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Directly Observed Transmetalation from Boron to Rhodium. β-Aryl Elimination from Rh(I) Arylboronates and Diarylborinates

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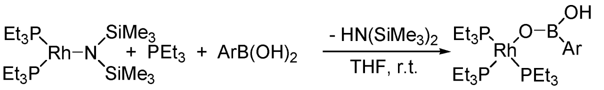
Transmetalation from organoboron compounds to late transition metal complexes is now a common route to catalytically active metal−hydrocarbyl intermediates.[1] Despite the importance of this transformation, details of its mechanism remain largely unknown.[2] A few groups have reported stoichiometric studies of reactions between arylboronic acids and organometallic complexes to generate metal aryl species.[3] However, the process by which the aryl group is transferred from boron to the metal is not well defined. Reactions of metal hydroxo complexes with boronic acids and reactions of hypervalent boronates have both been proposed. Reactions of hypervalent boron species have been studied by computational methods.[3c,4,5]

We report the isolation of a series of rhodium arylboronate and diarylborinate complexes that undergo intramolecular transfer of the aryl group from boron to rhodium by a β-aryl elimination pathway.[6] These studies uncover a new pathway to consider for the mechanism of transmetalation in several catalytic processes.

Triethylphosphine-ligated rhodium boronate complexes were prepared by treating the Rh(I) silylamido precursor $\{(PEt_3)_2Rh[N(SiMe_3)_2]\}$[7] (**1**) with arylboronic acids **2a**−**e** and added PEt_3 at room temperature (eq 1).



(1)

1

2a	Ar = Ph	**3a**	75%
2b	*p*-tolyl	**3b**	76%
2c	*p*-anisyl	**3c**	67%
2d	4-$CF_3C_6H_4$	**3d**	45%
2e*	*o*-anisyl	**3e***	

*unable to isolate due to low stability.

The proton exchange occurred smoothly to eliminate $HN(SiMe_3)_2$ and form the rhodium boronate complexes **3a**−**e**. The para-substituted aryl derivatives **3a**−**d** were stable enough to be obtained as crystalline solids in 45−76% isolated yields and were fully characterized. The *o*-anisyl derivative **3e** was unstable at room temperature, but it formed in quantitative yield at lower temperatures and was characterized in solution by NMR spectroscopic methods.

The structure of boronate complex **3b** was determined by X-ray diffraction (Figure 1). In the solid state, **3b** adopts a distorted square-planar geometry with P−Rh−O(1) angles of 80.21(5), 87.37(5), and 175.24(5)° for P(1), P(2), and P(3), respectively. The O(1−2)−B(1)−C(19−25) plane lies approximately perpendicular to the rhodium coordination plane, and the dihedral angle between these two planes is 83.4°. The Rh−O distance (2.102(2) Å) is slightly longer than those in Rh(I) alkoxides (2.05−2.07 Å)[8] but is very close to the Pt−O distance (2.09 Å) in a related Pt(II) boronate.[9]

Complexes **3a**−**e** underwent β-aryl elimination reactions at ambient temperatures to afford the corresponding rhodium aryl complexes **4a**−**e**. These reactions occurred over the course of 0.5−1 h in the absence of added ligand. The rhodium−aryl complexes were formed in 74−95% yield, as determined by ^1H NMR spectroscopy (eq 2). The boron product precipitated from solution and was insoluble in common solvents, but is likely to be boroxin oligomers $\{[O{=}B(OH)]_n\}$.[10] The closest transformations to the β-aryl eliminations are the reactions of a palladium siloxide complex[11] and reaction of a Pt(II) arylboronate with boronic acid and silver oxide.[9] In contrast to complexes **3a**−**e**, the platinum boronates were stable in the absence of additives.

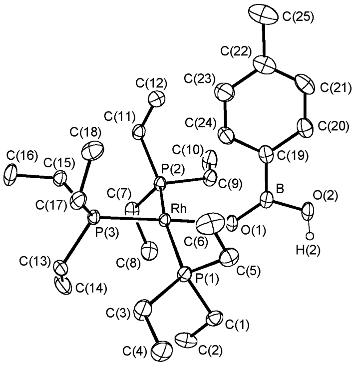
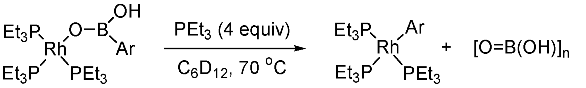


Figure 1. ORTEP diagram of $\{Rh(PEt_3)_3[OB(OH)(p\text{-tolyl})]\}$ (**3b**). Most hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Rh−O(1) = 2.102(2), O(1)−B = 1.330(3), B−C(19) = 1.593(4), B−O(2) = 1.382(3), Rh−P(1) = 2.336(1), Rh−P(2) = 2.324(1), Rh−P(3) = 2.204(1), P(1)−Rh−P(3) = 95.96(2), P(2)−Rh−P(3) = 96.97(2), O(1)−Rh−P(1) = 80.21(5), O(1)−Rh−P(2) = 87.37(5), Rh−O(1)-B = 134.3(2), O(1)−B−C(19) = 125.3(2), O(1)−B−O(2) = 121.3(3).



(2)

		$t_{1/2}$	yield	
3a	Ar = Ph	900 s	**4a**	78%
3b	*p*-tolyl	1400 s	**4b**	84%
3c	*p*-anisyl	1400 s	**4c**	74%
3d	4-$CF_3C_6H_4$	500 s	**4d**	82%
3e*	*o*-anisyl	<30 s	**4e**	>95%

*generated *in situ* (see supporting information).

A moderate electronic effect was observed for the rate of aryl group migration. The derivatives containing electron-donating groups (**3b**, **3c**) reacted slightly more slowly than those containing electron withdrawing groups (**3d**). However, the ortho-substituted, electron-rich **3e** reacted much faster than the other members of the series. These migratory aptitudes, including the fast rate for migration of the *o*-anisyl group, are comparable to those for β-aryl eliminations from isoelectronic PEt_3-ligated Rh(I) iminyl complexes.[12]

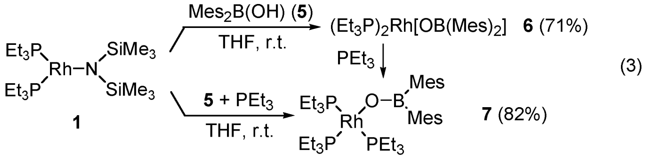
The mechanism of the β-aryl elimination from *p*-tolyl derivative **3b** in the presence of added PEt_3 was investigated by kinetic methods. Rate constants were measured by ^1H NMR spectroscopy for reactions at 70 °C containing an initial 0.014 M concentration of **3b** in cyclohexane. Reactions were conducted with concentrations of added PEt_3 varying from 0.014 to 0.112 M. A clear exponential decay of **3b** indicated that the reaction was first-order in rhodium. A plot of $1/k_{obs}$ versus $[PEt_3]$ (Figure S2 in Supporting Information)

10.1021/ja068587q CCC: $37.00

showed that the reaction was inverse first-order in added PEt$_3$. These results are most consistent with a pathway that occurs by reversible dissociation of PEt$_3$ to form a 14-electron intermediate, followed by β-aryl elimination to cleave the C−B bond. This mechanism would be analogous to that for β-aryl elimination to cleave the C−N and C−O bond in Rh(I) iminyl and alkoxo complexes reported recently.[8a,12] This mechanism would also parallel the classic one for β-hydrogen elimination from square-planar alkoxo complexes.[13]

The silylamido Rh(I) precursor **1** also underwent reaction with the diarylborinic acid (2-mesityl)$_2$B(OH) (**5**) to afford the corresponding bis(phospine) Rh(I) borinate complex, [(PEt$_3$)$_2$Rh[OB(Mes)$_2$] (**6**) in 71% isolated yield (eq 3).[14] This complex is unstable in solution but reacted with 1 equiv of added PEt$_3$ to quantitatively form a more stable, tris(phospine) Rh(I) borinate complex [(PEt$_3$)$_3$Rh[OB(Mes)$_2$] (**7**). Complex **7** was also prepared directly from silylamide **1** and boronic acid **5** in the presence of added PEt$_3$ in 82% isolated yield.

Heating of rhodium borinate **7** in cyclohexane at 80 °C led to β-aryl elimination. The corresponding [(PEt$_3$)$_3$Rh(Mes)] (**8**) and cyclic boroxin {[O═B(Mes)]$_3$}[15] (**9**) were formed in 87% and 91% yields after 4 h (eq 4). Reactions in the presence of 2 equiv of added PEt$_3$ were much slower, and at higher temperatures the mesitylrhodium product was unstable. Thus, quantitative rate studies were not conducted, but these qualitative data suggest that this reaction also occurs by initial, reversible dissociation of PEt$_3$.



$$(Et_3P)_3Rh[OB(Mes)_2] + PEt_3 \xrightarrow[80\ ^{\circ}C]{C_6D_{12}} (Et_3P)_3Rh(Mes) + [O{=}B(Mes)]_3 \qquad (4)$$

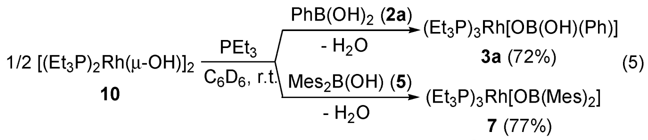
7			**8**	**9**
	0 equiv	4 h	87%	91%
	2 equiv	>12 h	<35%	<53%

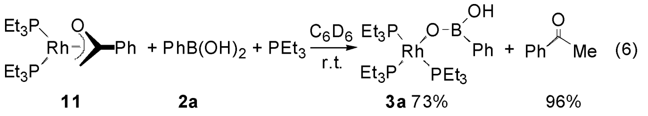
The transmetalation from boron to rhodium is a likely step in the catalytic asymmetric Michael additions of arylboronic acids.[1b,c] These catalytic processes are thought to occur by reaction of the product enolate with water to form a rhodium hydroxide complex, followed by transmetalation between the rhodium hydroxide and the boronic acid.[3b] To test the competence of rhodium boronates as intermediates in the transmetalation step, we monitored reactions of the boronic acid with rhodium hydroxide and enolate complexes.

Treatment of the hydroxorhodium complex [(PEt$_3$)$_2$Rh(μ-OH)]$_2$ (**10**)[16] with boronic acid **2a** and borinic acid **5** in the presence of added PEt$_3$ at room temperature eliminated H$_2$O (observed by ^{1}H NMR spectroscopy) and formed rhodium boronate and borinate complexes **3a** and **7**, respectively, in good yields (eq 5). Under these conditions, there was no detectable hypervalent boron species, such as {(PEt$_3$)$_3$Rh[B(Ph)(OH)$_3$]} or {(PEt$_3$)$_3$Rh[B(Mes)$_2$(OH)$_2$]}. This observation implies that metal-boronates can be intermediates in the transmetalation of aryl groups to replace hydroxo ligands on late metals.

In addition, boronic acid **2a** reacted with the PEt$_3$-ligated rhodium enolate **11**[17] shown in eq 6, in the presence of added PEt$_3$ to form the same boronate **3a**. These data imply that the transmetalation can occur directly with the enolate complex without the intermediacy of the hydroxo complex.

In summary, we have isolated a series of tris(phosphine) rhodium(I) arylboronate and diarylborinate complexes that allow direct observation of intramolecular transmetalation from boron to rhodium under mild conditions and without the participation of added activators. Kinetic studies are most consistent with β-aryl elimination from 14-electron boronate and borinate intermediates. This process appears competent to be a step in rhodium-catalyzed chemistry of boronic acids and should be considered as a possible pathway for transmetalation from boron to other late metals. Studies of transmetalation from boron to palladium by this pathway are ongoing.





Acknowledgment. Financial support for this work was provided by NIH (NIGMS Grant GM-58108).

Supporting Information Available: Experimental procedures, spectral data, and structural data (**3b**) (CIF and PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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JA068587Q