

After 1 h at room temperature, the reaction was concentrated in vacuo, and the residue was chromatographed on 10 g of silica gel. Elution with 1:2 hexane-ether gave 70 mg (82%) of (3 $\alpha$ ,4 $\alpha$ ,4 $\beta$ ,5 $\beta$ ,7 $\alpha$ ,8 $\alpha$ ,9 $\alpha$ )-3 $\alpha$ ,4,4 $\alpha$ ,5,7 $\alpha$ ,8,9,9 $\alpha$ -octahydro-3-methylene-4 $\alpha$ ,8-dimethyl-4,5-bis[(tetrahydro-2H-pyran-2-yl)oxy]azuleno[6,5-b]furan-2(3H)-one (**42**), which was used directly in the next reaction; IR (CCl<sub>4</sub>) 1775, 1660 cm<sup>-1</sup>.

A solution of 24 mg (0.053 mmol) of **42** in 0.7 mL of glacial acetic acid-water (60:40, v/v) was stirred at room temperature for 5 h. Removal of the solvent under reduced pressure (<0.1 mm) gave an oily residue, which was directly chromatographed on 5 g of silica gel. Elution with ether gave 12.9 mg (92% yield) of tricyclic  $\alpha$ -methylene lactone **43** as a crystalline material: mp 155-157 °C; *R*<sub>f</sub> 0.34 (ether); IR (CHCl<sub>3</sub>) 3600-3200, 3000, 2970, 2930, 1760, 1660, 1470, 1455, 1405, 1380, 1370, 1350, 1320, 1305, 1280, 1260, 1230, 1160, 1110, 1050, 1005 cm<sup>-1</sup>; NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  6.36 (d, 1 H, *J* = 1.75 Hz), 5.87 (d, 1 H, *J* = 1.75 Hz), 5.76-5.66 (m, 2 H), 4.96 (s, 1 H), 4.84-4.74 (m, 1 H), 3.78 (d, 1 H, *J* = 10.95 Hz), 3.43-3.35 (m, 1 H), 2.80 (br s, 1 H, OH), 2.60 (br s, 1 H, OH), 2.22 (d, 1 H, *J* = 11.4 Hz), 2.00-1.75 (m, 3 H), 1.12 (d, 3 H, *J* = 6.78 Hz), 1.09 (s, 3 H). Recrystallization from acetone-hexanes provided analytically pure **43**, mp 157-158 °C. Anal. Calcd for C<sub>15</sub>H<sub>20</sub>O<sub>4</sub>: C, 68.16; H, 7.63. Found: C, 68.09; H, 7.58.

***dl*-Helenalin (2)**. To a suspension of freshly prepared manganese dioxide (120 mg) in a mixture of dry methylene chloride (1.5 mL) and dry benzene (3.0 mL) was added 18 mg (0.040 mmol) of tricyclic alcohol **43**. After 2 h at room temperature, the mixture was diluted with 20 mL of ether and filtered. The solvent was removed under reduced pressure, and the residue was chromatographed on silica-AR-CC7. Elution with ether provided 12 mg (65%) of *dl*-helenalin as a crystalline compound: mp 223-226 °C; *R*<sub>f</sub> 0.51 (ether); IR (CHCl<sub>3</sub>) 3600, 3550-3200, 3020, 2975, 2940, 1765, 1710, 1660, 1580, 1460, 1380, 1360, 1340, 1320, 1200,

1275, 1210, 1160, 1110, 1050, 980, 945 cm<sup>-1</sup>; NMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  7.70 (dd, 1 H, *J* = 1.7, 6.0 Hz), 6.38 (d, 1 H, *J* = 3.1 Hz), 6.08 (dd, 1 H, *J* = 2.8, 5.9 Hz), 5.79 (d, 1 H, *J* = 3.1 Hz), 4.98 (td, 1 H, *J* = 8.9, 2.6 Hz), 4.46 (dd, 1 H, *J* = 1.7, 4.3 Hz), 3.56 (m, 1 H), 3.07 (dt, 1 H), 2.45 (d, 1 H, *J* = 4.3 Hz, OH), 2.28 (m, 1 H), 2.08 (m, 1 H), 1.80 (m, 1 H), 1.28 (d, 1 H, *J* = 7.5 Hz), 1.00 (s, 1 H). Recrystallization from acetone-hexane provided analytically pure *dl*-helenalin, mp 225-228 °C. Anal. Calcd for C<sub>15</sub>H<sub>18</sub>O<sub>4</sub>: C, 68.69; H, 6.92. Found: C, 68.60; H, 6.87.

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**Registry No.** **2**, 68330-47-2; **3**, 82041-93-8; **4**, 71748-37-3; **5**, 82043-27-4; **5** lactal, 71686-31-2; **5** (*E*)-enol ether derivative, 82010-13-7; **5** (*Z*)-enol ether derivative, 82043-28-5; **5** crude ketone derivative, 68241-51-0; **6**, 82043-29-6; **7**, 82043-30-9; **7** methyl ester, 82010-14-8; **8**, 68241-52-1; **9**, 71686-32-3; **10**, 71686-33-4; **10** mesylate, 82010-15-9; **10** THP, 68241-53-2; **10** THP alcohol, 82010-16-0; **10** THP mesylate, 82010-17-1; **10** hydroxy mesylate, 82010-18-2; **10** keto mesylate, 82010-19-3; **20**, 68241-54-3; **27**, 68241-55-4; **28**, 68306-73-0; **39**, 82010-20-6; **41**, 68257-98-7; **41** bis(THP), 68241-56-5; **41** hydroxy-methyl derivative bis(THP), 82010-21-7; **41** hydroxymethyl mesylate bis(THP), 82010-22-8; **42**, 82026-00-4; **43**, 68241-57-6; benzyl bromide, 100-39-0; (methoxymethylene)triphenylphosphorane, 20763-19-3.

## Communications to the Editor

### Mechanism of Arene Carbon-Hydrogen Bond Activation by [C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>Rh[P(CH<sub>3</sub>)<sub>3</sub>](H)(C<sub>6</sub>H<sub>5</sub>)]. Evidence for Arene Precoordination

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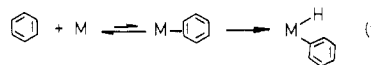
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The activation of unreactive carbon-hydrogen bonds is one of the most interesting yet elusive problems challenging chemists today. While significant advances in carbon-hydrogen bond activation by soluble transition-metal complexes have appeared in the literature over the past few years, the great majority of these reports involve oxidative addition of the metal to arene C-H bonds.<sup>1</sup> Homogeneous activation of alkane C-H bonds has also been observed by several workers recently.<sup>2</sup> In addressing the problem of C-H bond activation, we decided first to investigate in detail the nature of the activation process. While many types of activation mechanisms have been established in other metal systems (such as electrophilic attack<sup>3a</sup> or free radical<sup>3</sup>), we chose here to study exclusively activation by oxidative addition, where greater control of selectivity might be accomplished by varying

the properties of the metal complex.

The abundance of complexes that are capable of activating arenes but not alkanes is surprising in light of the difference in bond strengths involved (110 kcal/mol for benzene vs. ~95 kcal/mol for an alkane<sup>4</sup>) and suggests a kinetically higher reactivity for arenes. Parshall has proposed that arene coordination may precede oxidative addition of the C-H bond (eq 1), providing



an additional 5-10 kcal/mol of driving force through the  $T\Delta S^*$  term in the  $\Delta G^*$  for the oxidative addition,<sup>5</sup> although evidence for such an intermediate is lacking. This entropic contribution to  $\Delta G^*$  also manifests itself in the many examples of intramolecular alkyl and aryl C-H bond activation.<sup>1,6</sup> We report here chemical evidence for the intermediacy of an  $\eta^2$ -arene complex in the activation of aromatic C-H bonds involving the new rhodium complex [C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>Rh[P(CH<sub>3</sub>)<sub>3</sub>](H)(C<sub>6</sub>H<sub>5</sub>)].

Treatment of a 0.05 M THF solution of [C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>RhCl<sub>2</sub>[P(CH<sub>3</sub>)<sub>3</sub>]] with 1 equiv of 0.54 M (*p*-C<sub>6</sub>H<sub>4</sub>X)MgBr in THF at -40 °C results in the formation of [C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>RhBr[P(CH<sub>3</sub>)<sub>3</sub>](C<sub>6</sub>H<sub>4</sub>X)] in high yield (**1**, X = H; **2**, X = CH<sub>3</sub>).<sup>7</sup> Preparative chroma-

(4) Benson, S. W. "Thermochemical Kinetics"; Wiley, New York, 1968; p 309.

(5) If for the intramolecular oxidative addition  $\Delta S^*_{\text{intra}} \approx -5$  eu (small and negative) and for the intermolecular oxidative addition  $\Delta S^*_{\text{inter}} \approx -30$  eu and  $\Delta H^*_{\text{inter}} \approx \Delta H^*_{\text{intra}}$ , then  $\Delta\Delta G^* = \Delta G^*_{\text{intra}} - \Delta G^*_{\text{inter}} = T(\Delta S^*_{\text{inter}} - \Delta S^*_{\text{intra}}) = -7.5$  kcal/mol. See also: Ibers, J. A.; DiCosmo, R.; Whitesides, G. M. *Organometallics* **1982**, *1*, 13-20.

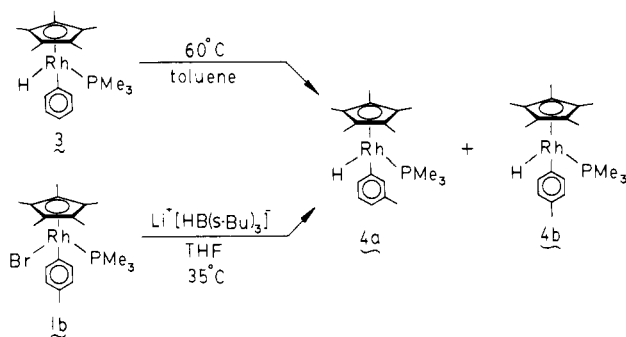
(6) See, for example: Cheney, A. J.; Mann, B. E.; Shaw, B. L.; Slade, R. M. *J. Chem. Soc. A* **1971**, 3833-3842. Masters, C. J. *Chem. Soc., Chem. Commun.* **1973**, 191-192. Laine, R. M.; Thomas, D. W.; Cary, L. W.; Buttrill, S. E. *J. Am. Chem. Soc.* **1978**, *100*, 6527-6528. Tulip, T. H.; Thorn, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 2448-2450. Moore, S. S.; DiCosmo, R.; Sowinski, A. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 948-949.

(1) (a) Parshall, G. W. *Acc. Chem. Res.* **1970**, *3*, 139-144. (b) Parshall, G. W. *Chem. Tech.* **1974**, *4*, 445-447. (c) Parshall, G. W. *Acc. Chem. Res.* **1975**, *4*, 113-117. (d) Halpern, J. *Discuss. Faraday Soc.* **1968**, *46*, 7-19. (e) Shilov, A. E.; Shteinman, A. A. *Coord. Chem. Rev.* **1977**, *24*, 97-143.

(2) Crabtree, R. H.; Melea, J. F.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 107-113. Baudry, D.; Ephritikhine, M.; Felkin, H. *J. Chem. Soc., Chem. Commun.* **1980**, 1243-1244. Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352-354.

(3) (a) For a representative overview of electrophilic-metal reactions, see: Parshall, G. W. "Homogeneous Catalysis"; Wiley: New York, 1980. (b) Sofranko, J. A.; Eisenberg, R.; Kampmeier, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 1163-1165.

## Scheme I



tography on silica gel using  $\text{CH}_2\text{Cl}_2$  and recrystallization from hexane afford the pure product as orange crystals in 85% yield. The  $^1\text{H}$  NMR of **1** and **2** both show complex patterns in the  $\delta$  6.5–8.0 region in addition to the  $\text{C}_5(\text{CH}_3)_5$  singlet and  $\text{P}(\text{CH}_3)_3$  doublet. Variable-temperature NMR experiments indicate restricted rotation about the rhodium–aryl bond, presumably due to steric interactions of the ortho hydrogens. The widely separated low-field resonances of **1** and **2** are assigned to the ortho-phenyl hydrogens on this basis.

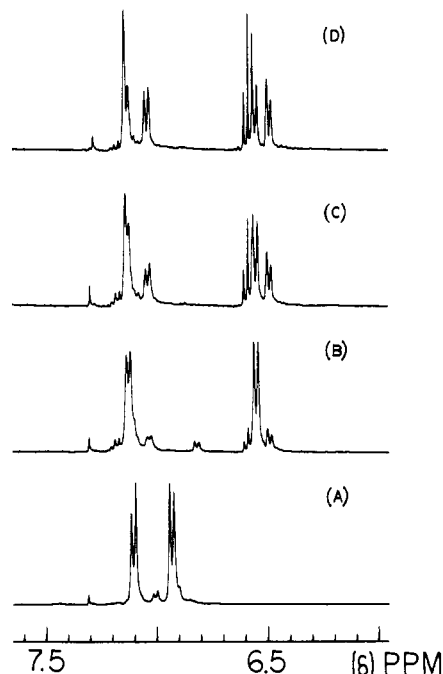
**1** can be converted to the highly air-sensitive hydride  $[\text{C}_5(\text{C}_6\text{H}_5)_5]\text{Rh}[\text{P}(\text{CH}_3)_3](\text{H})(\text{C}_6\text{H}_5)$  (**3**) by gentle heating of a concentrated solution of **1** and  $\text{Li}^+[\text{HB}(\text{s-Bu})_3]^-$  in THF followed by quick filtration of the solution through silica gel and removal of solvent.  $^1\text{H}$  NMR characterization of **3** ( $\text{C}_6\text{D}_6$ ) shows signals attributable to  $\text{C}_5(\text{CH}_3)_5$  ( $\delta$  1.79, d,  $J = 1.4$  Hz, 15 H),  $\text{P}(\text{CH}_3)_3$  ( $\delta$  0.90, dd,  $J = 9.8, 0.8$  Hz, 9 H), Rh–H ( $\delta$  –13.50, dd,  $J = 49.5, 32.8$  Hz, 1 H), and Rh( $\text{C}_6\text{H}_5$ ) ( $\delta$  7.64, d,  $J = 7.1$  Hz, 2  $\text{H}_{\text{ortho}}$ ;  $\delta$  7.10, m, 3  $\text{H}_{\text{meta+para}}$ ). As a solution of **3** is heated at 60 °C for 16 h in 100.0%  $\text{C}_6\text{D}_6$ , the resonances at  $\delta$  –13.50 (hydride) and  $\delta$  7.1–7.7 (phenyl) disappear as a new singlet at  $\delta$  7.15 appears, while the resonances at  $\delta$  1.79 and 0.90 remain unchanged. Analysis of the volatiles from the reaction by mass spectroscopy (5 eV) shows only peaks at  $m/e$  78 ( $\text{C}_6\text{H}_6$ ) and 79 ( $\text{C}_6\text{H}_5\text{D}$ , 14% of  $m/e$  78)<sup>8</sup> as well as the large peaks at  $m/e$  83 and 84 found in the pure solvent. When the nonvolatile organometallic product from this reaction is returned to  $\text{C}_6\text{H}_6$  solution, the solution heated at 60 °C for 16 h, the volatiles removed, and an NMR spectrum ( $\text{C}_6\text{D}_6$ ) of the product recorded, only the resonances attributable to **3** are observed. These observations can be explained in terms of a reversible intermolecular aromatic C–H bond-activation process involving oxidative addition and reductive elimination of the arene C–H bond. The half-life for arene exchange at 60 °C is about 4 h.

Heating a toluene solution of **3** at 60 °C for 16 h produces a 2:1 mixture of two compounds assigned structures **4a** and **4b**, in which the meta- and para-tolyl positions have been metalated.<sup>9</sup> This same mixture of compounds is produced upon treatment of **2** with  $\text{Li}^+[\text{HB}(\text{s-Bu})_3]^-$  in THF solution, followed by gentle

(7) **1**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , –35 °C)  $\delta$  1.41 (d,  $J = 10.3$  Hz, 9 H), 1.63 (d,  $J = 2.7$  Hz, 15 H), 6.95 (m, 3 H), 7.09 (d,  $J = 6.6$  Hz, 1 H), 7.96 (d,  $J = 7.3$  Hz, 1 H); mass spectrum (75 eV),  $m/e$  470/472 (Br isotope). Anal. ( $\text{C}_{19}\text{H}_{29}\text{BrPRh}$ ) C, H. **2**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , –55 °C)  $\delta$  1.63 (s, 15 H), 1.41 (d,  $J = 10.3$  Hz, 9 H), 2.25 (s, 3 H), 6.80 (d,  $J = 7.6$  Hz, 1 H), 6.84 (d,  $J = 7.9$  Hz, 1 H), 6.96 (d,  $J = 7.6$  Hz, 1 H), 7.81 (d,  $J = 7.9$  Hz, 1 H); mass spectrum (75 eV),  $m/e$  484/486. Anal. ( $\text{C}_{20}\text{H}_{31}\text{BrPRh}$ ) C, H.

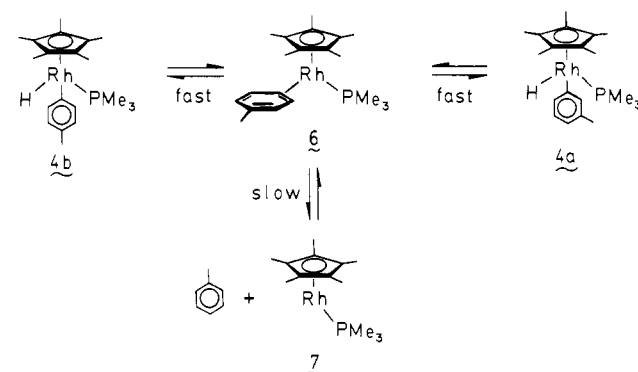
(8) No peaks were observed at  $m/e$  80, 81, or 82. The peak at  $m/e$  79 corresponds to a 93:7 mixture of  $\text{C}_6\text{H}_6/\text{C}_6\text{H}_5\text{D}$  after correction for natural abundance of  $^{13}\text{C}$ . The elimination is highly intramolecular.

(9) The tolyl resonances of **4a** and **4b** are fully resolved in  $\text{C}_6\text{D}_6$ , but not in THF- $d_6$ . **4a**:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  –13.52 (dd,  $J = 49.1, 33.7$  Hz, 1 H), 0.92 (d,  $J = 9.8$  Hz, 9 H), 1.81 (d,  $J = 1.3$  Hz, 15 H), 2.33 (s, 3 H), 6.91 (d,  $J = 7.2$  Hz, 1 H), 7.07 (t,  $J = 7.4$  Hz, 1 H), 7.43 (d,  $J = 7.3$  Hz, 1 H), 7.55 (s, 1 H). **4a**:  $^1\text{H}$  NMR (THF- $d_6$ )  $\delta$  –13.93 (dd,  $J = 49.5, 32.9$  Hz, 1 H), 1.14 (d,  $J = 9.8$  Hz, 9 H), 1.76 (d,  $J = 1.2$  Hz, 15 H), 2.08 (s, 3 H), 6.47 (d,  $J = 7.3$  Hz, 1 H), 6.56 (t,  $J = 7.5$  Hz, 1 H), 7.02 (d,  $J = 7.3$  Hz, 1 H), 7.12 (s, 1 H). **4b**:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  –13.52 (dd,  $J = 49.1, 33.7$  Hz, 1 H), 0.92 (d,  $J = 9.8$  Hz, 9 H), 1.81 (d,  $J = 1.3$  Hz, 15 H), 2.30 (s, 3 H), 6.99 (d,  $J = 7.5$  Hz, 2 H), 7.55 (br s, 2 H). **4b**:  $^1\text{H}$  NMR (THF- $d_6$ )  $\delta$  –13.93 (dd,  $J = 49.5, 32.9$  Hz, 1 H), 1.14 (d,  $J = 9.8$  Hz, 9 H), 1.76 (d,  $J = 1.2$  Hz, 15 H), 1.96 (s, 3 H), 6.53 (d,  $J = 8.8$  Hz, 2 H),  $\delta$  7.10 (s, 2 H).



**Figure 1.**  $^1\text{H}$  NMR spectra of  $[\text{C}_5(\text{CH}_3)_5]\text{Rh}[\text{P}(\text{CH}_3)_3](\text{H})(p\text{-C}_6\text{H}_4\text{CH}_3)\text{Br}$  in THF- $d_6$ : (A) after treatment with  $\text{AgPF}_6$  at –40 °C; (B) after addition of 1 equiv of  $\text{Li}^+[\text{HB}(\text{s-Bu})_3]^-$  at –25 °C; (C) after 35 min at –10 °C; (D) after 110 min at +25 °C.

## Scheme II



warming (<35 °C).<sup>10</sup> Apparently, the tolyl ligand in the initially formed product **4b** isomerizes to give **4a** under conditions that are less severe than those required for toluene exchange with external arene (Scheme I). The tolyl compounds **4a** and **4b** only exchange with  $\text{C}_6\text{H}_6$  above 60 °C.<sup>11</sup>

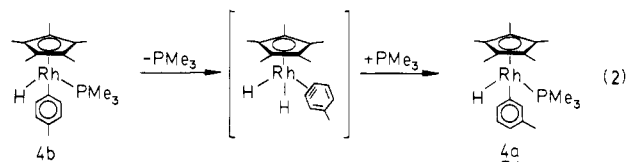
For proof that **4b** was being formed initially and then isomerizing to **4a**, a solution of **2** in THF- $d_6$  (0.08 M) was treated with 1 equiv of  $\text{AgPF}_6$  at 25 °C and filtered through a cotton plug to remove  $\text{AgBr}$ . An NMR spectrum recorded at –40 °C showed a  $\text{C}_5(\text{CH}_3)_5$  doublet at  $\delta$  1.56 ( $J = 2.5$  Hz, 15 H), a  $\text{P}(\text{CH}_3)_3$  doublet at  $\delta$  1.48 ( $J = 10.4$  Hz, 9 H), a methyl singlet at  $\delta$  2.23 (3 H), and two tolyl resonances at  $\delta$  6.93 (d,  $J = 7.9$  Hz, 2 H) and 7.11 (d,  $J = 7.9$  Hz, 2 H). The compound is stable for hours in THF solution, but attempts to isolate the material by removal of solvent under vacuum result in decomposition. On the basis of the NMR spectrum and the chemical reactivity of the complex (vide infra), we believe this compound to be the THF adduct

(10) On several occasions, the hydride exchange occurred at lower temperatures as denoted by a change in the color of the solution from orange to straw yellow. The erratic substitution behavior and the observation of an induction period of variable length suggests a free-radical hydride-exchange mechanism.

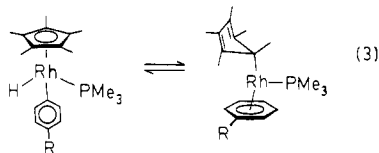
(11) Solvent effects do not appear to be important in the arene exchange reaction. If  $[\text{C}_5(\text{CH}_3)_5]\text{Rh}[\text{P}(\text{CH}_3)_3](\text{H})(\text{C}_6\text{H}_4\text{CH}_3)$  is dissolved in 25%  $\text{C}_6\text{D}_6/75\%$  THF- $d_6$ , arene exchange is still not observed below 60 °C.

$[(C_5(CH_3)_5)Rh(p-C_6H_4CH_3)(THF-d_8)[P(CH_3)_3]]^+$  (**5**). Treatment of this solution of **5** with 1 equiv of  $Li^+[HB(s-Bu)_3]^-$  at  $-40^\circ C$  followed by warming to  $-25^\circ C$  in the probe of an NMR spectrometer showed  $\sim 90\%$  conversion to the hydrido derivative **4b**. The interconversion of **4b** to **4a** was observed upon warming the solution to  $-10^\circ C$ , giving an equilibrium **4a/4b** ratio of 2:1 (Figure 1).

The above experiments indicate that facile interchange of the site of attachment of the aromatic ligand to the metal occurs at  $-10^\circ C$  without dissociation of the arene. The most plausible mechanism for this isomerization involves a reductive elimination process to form **6** in which the arene remains coordinated to the metal in an  $\eta^2$  fashion (Scheme II). An alternative mechanism, involving phosphine dissociation and formation of a dihydrido-benzene complex (eq 2), could also explain the observed isom-



erization of **4a** and **4b** at  $-10^\circ C$ .<sup>12</sup> However, no phosphine exchange is observed upon treatment of **3** with  $P(CD_3)_3$  in  $C_6D_6$  after 1 h at  $25^\circ C$ , thereby ruling out this possibility. Another possible mechanism would involve shifting the  $C_5(CH_3)_5$  ring from  $\eta^5$  to  $\eta^1$  coordination while forming an  $\eta^6$ -arene complex (eq 3).



This variation in cyclopentadienyl coordination has been postulated<sup>13</sup> and observed<sup>14</sup> by others in intermolecular reactions of ligands with cyclopentadienyl complexes. However, when  $[(C_5(CH_3)_5)Rh[P(CH_3)_3](H)(C_6D_5)]$  is prepared at  $-20^\circ C$  in  $THF-d_8$  and then allowed to warm to  $-10^\circ C$ , the aromatic region of the  $^1H$  NMR shows rapid growth of a singlet at  $\delta$  7.27 ( $H_{ortho}$ ) followed by singlets at  $\delta$  6.70 ( $H_{meta}$ ) and 6.67 ( $H_{para}$ ). These observations clearly rule out an  $\eta^6$ -arene intermediate<sup>15</sup> and offer strong support for the  $\eta^2$ -arene sequence shown in Scheme II.

The observation of intermolecular arene exchange only above  $60^\circ C$  indicates that arene dissociation from the metal to form the coordinatively unsaturated complex  $[C_5(CH_3)_5)Rh[P(CH_3)_3]]$  (**7**) is a kinetically unfavorable process with respect to the oxidative addition and reductive elimination to arene C-H bonds. The only other report of arene precoordination followed by intramolecular C-H activation involves the complex  $(\eta^6-C_6H_6)Os(C_2H_4)[P(CH_3)_3]$ , in which arene dissociation is quite unfavorable.<sup>16</sup>

In order to evaluate the barrier to arene coordination in the reaction of **7** with benzene, a solution of  $[C_5(CH_3)_5)Rh[P(CH_3)_3](H)_2]$  (**17**) in  $C_6D_6$  was irradiated at  $25^\circ C$  with a medium-pressure Hg lamp.  $^1H$  NMR spectra showed the disappearance of the dihydride and the appearance of resonances at  $\delta$  1.79 (d,  $J = 1.4$  Hz, 15 H) and 0.90 (d,  $J = 9.8$  Hz, 9 H) attributable to  $[C_5(CH_3)_5)Rh[P(CH_3)_3](D)(C_6D_5)]$ , indicating a low barrier for arene coordination to **7**.

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(15) Alternatively, an  $[\eta^3-C_5(CH_3)_5)Rh[P(CH_3)_3](\eta^4-C_6H_5D)]$  complex could be postulated as an intermediate. However, the rapid initial formation of the ortho-H phenyl- $d_4$  species rules out this mechanism also.

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In conclusion, facile oxidative addition and reductive elimination of arene C-H bonds occurs in these permethylcyclopentadienyl rhodium complexes at or below room temperature, while dissociation of an  $\eta^2$ -bound arene requires heating to  $60^\circ C$ . The coordinatively unsaturated intermediate **7**, on the other hand, reacts rapidly with arene C-H bonds to produce aryl hydrides, indicating that arene coordination plays an important role in the oxidative-addition reaction. Studies are underway to elucidate the importance of this coordination in arene activation and its relevance to alkane activation.

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**Registry No.** **1**, 81971-44-0; **2**, 81971-45-1; **3**, 81971-46-2; **4a**, 81971-47-3; **4b**, 81971-48-4; **5**, 81971-49-5;  $[C_5(CH_3)_5)RhCl_2[P(CH_3)_3]$ , 80298-79-9.

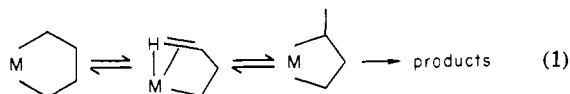
## Metallacyclobutane to Metallacyclopentane Ring-Expansion Reactions

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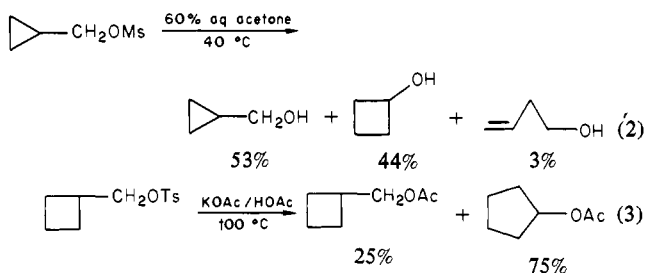
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Although there is much interest in metallacycles  $M(CH_2)_n$  due to their proposed roles as intermediates in transition-metal-catalyzed reactions, few examples of interconversion between metallacycles of order  $n$  and  $n + 1$  are known.<sup>1,2</sup> Schrock has proposed that short-lived tantalacyclobutane intermediates are formed from tantalacyclopentanes during some catalytic alkene dimerization reactions (eq 1),<sup>1</sup> but the reverse reaction, which should be favored thermodynamically,<sup>2,3</sup> has not been observed.<sup>4</sup>



We report the first examples of metallacyclopentane to metallacyclobutane ring-expansion reactions in which both starting materials and products are isolable crystalline solids. Our approach was based on analogy with the solvolysis of cyclopropylmethyl or cyclobutylmethyl esters which occurs with at least partial rearrangement to cyclobutyl or cyclopentyl derivatives, respectively<sup>5-7</sup> (eq 2 and 3, OMs = mesylate, OTs = tosylate).



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