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Synthesis, Characterization, and Reactivity of N-Heterocyclic Carbene Palladium(II) Hydroxide Dimers

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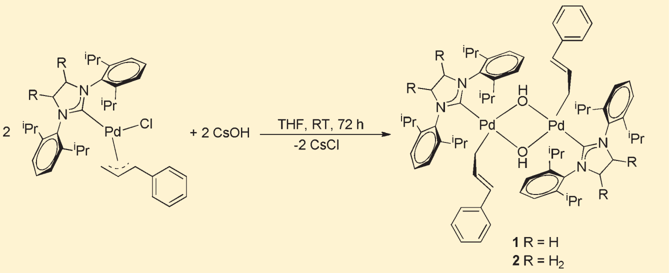
S *Supporting Information*

ABSTRACT: Palladium hydroxide dimers were prepared by reactions of CsOH with monomeric [Pd(NHC)(η^3-allyl)Cl] starting materials. The dimers represent species proposed as intermediates in important cross-coupling reactions. These complexes were tested for their catalytic activity in Suzuki–Miyaura coupling and Buchwald–Hartwig aryl amination. The hydroxide complexes were susceptible to hydrogenolysis on exposure to H_2 gas. Following H_2O elimination and β-hydride elimination of an additional cinnamyl ligand, a Pd(0) species is formed which can react with other available ligands.



Transition-metal hydroxides are receiving increasing attention due to their importance as intermediates in catalytic cycles.[1] Of interest to us is the recent attention devoted to isolation of organometallic Pd–OH complexes in order to study their structures and reactivity.[2–4] Additionally, the recent emergence of N-heterocyclic carbenes (NHCs) as ligands has led to the invention of many catalysts with superior activity and stability compared to those of their phosphine analogues, for which they were once thought to be simple mimics.[5] Our targeted system combines these two burgeoning areas of research. This contribution reports on the reactivity of newly prepared NHCs containing Pd–OH dimers.

Palladium(II) halides, including the Pd–Cl monomers from which our Pd–OH dimers are derived, often serve as precatalysts for cross-coupling reactions that require a Pd(0) active species.[6] This often requires initiation by either alkoxide or hydroxide bases.[6,7] One proposed mechanism for this activation involves an inner-sphere attack by RO^- with elimination of Cl^- (Scheme 1, left).

In order to isolate a well-defined congener of compound A (Scheme 1), excess CsOH was reacted with [(L)PdCl(cinnamyl)],[6] yielding the new complexes [(L)Pd(η^1-cinnamyl)(μ-OH)]$_2$ (L = IPr = *N*,*N*′-bis(2,6-(diisopropyl)phenyl)imidazol-2-ylidene (**1**), SIPr = *N*,*N*′-(bis(2,6-diisopropylphenyl)imidazolidine (**2**)) (Scheme 2).

The ^{1}H NMR spectra of **1** and **2** contain upfield resonances at −4.25 and −4.29 ppm, respectively, corresponding to the proton of the bridging hydroxide moieties. Crystals of either **1** or **2** suitable for X-ray diffraction can be grown from concentrated pentane solution at ambient temperature. Structural data confirm that both **1** and **2** are dimers in the solid state (Figure 1).[8]

The cinnamyl ligands have also transitioned to η^1 from the η^3 bonding mode adopted in the chloro precursors. The tendency of allyl ligands bound to group 10 metals containing three other bound ligands to take on a η^1 bonding mode is consistent with literature precedent and facilitates the desired square-planar geometry.[9] The palladium atoms and those atoms attached directly to the metal all exist in a single plane. The additional atoms of the cinnamyl ligands exist on the same side of this plane. The imidazolium moieties of the NHCs are both twisted 63° in opposite directions of the metal–ligand plane.

The resonance resulting from the cinnamyl proton nearest the phenyl (6.12 ppm) in the ^{1}H NMR spectrum of **1** is close to the resonance of the free alkene (6.37 ppm), as opposed to the resonance of the chloro starting complex (5.07 ppm). Additionally, in **1** the two cinnamyl protons farthest from the phenyl give a single resonance at 1.75 ppm. This is in contrast to the case for the chloro starting complex, in which these two hydrogens are nonequivalent and give two separate resonances at 1.80 and 3.02 ppm. These cinnamyl resonances are consistent with both the solution and solid-state structures having the same configuration. Overall the two complexes appear to be nearly identical by comparison of the atoms bound to Pd: bond lengths of the two complexes Pd–O (**1**, 2.10 Å; **2**, 2.07 Å) and Pd–C(cinnamyl) (**1** and **2**, 2.05 Å). The NHC ligands within the two complexes also have very similar steric requirements, from calculation of the percent buried volumes of complexes **1** (39.4%) and **2** (41.8%).[10] For complex **2**, the crystal structure was found to contain bridging Cl atoms in place of OH in approximately 10% of the complex. This impurity formed during the reaction with CsOH, and attempts to separate the very similar complexes have been unsuccessful.

Both **1** and **2** were tested as catalysts for Buchwald–Hartwig aryl aminations and Suzuki–Miyaura type couplings. We had previously reported the use of [Pd(NHC)(cinnamyl)Cl]

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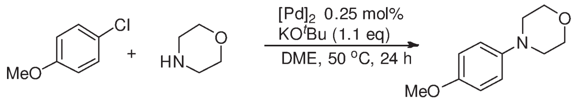
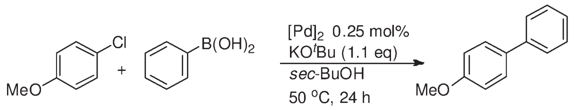
(NHC = IPr, SIPr) as precatalysts for both reactions.[6] In both reactions the active [Pd^0(NHC)] catalyst must first be formed by reaction of the chloro/allyl precatalyst with KO^{t}Bu. With that in mind, we were interested in learning what effect having a basic HO$^-$ in place of the Cl$^-$ in the precatalyst would have on catalytic activity.

Compounds **1** and **2** were tested for their ability to carry out aryl amination reactions (eq 1). Using 0.25 mol% of **1** as catalyst loading, the reaction between *p*-chloroanisole and morpholine at 50 °C yielded 4-(4-methoxyphenyl)morpholine in 92% GC conversion. The same reaction using **2** gave >99% conversion by GC (89% isolated). Additionally, the catalytic activity was tested for a Suzuki–Miyaura coupling (eq 2). Using 0.25 mol% of **1** at 50 °C, the reaction between *p*-chloroanisole and phenylboronic acid yielded 4-methoxybiphenyl in 78% conversion, as quantified by GC (64% isolated yield). Additionally, 21% of the reduction product methoxybenzene was observed. The same reaction using **2** yielded 58% coupling product and 36% reduction product (GC).



(1)



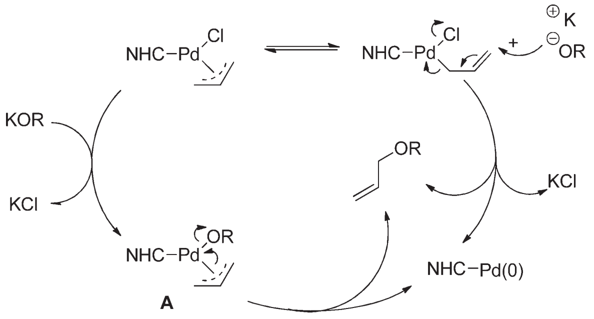
(2)

In the case of aryl amination, the SIPr ligand containing **2** proved to be the more viable catalyst. This is in agreement with the observed catalytic activity for the chloro/allyl complexes. Most notably, for Suzuki–Miyaura couplings, the IPr-containing **1** performs most efficiently. Both **1** and **2**, however, lead to significant amounts of dehalogenated aryl chloride forming as a side product, a side reaction that was avoided in the chloro systems by using cinnamyl instead of the allyl fragment.[6]

Additionally, a potentially valuable yet rarely documented catalytic step is the release of H_2O from M–OH in the presence of molecular hydrogen to form a metal hydride.[1b,11] Model systems demonstrating this step, however, remain rare.[3] The Pd–OH complexes reported here were exposed to H_2 in order to observe this reaction.

The hydroxide complex **1** is susceptible to hydrogenolysis in the presence of molecular hydrogen. Reaction of **1** with H_2 gas (1 atm) when monitored by ^{1}H NMR spectroscopy shows the formation of H_2O, [Pd(IPr)$_2$] (**3**), and propylbenzene, with the last two products in a 1:2 ratio (eq 3). In this reaction palladium black is also precipitated. Presumably the initial hydrogenolysis forms [Pd(IPr)(cinnamyl)(H)], which may then reductively eliminate to form unstable 12e$^-$ [Pd(IPr)]. The 12e$^-$ species would then decompose to form Pd(0) and free IPr. The IPr ligand is then available to react with subsequently formed 12e$^-$ [Pd(IPr)]. This ligand scrambling is similar to the Pd hydrogenolysis reaction recently reported by Fulmer *et al.*,[3b] in which a "PCO" pincer ligated a Pd hydroxide moiety. On exposure to H_2,

Scheme 1. Plausible Mechanisms of Pd(0) Formation



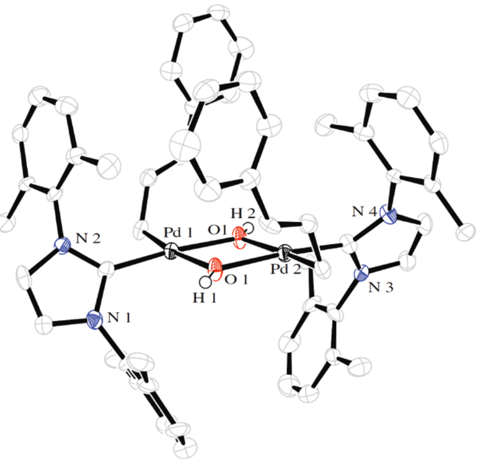
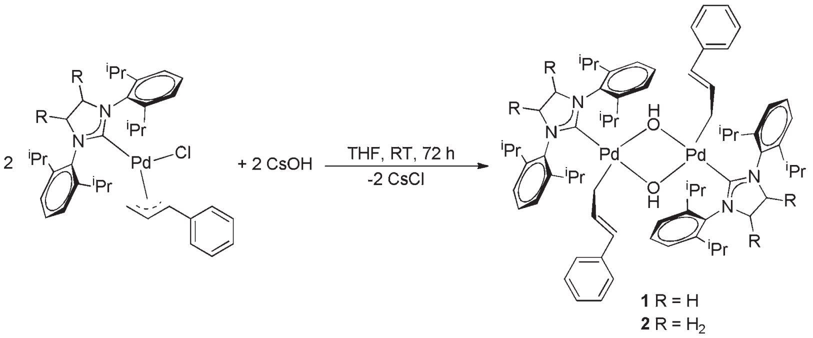


Figure 1. Crystal structure of [Pd(IPr)(η^1-cinnamyl)(μ-OH)]$_2$ (**1**) with thermal ellipsoids drawn at the 50% probability level. Nonhydroxide hydrogen atoms have been omitted, and isopropyls have been abbreviated for clarity. Selected bond distances (Å) and angles (deg): Pd–O = 2.10 (average), Pd1–C(carbene) = 1.951(6), Pd1–C(cinnamyl) = 2.049(6), Pd1–Pd2 = 3.1720(13); O2–Pd1–O1 = 81.80(14), C(carbene)–Pd–C(cinnamyl) = 91.2(2).

Scheme 2. Synthesis of Pd(II) Hydroxides



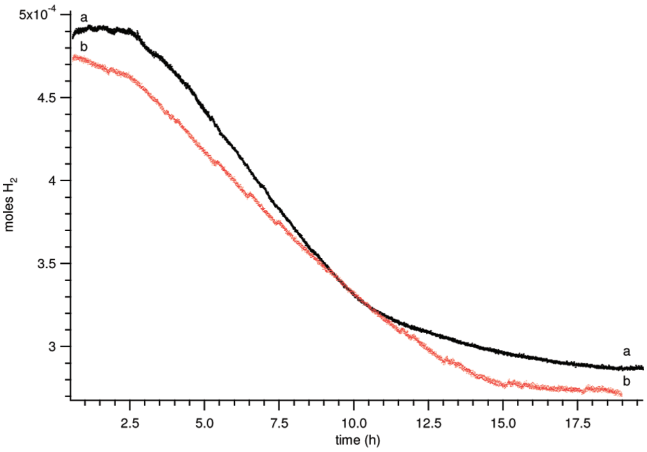
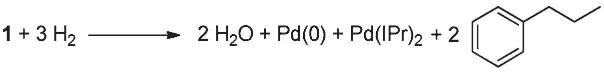


Figure 2. Moles of H_2 present in reactor calculated from H_2 pressure: (a) reactor loaded with 84.7 mg of **1** (0.67×10^{-4} mol); (b) reactor loaded with 83.8 mg of **1** (0.66×10^{-4} mol).

[Pd(PCO)(OH)] eliminates H_2O with a final product having two of the PCO ligands only bound through their P atoms in a new Pd(0) complex. The isopropylbenzene presumably forms via hydrogenation of 1-benzyl-1-propene by **3**, which is similar to the case for the known hydrogenation catalyst [Pd(SIPr)(PCy_3)],[12] which interacts with H_2.[13] Alternatively, the 12e⁻ [Pd(IPr)] intermediate may have acted as the active catalyst in the hydrogenation of 1-benzyl-1-propene.



(3)

Additional confirmation of the reaction stoichiometry was garnered from *in situ* measurement of the hydrogen pressure change. The change in hydrogen pressure over the course of the reaction showed that 3 equiv of H_2 gas were consumed for every 1 mol of **1** loaded into the reactor (Figure 2).

Reaction of **1** with PCy_3 in THF at reflux yields the previously described Pd(0) complex [Pd(IPr)(PCy_3)] (**4**). This, however, is not an efficient reaction, due to thermal decomposition of **1**. This also is in contrast with previous reports on similar phosphine complexes of the form $[Pd(PR_3)(OH)L]_2$, in which phosphine addition resulted in phosphine ligation to form an equilibrium with monomeric species, of the form $[Pd(PR_3)_2(OH)L]$.[14] Hydrogenolysis was also performed in the presence of added PCy_3 to give complex **4** in quantitative yields in reactions monitored by NMR spectroscopy. Attempts to scale this reaction for an improved synthesis of **4**, however, were unsuccessful, and on a larger scale reactions resulted in mixtures of **3** and **4**.

In summary, the use of Pd−OH complexes as precatalysts for Buchwald−Hartwig aryl amination and Suzuki−Miyaura couplings confirms the possibility of Pd−OR species being intermediates in the formation of catalytically active Pd(0) from Pd(II)−Cl complexes. Additionally, the newly reported Pd−OH complexes are susceptible to hydrogenolysis, modeling this potentially valuable catalytic step. Studies aimed at exploring further the role of M−OH species in catalysis are ongoing.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Text and figures giving experimental details and characterization data for **1** and **2** and CIF files giving X-ray crystallographic data for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) CCDC-831869 (**1**) and CCDC-831870 (**2**) contain supplementary crystallographic data for this contribution. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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