

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

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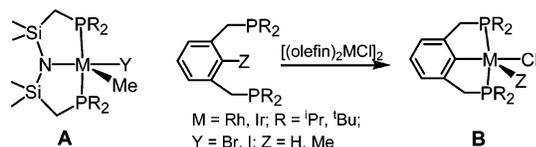
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Tremendous advances in transition metal-catalyzed aromatic amination over the past decade have made it a practical, widely used reaction.¹ Formation of C–N bonds via reductive elimination (RE) is a crucial step of this process that has received substantial 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 rare⁵ 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

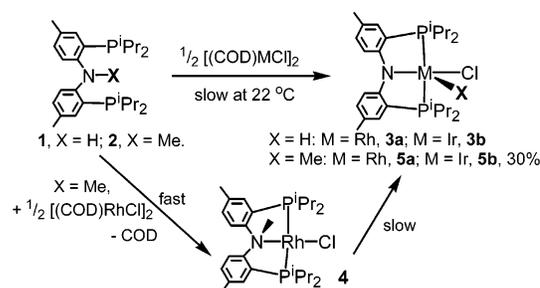
We report here our direct observations of oxidative addition of N–H and N–C bonds to Rh^I and to Ir^I. The C–N OA examples described here are unique in that they involve unstrained N–C(sp³) bonds.

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 ³¹P 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 d⁶ metals (e.g., (R₃P)₂M(H)Cl(CO) for M = Ru, Os, or (R₃P)₂MHCl₂ 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 C₆D₆ solvent at ambient temperature (50% exchange in 10–15 h).

Mixing **2** and 0.5 equiv of [(COD)RhCl]₂ in ether or C₆D₆ 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 ¹³C 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 (³¹P 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 ¹³C NMR spectrum of the mixture are assigned to Ir–CH₃. Under selective irradiation of the ³¹P 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) ³¹P NMR kinetic studies in C₆D₆. At all temperatures the reaction followed a first-order rate law (d(ln[**4**])/dt = –k; k₂₉₈ = 1.45(3) × 10^{–5} s^{–1}; t_{1/2}(298 K)·13 h), consistent with an intramolecular process. The activation parameters were determined (ΔH^\ddagger = 23.5(9) kcal/mol; ΔS^\ddagger = –2(3) kcal/mol; ΔG^\ddagger_{298} = 24.0(18) kcal/mol). The near-zero ΔS^\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 =

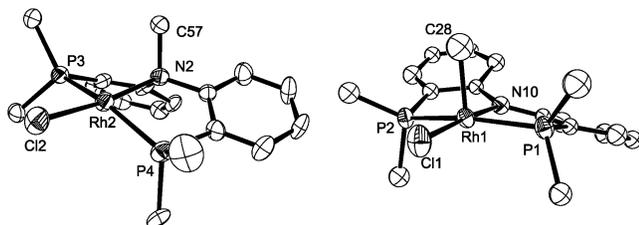


Figure 1. ORTEP drawing (30% probability ellipsoids) of **4** (left, **I** of **D1**) and **5a** (right, **II** of **D2**) showing selected atom labeling. Omitted for clarity: H atoms and Me groups except for Rh–Me.

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 $(\text{Bu}_3\text{SiO})_3\text{Ta}$ was favored by the increased positive charge on the $\alpha\text{-C}$.^{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 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 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 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–CH₃ distance (2.01(2) Å) in **5a** is slightly shorter than the 2.06–2.08 Å Rh–CH₃ distances calculated for various **B**.^{11d}

In summary, we present here an investigation of a well-defined oxidative addition of a $\text{C}(\text{sp}^3)\text{-N}$ 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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