C–H Bond Activation

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C–H Bond Activation by Rhodium(I) Hydroxide and Phenoxide Complexes**

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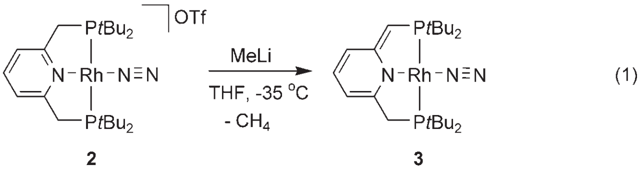
Catalysts for selective hydrocarbon oxidation are crucial to more efficient utilization of our hydrocarbon resources. In recent years, a substantial number of metal complexes capable of the selective activation of C–H bonds under mild conditions have been discovered.[1] In spite of these advances, practical catalysts for C–H bond functionalization remain elusive, owing in part to the fact that the C–H bond activation reaction is often inhibited by water or by the alcohol product eliminated from the metal complex, particularly for low-valent late-metal complexes.[1a,2] In this context, a desirable reaction would be the addition of a C–H bond across a metal alkoxide or hydroxide complex, releasing an alcohol and generating a new metal–carbon bond in one step. In 2005, the first examples of this reaction class were reported by the groups of Periana and Gunnoe, who documented the C–H bond activation of arenes by iridium(III) methoxide and ruthenium(II) hydroxide complexes, respectively.[3] These reactions begin with saturated 18-electron metal complexes, and are proposed to proceed by ancillary ligand dissociation and subsequent σ-bond metathesis for the arene activation step.[4] In this contribution, we report arene activation by rhodium(I) hydroxide, trifluoroethoxide, and aryloxide complexes bearing a PNP pincer ligand (PNP = 2,6-bis[(di-*tert*-butylphosphino)methyl]pyridine). A similar σ-bond metathesis pathway for the C–H bond activation may also be involved in these reactions. However, in contrast to the previously reported systems, the open site for arene interaction is readily available in these rhodium(I) 16-electron complexes and ancillary ligand dissociation is not required. The results reported herein not only increase the generality of the novel mode of C–H bond activation but also provide new opportunities for the development of more active systems.

The rhodium(I) triflate complex [(PNP)Rh(OTf)] (**1**) was prepared by the reaction of [{Rh(coe)$_2$Cl}$_2$] (coe = cyclooctene) with silver triflate, filtration, and addition of the PNP ligand. This complex was characterized by NMR spectroscopy and elemental analysis. The triflate ligand in **1** is bound quite weakly; in the presence of nitrogen, an equilibrium between **1** and the monomeric dinitrogen complex [(PNP)Rh(N$_2$)]OTf (**2**) was observed. Complex **2** has been characterized by NMR and IR spectroscopy, and elemental analysis.

Despite the lability of the triflate ligand, the corresponding Rh^{I} alkyl and alkoxide complexes cannot be easily prepared by salt metathesis; the CH$_2$ groups on the PNP ligand of **2** are deprotonated by strong bases (MeLi, KO*t*Bu), generating the neutral dinitrogen complex [(PN^{-}P)Rh(N$_2$)] (**3**) [Eq. (1)].



(1)

Complex **3** was characterized by NMR spectroscopy and elemental analysis, and displays a characteristic AB pattern of doublets in the ^{31}P NMR spectrum, indicating inequivalent phosphorus atoms. The IR spectrum of **3** shows an N–N stretch at 2122 cm^{-1}, slightly shifted from the N–N stretch of **2** (2153 cm^{-1}), thus consistent with a greater degree of back-bonding to the nitrogen ligand in the neutral compound **3**. Similar deprotonation reactions of the methylene positions in pincer ligands on Pd, Pt, Ir, and Ru centers have previously been reported.[5,6]

Use of the milder alkylating reagent ZnMe$_2$ avoids the problem of deprotonation of the ligand backbone; the rhodium(I) methyl complex [(PNP)Rh(CH$_3$)] (**4**) was efficiently prepared by the reaction of **1** or **2** with ZnMe$_2$. The initial product of this reaction was a rhodium–zinc adduct, formulated as [(PNP)Rh(CH$_3$)Zn(CH$_3$)]OTf based on NMR spectroscopy and elemental analysis. Addition of one equivalent of 2,2′-bipyridyl (bipy) to a dark yellow solution of the rhodium–zinc adduct resulted in an immediate color change to dark pink and release of **4**, as shown in Scheme 1. Complex **4** was isolated by extraction with pentane.[7]

The isolation of [(PNP)Rh(CH$_3$)] (**4**) provided a viable synthetic route to the previously unavailable hydroxide and alkoxide complexes. Reaction of **4** with water or the appropriate alcohol in THF at room temperature generated the rhodium(I) hydroxide, trifluoroethoxide, and phenoxide complexes [(PNP)Rh(OR)] (R = H (**5**), CH$_2$CF$_3$ (**6**), C$_6$H$_5$ (**7**); Scheme 1). Complexes **5**, **6**, and **7** were characterized by NMR spectroscopy and elemental analysis.[7]

The thermal reactivity of the {(PNP)Rh} complexes **4**–**7** was investigated. When **4** was heated (80 °C) in [D$_6$]benzene,

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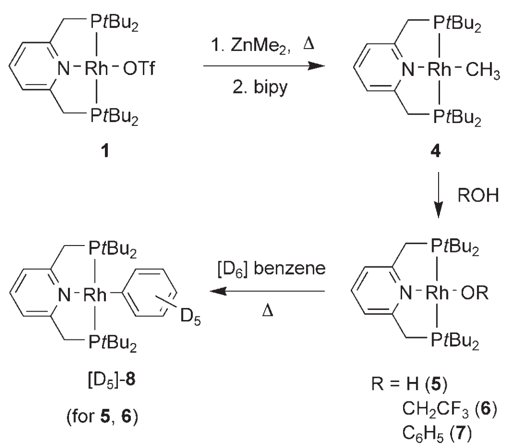
Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.



Scheme 1. Synthesis of complexes **4**–**7**.

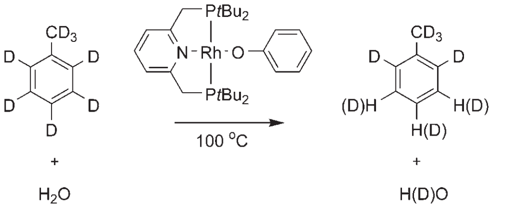
the deuterated phenyl complex $[(PNP)Rh(C_6D_5)]$ ($[D_5]$-**8**) was produced in 95% yield. Complex **8** was independently prepared from **1** and $ZnPh_2$, and characterized by NMR spectroscopy and elemental analysis.[7] Remarkably, the other product of the thermolysis reaction was not CH_3D but rather CH_4. This result led us to consider the possibility of contamination of the reaction by adventitious water. Consistent with this proposal, we found that simply dissolving **4** in $[D_6]$benzene saturated with H_2O (approximately 1–2 equiv) *at room temperature* resulted in the formation of both the hydroxide complex **5** (21%) and the phenyl complex $[D_5]$-**8** (73%). In the absence of water, no reaction occurred between complex **4** and $[D_6]$benzene at room temperature. Thus, water appears to play an important role in the C–H activation reaction involving the Rh^I methyl complex, suggesting the Rh^I hydroxide **5** might be an active species for benzene activation.

Heating a sample of isolated $[(PNP)Rh(OH)]$ in $[D_6]$benzene at 60 °C for 95 h resulted in formation of the deuterated phenyl complex $[(PNP)Rh(C_6D_5)]$ ($[D_5]$-**8**) in 60% yield (Scheme 1). An intractable yellow solid precipitate was also formed during the reaction; the identity of this material remains unclear. At 25 °C, no reaction occurred between **8** and 1.6 equivalents of H_2O in $[D_6]$benzene solution. Similarly, heating a solution of trifluoroethoxide complex **6** in $[D_6]$benzene at 100 °C for 158 h resulted in partial conversion into the deuterated phenyl complex $[D_5]$-**8** (40%), with unreacted **6** also present (40%). This reaction was accompanied by some decomposition in the form of a solid precipitate. Prolonged reaction led to increased decomposition with no increase in the yield of **8**.

In the reactions of **5** and **6** in $[D_6]$benzene, partial deuterium incorporation (40–60%) into the methylene bridges of the PNP ligand on the product $[D_5]$-**8** was observed. Efficient deuterium exchange into the methylene positions of **8** was subsequently demonstrated through a control experiment in which reaction of the phenyl complex **8** with D_2O (10 equiv) in C_6H_6 resulted in deuterium incorporation (approximately 75%) into the methylene groups over the course of 24 h *at room temperature*, as determined by ^2H and ^1H NMR spectroscopy. Thus, the deuterium incorporation into the methylene positions can be most directly explained by proton/deuterium exchange with the deuterated water or alcohol product of the reaction. The protons at these positions have already been observed to be acidic (see above). It is of interest that for the analogous $[(PNP)IrPh]$ complex, deuteration of the methylene groups on the PNP ligand with the addition of D_2 was proposed to result from the proton transfer from the methylene position to the metal center with formation of Ir^{III} and subsequent D_2 activation at the Ir^{III} center.[6] A related mechanism for the Rh system cannot be excluded, although C–D activation of $[D_6]$benzene by Rh^{III} seems unlikely.

Unlike the hydroxide and trifluoroethoxide complexes, phenoxide complex **7** was stable to prolonged heating in $[D_6]$benzene at 100 °C. No conversion into $[D_5]$-**8** was observed, and reaction of a benzene solution of **8** with 2.5 equivalents of phenol resulted in quantitative conversion into **7**, suggesting that phenoxide complex **7** is the thermodynamically preferred product. However, complex **7** proved to be an effective catalyst for H/D exchange between D_2O and benzene. A solution of **7**, D_2O, and benzene was heated at 100 °C under Ar and the intensity of the residual [D]benzene signal was monitored by ^2H NMR (integration against a $[D_8]$THF internal standard). The $[D_1]$benzene signal was found to increase linearly with time, so that approximately 15 turnovers were observed after 100 h (where a turnover is defined as mol ^2H incorporated per mol catalyst). The catalyst showed no decomposition under these conditions. This reaction is uncommon for transition metals; few examples of the homogeneously catalyzed H/D exchange between D_2O and organic molecules have been reported.[3,8]

As strong acids are known to react with arenes through electrophilic aromatic substitution pathways,[9] control experiments were performed to confirm that the observed H/D exchange was in fact metal-catalyzed. The possibility that a small amount of phenol could be produced from **7** under the reaction conditions and might facilitate the exchange process was considered. However, when phenol was dissolved in a mixture of $[D_8]$toluene and H_2O and heated at 100 °C, no increase in the residual $[D_7]$toluene signals was detected, even after 360 h (as determined by integration of the ^1H NMR spectrum against an internal standard). A similar reaction was conducted with complex **7** in $[D_8]$toluene containing H_2O [Eq. (2)].



(2)

After 335 h at 100 °C, approximately 47 turnovers were observed, with a selectivity (statistically corrected) of 1.2:1:0:0 *meta*/*para*/*ortho*/CH_3. This selectivity is consistent with a metal-catalyzed reaction, as opposed to an electrophilic aromatic substitution mechanism, in which *ortho* and *para* activation dominate.[9]

In contrast to the reactivity of **5** and **6**, but similar to that observed for **7**, when the Rh^I triflate **1** was heated in [D$_6$]benzene at 100 °C, no conversion into **8** was observed. However, complex **1** was found to be a much less effective catalyst for the exchange between benzene and D_2O than **7**, resulting in approximately 1.5 turnovers after 100 h at 100 °C. Thus, the basicity of the phenoxide ligand of complex **7** appears to play an important role in the observed H/D exchange reactions. However, the lone electron pair appears to also be needed to mediate the σ-bond metathesis. The methyl complex **4** did not react in dry [D$_6$]benzene at room temperature, with conversion into **8** occurring only in the presence of H_2O, presumably by formation and reaction of the Rh^I hydroxide **5** (see above).

In conclusion, new Rh^I hydroxide, phenoxide, and trifluoroethoxide complexes are shown to be capable of arene C−H bond activation. This reaction may proceed through a mechanism similar to the two previous examples of C−H bond activation by high-valent transition-metal alkoxide/hydroxide complexes,[3] but with the important distinction that the low-valent Rh^I complexes reported herein do not require loss of an ancillary ligand to facilitate the C−H bond activation. It may be possible to expand these Rh^{I}OR complexes to create a new general class of square-planar d^8 metal complexes, which show high activity for this unusual C−H bond activation in the presence of water or alcohol. Future work will focus on determining the mechanism of these activation reactions and exploring the range of d^8 square-planar metal/ligand complexes that can promote this exciting reactivity.

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