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Facile Oxidative Addition of N−C and N−H Bonds to Monovalent Rhodium and Iridium

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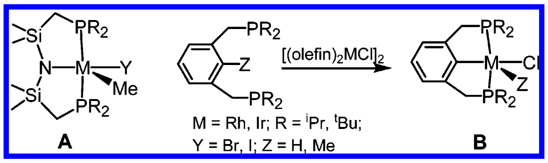
Tremendous advances in transition metal-catalyzed aromatic amination over the past decade have made it a practical, widely used reaction.[1] Formation of C−N bonds via reductive elimination (RE) is a crucial step of this process that has received substantial attention.[2] Its microscopic reverse, oxidative addition (OA) of a C−N bond, may be essential for hydrodenitrogenation of petroleum.[3] The related OA of N−H bonds is of relevance to hydroamination of alkenes.[4] However, well characterized examples of OA of C−N bonds are exceedingly rare[5] and those of OA of N−H bonds are relatively few, as well.[6] Investigations of well-defined elementary steps *and their microscopic reverses* provide thermodynamic and kinetic information that is vital to our ability to design and improve catalytic processes. A recent mechanistically fruitful example of the microscopic reverse approach is the studies of C−C and C−H RE on Pt.[7]

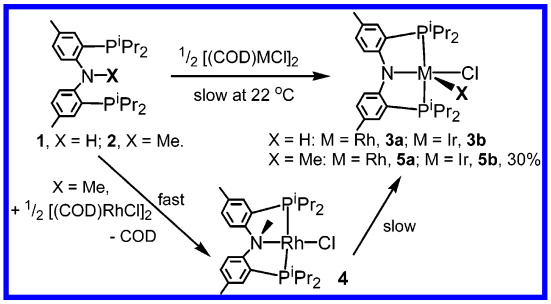
We report here our direct observations of oxidative addition of N−H and N−C bonds to Rh^I and to Ir^I. The C−N OA examples described here are unique in that they involve unstrained N−C(sp^3) bonds.

We have previously reported the synthesis of ligand **1** (Scheme 1) and its N−H cleavage chemistry with Pd.[8,9] The N−Me derivative **2** (Scheme 1) was prepared in an analogous fashion. Our anticipation of the OA of N−H and N−C bonds of **1** or **2** to Rh^I and Ir^I was based partly on the apparent stability (toward RE of C−N) of related compounds prepared by Fryzuk et al.[10] (**A**) and on the facile C−H and C−C oxidative addition processes described by Shaw et al. and Milstein et al. for the topologically similar PCP ligand on Rh and Ir (**B**).[11a−e] Activation of C−O bonds by pincer-ligated Rh, Pd, and Ni complexes has also been reported.[11f,g]



Mixtures of several new PNP complexes are formed upon allowing **1** to react with 0.5 equiv of $[(COD)MCl]_2$ (M = Rh, Ir; COD = cyclooctadiene) in an aromatic solvent at ambient temperature. Free COD is concomitantly produced. Over time these mixtures evolve into **3a** or **3b** nearly quantitatively. Conversion in excess of 98% (by ^{31}P NMR) is reached after 10 h (5 h) for **3a** (**3b**) at 22 °C and in less than 1 h for both **3a** and **3b** at 65 °C. The distinctive spectroscopic feature of compounds **3a** and **3b** is the upfield M−H resonance, found at −29.91 (−45.61) ppm for **3a** (**3b**). Such strongly upfield shifts are typical for five-coordinate square pyramidal complexes of d^6 metals (e.g., $(R_3P)_2M(H)Cl(CO)$ for M = Ru, Os, or $(R_3P)_2MHCl_2$ for M = Rh, Ir)[12,13] where the hydride is trans to an empty site. A related N−H oxidative addition to Rh^I to give a saturated product for a similar PNP ligand has been recently reported.[9b]

Scheme 1



During the course of the formation of **3a** and **3b**, the initially produced 1,5-COD is isomerized into 1,3-COD. It seems likely that the isomerization of COD by the unsaturated hydrides **3** proceeds by an insertion/β-H elimination pathway.[14] Complexes **3a** and **3b** also undergo H/D exchange with the C_6D_6 solvent at ambient temperature (50% exchange in 10−15 h).

Mixing **2** and 0.5 equiv of $[(COD)RhCl]_2$ in ether or C_6D_6 results in the rapid formation of **4** and 1 equiv of free 1,5-COD. Over time, yellow **4** slowly evolves into deep-green **5a**, a product of N−C oxidative addition. The most revealing indicators of the migration of the Me group are its ^1H (**4**: s, 3.72 ppm; **5a**: td, 2.33 ppm, $J_{H-Rh} = 3$ Hz, $J_{H-P} = 5$ Hz) and ^{13}C NMR (**4**: app q, 62.7 ppm, J_{CP}•J_{C-Rh}•2 Hz; **5a**: dt, 1.9 ppm, $J_{C-Rh} = 29$ Hz, $J_{C-P} = 5$ Hz) characteristics. In addition, the similarity of J_{Rh-P} in **3a** and **5a** (106 and 109 Hz, respectively) is consistent with the Rh^{III} formulation, different from the Rh^I in **4** ($J_{Rh-P} = 154$ Hz).

Thermolysis of a mixture of **2** and 0.5 equiv of $[(COD)IrCl]_2$ in an aromatic solvent (12 h, 85 °C) produces a green-colored mixture of **5b** and a pair of as yet unidentified Ir complexes (^{31}P NMR evidence). The ^1H resonances of the PNP ligand in **5b** are very similar to those of **5a** (but not to those of **4**). The triplet ($^2J_{PH} = 5.5$ Hz) signal at 2.33 ppm in the ^1H NMR spectrum and the triplet at −28.2 ppm in the ^{13}C NMR spectrum of the mixture are assigned to $Ir-CH_3$. Under selective irradiation of the ^{31}P NMR frequency of **5b**, the former peak appears as a singlet. The NMR data for **5a**,**b** are thus in good agreement with those of the structurally similar **A** and **B**.[10,11]

The transformation of **4** to **5a** was investigated by variable-temperature (25−62 °C) ^{31}P NMR kinetic studies in C_6D_6. At all temperatures the reaction followed a first-order rate law ($d(\ln[\mathbf{4}])/dt = -k$; $k_{298} = 1.45(3) \times 10^{-5}\ s^{-1}$; $t_{1/2}$(298 K)•13 h), consistent with an intramolecular process. The activation parameters were determined ($\Delta H^\ddagger = 23.5(9)$ kcal/mol; $\Delta S^\ddagger = -2(3)$ kcal/mol; $\Delta G^\ddagger_{298} = 24.0(18)$ kcal/mol). The near-zero $\Delta S^\ddagger$ is consistent with little increase in order in the transition state. This particularly argues against dissociation of N or P in the transition state and is most consistent with a least motion 1,2-shift of Me^+. It is conceivable that such a mechanism (coordination of the heteroatom followed by "slip" of R^+) may sometimes be operative for OA of RX (X =

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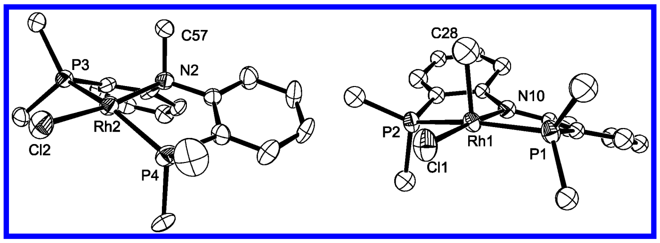

Figure 1. ORTEP drawing (30% probability ellipsoids) of **4** (left, **I** of **D1**) and **5a** (right, **II** of **D2**) showing selected atom labeling. Omitted for clarity: H atoms and Me groups except for Rh−Me.

heteroatom) in general. The kinetic importance of coordination of aryl halide to Pd during amination reactions has been demonstrated in some instances.[15]

An equivalent description is that of an intramolecular attack by a nucleophilic Rh on an electrophilic Me. This is in line with the finding of Wolczanski et al. that the C−N oxidative addition of arylamines to $(^t\mathrm{Bu}_3\mathrm{SiO})_3\mathrm{Ta}$ was favored by the increased positive charge on the α-C.[5d] Isomerization of **4** into **5a** occurs even in the solid state. Heating of a microcrystalline sample of **4** for 3 h at 70 °C resulted in >99% conversion to **5a**, as confirmed by dissolution and NMR analysis. The apparent rate of the solid-state reaction relative to the solution rate is in accord with the trends for organic solid-state reactions.[16] Crystals of **4** suitable for an X-ray diffraction study were grown from $\mathrm{Et_2O}$/pentane at −35 °C. Freshly grown crystals from this and similarly prepared batches give solutions of pure **4** when isolated and redissolved in $\mathrm{C_6D_6}$ within <30 min. The X-ray diffraction study (**D1**)[17] revealed that the asymmetric unit contained two independent molecules. One of these molecules (**I**) is a molecule of **4**, while the other crystallographic position (**II**) is occupied by molecules of **4** or **5a** (content of **4** in **II** is 53(2)%). The same crystal was subjected to another X-ray diffraction study (**D2**)[17] 16 days later. It registered a decay in intensity of the signal, yet the data obtained was satisfactory for unambiguous stereochemical determination. This second study (**D2**) revealed that while **I** remained an unchanged **4**, **II** now was >95% occupied by molecules of **5a**. Thus, it appears that for the transformation of **4** to **5a** in the crystal, *the activation energies for the two independent molecules are different*.[18]

The environment about Rh in **4** can be described as distorted square planar or flattened tetrahedral. The P−Rh and Rh−Cl distances are unremarkable. The N2−Rh2−Cl2 angle (171.6(3)°) only slightly deviates from linearity, but the P3−Rh2−P4 angle is merely 155.4(2)°. This showcases the inability of the ligand **2** to maintain idealized meridionality *and* a tetrahedral *amino* N.

On the other hand, the anionic *amido* PNP form of the ligand in **5a** possesses a planar N and is well suited to occupy three meridional coordination sites. The crystallographic data confirm that **5a** is a $\mathrm{Rh^{III}}$ square pyramidal compound with the Me group in the apical site. The preference of the Me in **5** and of hydride in **3** for the apical position is ascribed to their high trans influence.[19] The Rh−N distance in **5a** (2.059(4) Å) is shorter than that in **4** (2.134(10) Å), as is expected for *amido* vs *amine* donor sites. The Rh−$\mathrm{CH_3}$ distance (2.01(2) Å) in **5a** is slightly shorter than the 2.06−2.08 Å Rh−$\mathrm{CH_3}$ distances calculated for various **B**.[11d]

In summary, we present here an investigation of a well-defined oxidative addition of a C(sp^3)−N bond to a transition metal center. In addition, related N−H oxidative addition reactions are reported. These N−H and N−C bonds are slightly weaker than those in aliphatic and monoaromatic amines.[20] That and the product-adapted geometry of the PNP ligand contribute to the overall ease and favorability of N−C (and N−H) OA. Solution kinetic studies suggest a simple migration of Me from a coordinated amine functionality to Rh. Remarkably, in the solid state the oxidative addition of N−C to Rh proceeds in a crystal-to-crystal fashion, transforming only one of the two independent molecules in the crystal.

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Supporting Information Available: Experimental details, characterization data, and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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