond Making and Breaking: First Direct Evidence for a Reversible Migration of a Benzyl Group along a Metal–Carbon Bond

Martin Albrecht,<sup>†</sup> Robert A. Gossage,<sup>†,§</sup>  
Anthony L. Spek,<sup>‡</sup> and Gerard van Koten\*<sup>†</sup>

Debye Institute, Department of Metal-Mediated  
Synthesis and Bijvoet Center for Biomolecular Research  
Department of Crystal and Structural Chemistry  
Utrecht University, Padualaan 8  
3584 CH Utrecht, The Netherlands

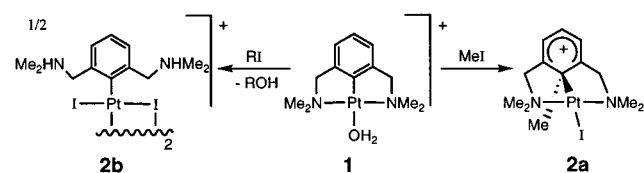
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Considerable effort has been directed toward the metal-mediated activation of C<sub>aryl</sub>–C<sub>alkyl</sub> bonds in C-substituted benzene derivatives, mainly because of their importance in a number of bulk and specialty chemical syntheses.<sup>1,2</sup> In particular, potentially terdentate coordinating aryl-carbanions of the “pincer” class ligands (e.g., the NCN<sup>3</sup> or PCP-type<sup>2,4</sup>) have been shown to be very versatile in providing insight into mechanistic details of such reactions.<sup>5</sup>

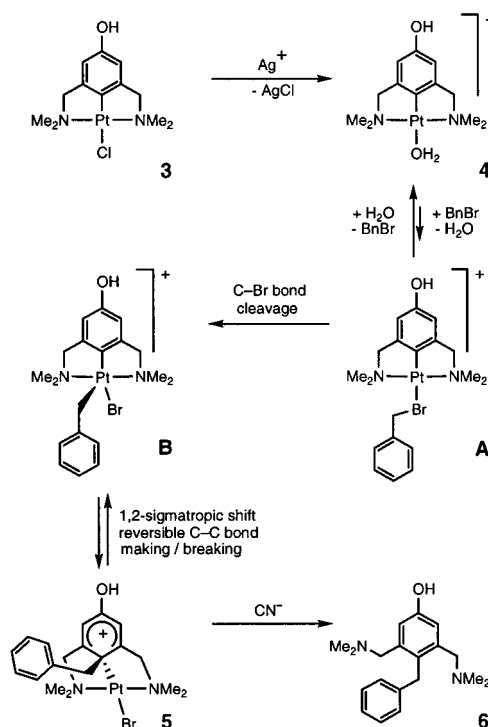
The arylplatinum aqua cation **1** containing the ligand [C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-2,6]<sup>−</sup> (abbreviated as NCN) reacts with MeI to afford an air-stable methyl arenium ion **2a** (Scheme 1).<sup>6,7</sup> Formation of **2a**, which is equivalent to a platinum(II)-mediated C<sub>aryl</sub>–C<sub>alkyl</sub> bond-making process, has been demonstrated to be reversible.<sup>6b</sup> Computational studies suggested that the observed C<sub>aryl</sub>–C<sub>alkyl</sub> bond formation most probably involves S<sub>N</sub>2 attack of MeI on the cationic Pt(II) center which is followed by a 1,2-sigmatropic shift of the Me group to C<sub>aryl</sub>.<sup>6c</sup> Interestingly, reaction of cation **1** with higher alkyl halides (RX, R = Et, Bn, allyl) resulted in a cascade of reactions which slowly afforded the corresponding alcohol (ROH) and an unusual zwitterionic Pt dimer **2b** (Scheme 1).<sup>8</sup>

Here we demonstrate that the application of a simple concept derived from electrophilic aromatic substitution theory<sup>9</sup> circumvents this restriction in alkyl halide reactant: the introduction of electron-releasing substituents as activators on the aromatic ring (i.e., in this case on the NCN ligand) allows reversible C–C bond making and arenium formation with various alkyl halides. This provides a basis for the mechanistic understanding of metal-mediated C<sub>aryl</sub>–C<sub>alkyl</sub> bond-making and -breaking processes.<sup>2,10</sup>

**Scheme 1.** Discriminating Reactivity of the Platinum(II) Solvato Complex **1** toward Alkyl Halides, Leading to Arenium Ion **2a** (R = Me) or to a Dimeric Zwitterion **2b** (R ≠ Me)



**Scheme 2.** Proposed Steps for the Formation of the New C<sub>aryl</sub>–C<sub>alkyl</sub> Bond Affording **6**



When a colorless acetone solution of the cationic aqua-complex **4** containing a hydroxyl group at C<sub>para</sub> (derived from the corresponding neutral chloroplatinum complex **3**)<sup>11</sup> is treated with benzyl bromide (BnBr), a deep purple color develops within a few minutes. This is followed by a second slower color change to yield eventually an orange solution.<sup>12</sup> Spectroscopic analyses (multinuclear NMR, UV–vis) are in agreement with the latter (orange) complex being a stable benzyl arenium species (**5**; Scheme 2).<sup>13</sup>

Formation of a new C<sub>aryl</sub>–C<sub>benzyl</sub> bond in **5** has been confirmed unequivocally by single-crystal structure analysis (Figure 1).<sup>14</sup> The intriguing features of the molecular structure (e.g., geometry around C1, alternating bond length in the aryl unit)<sup>6b,15</sup> correspond well with recently reported data on organic chloro and rhodium arenium species.<sup>16</sup>

Mechanistic insight into the reaction pathway from **4** to **5** has been obtained by photospectroscopic monitoring of the two

<sup>†</sup> Debye Institute.

<sup>‡</sup> Bijvoet Centre for Biomolecular Research.

<sup>§</sup> Present address: AnorMED Inc., Langley, BC V2Y 1N5, Canada.

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(3) NCN = [C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NR<sub>2</sub>)<sub>2</sub>-2,6]<sup>−</sup>. See e.g.: van Koten, G. *Pure Appl. Chem.* **1989**, *61*, 1681.

(4) PCP = [C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>PR<sub>2</sub>)<sub>2</sub>-2,6]<sup>−</sup>. See e.g.: (a) Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1020. (b) Rimmel, H.; Venanzi, L. M. *J. Organomet. Chem.* **1983**, *259*, C6. (c) Nemeš, S.; Jensen, C.; Binamira-Soriaga, E.; Kaska, W. C. *Organometallics* **1983**, *2*, 1447. (d) Dani, P.; Karlen, T.; Gossage, R. A.; Kooijman, H.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1997**, *119*, 11317.

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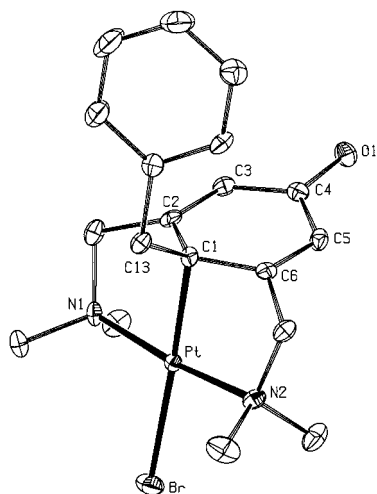
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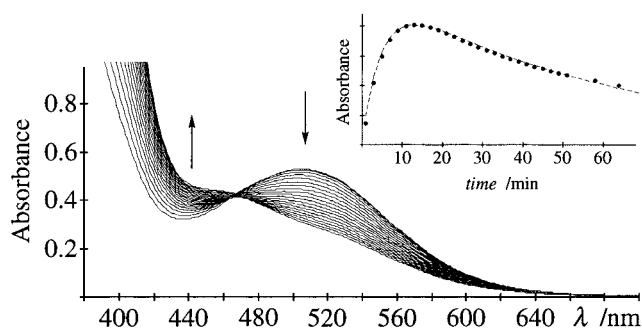
(12) Similar orange colors have been previously observed in methyl arenium compounds containing a Pt-bound bromide ion: Terheijden, J.; van Koten, G.; Vinke, I. C.; Spek, A. L. *J. Am. Chem. Soc.* **1985**, *107*, 2891.

(13) Unlike in earlier investigated, unsubstituted arenium ions, mesomeric stabilization is found in **5** due to the hydroxyl substitution and C<sub>ipso</sub> has been found at δ<sub>C</sub> = 79.8 ppm.

(14) Crystals of **5** were grown from an acetone solution layered with pentane. For crystal data see Supporting Information.



**Figure 1.** Perspective view (ORTEP 50% probability) of the arenium cation **5** (all hydrogens and  $\text{BF}_4^-$  anion omitted for clarity).



**Figure 2.** The overlapping absorption spectra (2 min interval) showing the color change of the reaction solution (acetone) from purple (intermediate **B**) to orange (arenium **5**). Inset: Time-dependent absorbance of the reaction from the aqua-ion **4** to arenium **5** via intermediate **B**, monitored at 505 nm.

consecutive color changes. The initially formed purple solution is characterized by a broad band with an absorption maximum at 505 nm (acetone). Subsequently, a decrease of the absorbance at this wavelength occurs, concomitant with an increase of the absorption activity at the local minimum around 430 nm (Figure 2). The isosbestic point at 472 nm demonstrates this transformation to be an equilibrium process between two species only. When cation **4** is treated with a large excess of  $\text{BnBr}$ , time-dependent measurements of the absorbance at 505 nm allow for monitoring the reaction rate under pseudo-first-order conditions. Two consecutive reaction sequences can be distinguished (Figure 2, inset): first, formation of an intermediate **B** having an absorption maximum at 505 nm, followed by a consumption of this intermediate, which is nearly linear in time.<sup>17</sup>

The low solubility properties of **4** as well as signal overlap of **4** and intermediates hampered the monitoring of the reaction by  $^1\text{H}$  NMR spectroscopy. However, a significant line broadening of the signal due to coordinated water in **4** ( $\delta = 2.85$  ppm) is noted ( $\Delta w_{1/2} = 25$  Hz) in the initial few minutes of the reaction, presumably because of  $\text{BnBr}$  coordination (see **A**, Scheme 2).

(15) Pertinent angles (deg) in **5**: C2–C1–C6 114.8(4); C2–C1–C13 117.4(4); C6–C1–C13 119.4(4); C13–C1–Pt 112.2(3). Selected bond lengths (Å): C1–C13 1.538(7); C1–Pt 2.106(4). The presence of the hydroxyl proton (not detected by NMR) has been confirmed unequivocally by the existence of a  $\text{O–H}\cdots\text{F–B}$  hydrogen bond between the phenol of the arenium cation and the anionic  $\text{BF}_4^-$  unit; for details, see the Supporting Information.

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(17) Approximation of the measured data points by the expected concentration of **B** during a consecutive reaction  $\mathbf{4} \rightarrow \mathbf{B} \rightarrow \mathbf{5}$  gives an excellent correlation ( $R > 0.997$ ).

Simultaneously, a new set of signals appears, which points to diastereotopic  $\text{CH}_2\text{N}$  protons (AB pattern at 3.58 and 5.06 ppm, respectively) and  $\text{NMe}_2$  groupings (two singlets).<sup>18</sup> At a later stage, a new final set of signals gradually appears which is characteristic for the benzyl arenium product **5**. The transformation to **5** can be accelerated by heating the reaction solution to 50 °C.

Dissolution of crystals of **5** in acetone produces two sets of signals in the  $^1\text{H}$  NMR spectrum, i.e., of **5** and of **B**, pointing to the reversibility of the  $\text{C}_{\text{aryl}}\text{–C}_{\text{alkyl}}$  bond-formation process.

On the basis of these results a proposal for the intimate steps during the transformation of **4** to **5** and the reverse is shown in Scheme 2. This involves the following: (1) transient coordination of  $\text{BnBr}$  via bromide (i.e., formation of **A**; cf. broadening of the signal due to water in the  $^1\text{H}$  NMR);<sup>19</sup> (2) oxidative addition by heterolytic cleavage of the  $\text{Br–C}_{\text{benzyl}}$  bond resulting in the formation of **B** (first reaction intermediate observed by UV–vis spectroscopy); and (3) as the slowest step, an intramolecular rearrangement, i.e., the occurrence of a (reversible) 1,2-shift of the benzyl group from the metal center to  $\text{C}_{\text{ipso}}$  thus forming the thermodynamically more stable benzyl arenium product **5**. This is fully consistent with all of the experimental observations, i.e., (i) the absorption spectrum of intermediate **B**, (ii) the kinetics deduced for the formation of **5**, and (iii) a strong structural similarity (NMR) between the intermediate **B** and the final product **5**. These results provide for the first time direct evidence for a reversible migration of a benzyl cation along a metal–carbon bond: the observations visualize the reaction trajectory for a reductive elimination process (i.e. C–C bond forming) taking place at a metal center, and in particular, also demonstrate the microscopic reverse, i.e. that for a metal-mediated C–C bond cleavage process. In either reaction direction, the formation of the thermodynamically stable arenium ion is crucial.<sup>6c</sup>

Finally, elimination of a cationic species from **5** (formally  $\text{PtBr}^+$ ; mediated, e.g., by aqueous cyanide solution) and concomitant re-aromatization takes place (formation of **6**).

In conclusion, we have shown that arenium formation of platinum complexes containing the NCN pincer ligand can be extended to other alkyl halides by introducing an activating hydroxyl group on the aryl ring, which displays a basic principle of electrophilic aromatic substitution. For the first time, direct evidence is provided for the indirect attack of a carbocation via the metal center onto an aromatic system as a key step in the formation of such an arenium ion. The activation of a  $\text{C}_{\text{aryl}}\text{–Pt}$  platinum bond, the initial stage of the formation of a  $\text{C}_{\text{aryl}}\text{–C}_{\text{alkyl}}$  bond and de-metalation, is shown to take place by an electrophilic aromatic substitution process, involving attack on the metal center<sup>20</sup> followed by 1,2-migration of the alkyl cation along the metal– $\text{C}_{\text{aryl}}$  bond. Moreover, this work indicates that a reverse metalation reaction, i.e.,  $\text{C}_{\text{aryl}}\text{–metal}$  bond formation via  $\text{C}_{\text{aryl}}\text{–C}_{\text{alkyl}}$  bond activation and cleavage,<sup>2,21</sup> presumably occurs through a similar mechanism, viz. the microscopic reverse of the de-metalation process presented here, which would require chelate  $\text{Pt–N}$  coordination to **6**.<sup>21b</sup>

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**Supporting Information Available:** Tables with microanalyses, spectroscopic and crystal data for **5**, the synthesis of **6**, and UV–vis data for the transformation of **4** to **B** (PDF). The material is available free of charge via the Internet at <http://pubs.acs.org>.

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(18)  $\text{NMe}_2$ :  $\delta_{\text{H}} = 3.12$  ( $^3J_{\text{PH}} = 28.5$  Hz) and 2.83 ppm ( $^3J_{\text{PH}}$  not resolved), respectively; these data corroborate with a structure **B** representing a 5- or 6-coordinate Pt(IV) species, see the Supporting Information.

(19) Associative solvent exchange on cationic platinum(II) solvato complexes containing the NCN pincer ligand is fast, see: Frey, U.; Grove, D. M.; van Koten, G. *Inorg. Chim. Acta* **1998**, *269*, 322.

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