

## Pt and Pd 1,4-Shifts at the Edge of Dibenz[*a,c*]anthracene

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C–H activation by transition metals is an active research area with increasing applications.<sup>1</sup> Catalytic aromatic C–H activation provides simple access to a range of compounds. In some cases, products are explained by metal shifts or migration where a carbon-bound Rh or Pd exchanges positions with a nearby carbon-bound hydrogen (Scheme 1).<sup>2</sup> We report here such shifts in isolated Pt and Pd complexes.<sup>3</sup>

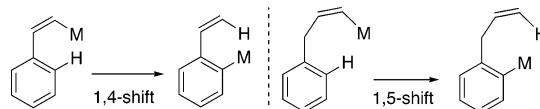
The chemistry of the complexes is shown in Scheme 2. Colorless **1a** (M = Pt) and **1b** (M = Pd) are prepared by oxidative addition of 9-bromodibenz[*a,c*]anthracene<sup>4</sup> to ML<sub>4</sub> (L = PEt<sub>3</sub>). <sup>31</sup>P NMR data indicate a *cis* configuration around the metal centers. <sup>1</sup>H NMR spectra show a strongly shifted signal for the *bay*-proton in the 8-position of the dibenz[*a,c*]anthracene moiety (10.95 ppm for **1a**, 10.92 ppm for **1b**). Similar values have been reported for aromatic CH's in other square planar d<sup>8</sup> metal complexes and are attributed to "pre-agostic" metal–CH interactions where the hydrogen atom is in close proximity to the metal.<sup>5</sup> This situation is confirmed for H8 of **1** by X-ray crystal structure determinations (see below).

Heating sealed-tube toluene solutions of **1** at 160 °C results first in isomerization to the *trans* complexes **2** (Scheme 2). The isomerization is accompanied by an increase in the H8 <sup>1</sup>H NMR resonance from ~10.9 to 12.07 ppm for **2a** and 11.63 ppm for **2b**. After the isomerization is nearly complete (~48 h), the concentration of **2** begins to decrease with the concomitant appearance and increase of a new complex. For **2a** the conversion is clean and follows first-order kinetics (*k* = 0.022 h<sup>-1</sup>). Isolation of the new complex at the end of the reaction (~5 days) reveals the 8-substituted<sup>6</sup> dibenz[*a,c*]anthracene complex **3a** (Scheme 2), formed by a 1,4-shift or -migration of the Pt center. The <sup>31</sup>P NMR signal for **3** is a singlet, consistent with a *trans* isomer, and is at a slightly higher frequency from that for **2**. <sup>195</sup>Pt satellites indicate <sup>31</sup>P–<sup>195</sup>Pt coupling nearly identical to that in **2**. Most diagnostic of the structure of **3** is the appearance of a new singlet in the aromatic region of the <sup>1</sup>H NMR spectrum, resulting from the H9 proton now at the position formally occupied by the Pt center. NMR data for **3b** (M = Pd) are similar to those for the Pt complex, but its formation from **2b** is slower (~10 days at 160 °C) and several other products are formed, including free PEt<sub>3</sub> and a black precipitate assumed to be Pd.

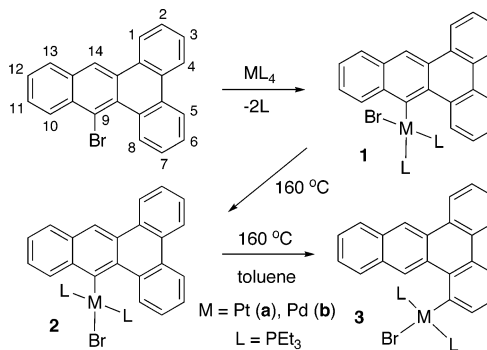
The effect of solvents and additives on the **2a** → **3a** conversion was investigated. Clean conversion is observed in polar C<sub>6</sub>H<sub>5</sub>CF<sub>3</sub> at 160 °C, with a rate constant (0.071 h<sup>-1</sup>) ~3 times that in toluene. In DMF conversion occurs at 110–130 °C, but additional products form. D<sub>2</sub>O addition (25 mg) to a toluene reaction (0.7 mL) also gives clean conversion, with a rate constant (160 °C, *k* = 0.052 h<sup>-1</sup>) ~2 times that in dry toluene. No deuterium incorporation into **3a** or remaining **2a** is detected. Finally, 10 mol % free PEt<sub>3</sub> slowed the conversion in toluene at 160 °C (*k* = 0.0094 h<sup>-1</sup>).

The solid-state structures of **1a**, **2a**, and **3a** are shown in Figure 1. In **1a** the aromatic system is strongly distorted from planarity and twisted up toward the Br atom. The twist angle, as measured by the torsion angle between the vectors from C9 to C14 and C2

Scheme 1



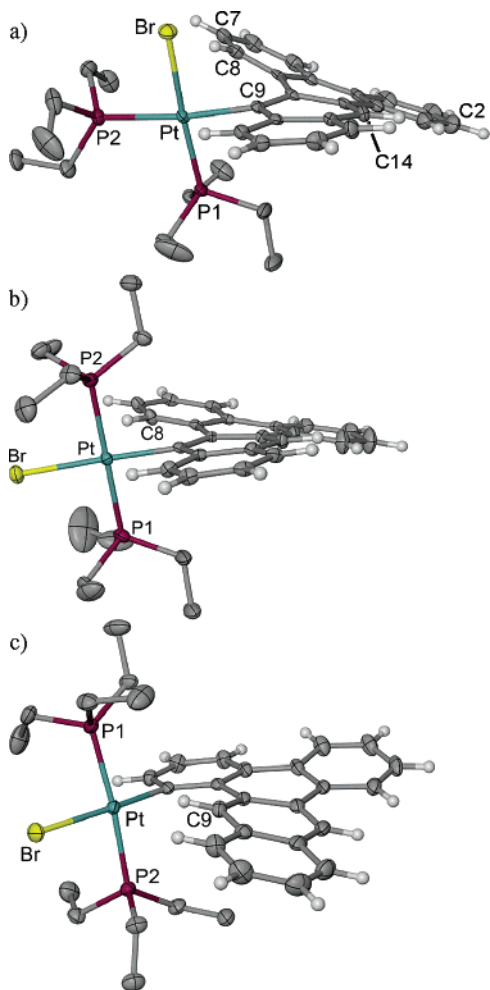
Scheme 2



to C7, is 20.5°. The distortion reduces the contact of the hydrogen atom at C8 with the Pt center. The calculated Pt–H8 distance is still quite small at 2.548 Å. An additional close Pt–H contact (2.720 Å) occurs between the Pt center and the *peri*-hydrogen atom at the 10-position of the dibenz[*a,c*]anthracene moiety.

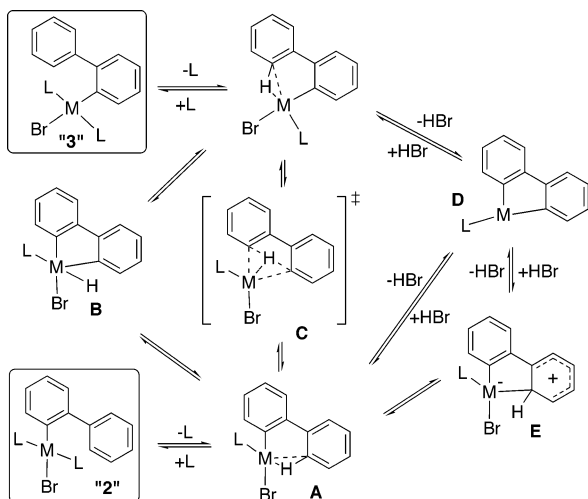
Isomerization to the *trans* structure **2** exchanges the Br atom with the more sterically demanding PEt<sub>3</sub> ligand, sandwiching the aromatic system between the two *trans*-PEt<sub>3</sub> ligands. This apparently reduces the aromatic system twist angle (14.8°) and forces a closer approach of H8 to the Pt center. The calculated Pt–H8 distance of 2.303 Å in **2a** is nearly 0.25 Å shorter than that in **1a**. An increase of 1.2 ppm in the <sup>1</sup>H NMR shift of H8 accompanies the shorter distance. The Pt–H10 distance is also shortened (2.597 Å) but by a smaller amount of 0.12 Å. The *trans* placement of the PEt<sub>3</sub> ligands also results in a lengthening of the *cis*-to-carbon Pt–P distance. Changing from a weak Br<sup>-</sup> *trans* influence<sup>7</sup> to a strong PEt<sub>3</sub> *trans* influence increases the distance (Pt–P1) from 2.2382 (8) Å in **1a** to 2.306(1) (Pt–P1) and 2.317(1) Å (Pt–P2) in **2a**. The resulting stronger *trans* effect<sup>7</sup> of PEt<sub>3</sub> gives a more labile *cis*-to-carbon PEt<sub>3</sub> in **2a** than in **1a** that may be important in the shift mechanism (see below). Similar changes are observed in the structures of the Pd complexes **1b** and **2b**.

A comparison of the structures of **2a** and **3a** shows a slightly greater aromatic system twist in **3a** and a slightly greater Pt–*bay*-hydrogen atom distance. The Pt–H9 distance in **3a** is 2.354 Å, while the Pt–H8 distance in **2a** is 2.303 Å. The twist angle is 17.0° in **3a** and 14.8° in **2a**. In addition, there is no *peri*-hydrogen interaction with the Pt center in **3a** as there is in **2a**, and the Pt–H10 distance of 2.597 Å in **2a** has been replaced with a much longer Pt–H7 distance of 2.828 Å. These features suggest a less constrained structure for **3** that may account for its greater stability over **2**.



**Figure 1.** Solid-state structures of (a) **1a**, (b) **2a**, and (c) **3a**, with 50% (30% **2a**) probability ellipsoids. Hydrogen atoms are omitted from the PEt<sub>3</sub> ligands.

### Scheme 3



Several mechanistic pathways considered for 1,4- and 1,5-shifts and related arylation reactions are illustrated for an abbreviated **2** in Scheme 3.<sup>8</sup> A reasonable first step is phosphine ligand substitution by the pre-agostic C–H, which moves into a full agostic interaction in **A**. The slowing of the reaction with added PEt<sub>3</sub> and the required cis-to-trans isomerization that gives a more labile PEt<sub>3</sub> (see above) support this. Subsequent pathways may involve C–H

oxidative addition (**B**),  $\sigma$ -bond metathesis (**C**), deprotonation of an acidic agostic C–H (**D**), or electrophilic attack (**E**). Pathways involving the formation of HBr can be eliminated by the lack of deuterium incorporation into **3a** (or remaining **2a**) with added D<sub>2</sub>O.<sup>9</sup> This leaves the oxidative addition or  $\sigma$ -bond metathesis pathways. Either way, the increased rate with solvent polarity and polar additives suggests significant polarization in the process. For example, the  $\sigma$ -bond metathesis (**C**) may have significant proton-transfer character.<sup>8a</sup>

In conclusion, we have demonstrated 1,4-shifts in isolated Pt(II) and Pd(II) complexes analogous to shifts postulated to occur in Rh- and Pd-catalyzed reactions. The process does not appear to involve acidic intermediates but is sensitive to the environmental polarity, suggesting an increase in polarity during the process.

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**Supporting Information Available:** Experimental procedures and characterization; kinetic and structural data (PDF, CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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