N-Heterocyclic Carbene Complexes

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Reduction of a Chelating Bis(NHC) Palladium(II) Complex to [{μ-bis(NHC)}$_2$Pd$_2$H]$^+$: A Terminal Hydride in a Binuclear Palladium(I) Species Formed under Catalytically Relevant Conditions**

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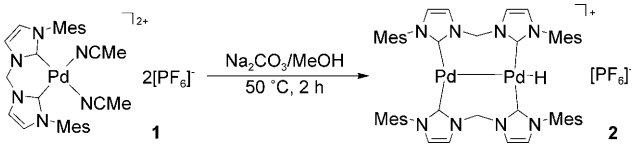
Catalytic processes featuring N-heterocyclic carbene (NHC) ligands have been extensively studied following the isolation of free imidazol-2-ylidenes.[1] An important reaction class is the base-assisted palladium-mediated C–C/N coupling, such as the Sonogashira, Buchwald–Hartwig, and Mizoroki–Heck reactions.[2] Interestingly, mechanistic debate spans from the in situ generation of active NHC complexes by reaction of simple palladium(0) or palladium(II) species with imidazolium-based ionic liquid solvents[3] to the extreme of NHC complexes being precatalysts to NHC-free colloidal palladium materials effecting heterogeneous catalysis.[4] Pd^{II} NHC precatalyst usage prevails, and is generally thought to give an active palladium(0) species; however, the first palladium(IV) NHC complex was recently reported via a catalytically relevant oxidative addition to a palladium(II) precursor.[5] Pd^0 NHC complexes have been prepared from palladium(0) sources and used as catalysts.[6] However, we are unaware of any isolated, well-characterized, low-valent Pd NHC complexes (Pd^0 or Pd^I) prepared by reduction of palladium(II) precursors under conditions that are relevant to the catalysis of C–C/N coupling reactions.[7]

Herein we present high-yield access to a Pd$_2$H$^+$ species, **2**, stabilized by a bulky bridging bis(NHC) ligand by base-assisted reduction of a chelating bis(NHC)Pd^{II} complex. DFT calculations have established the bonding in **2** and its fluxional behavior is described. To the best of our knowledge, **2** is the first reported well-characterized 1) Pd^I NHC complex, 2) Pd NHC complex prepared via base-assisted reduction, and 3) structurally authenticated Pd$_2$H$^+$ complex and Pd–Pd bonded complex of any oxidation state with a terminal hydride ligand.

A colorless solution of **1** over anhydrous Na_2CO_3 in dry MeOH was heated at 50 °C for two hours to give a red solution, from which red crystals of **2** were obtained in 84% yield after filtration and concentration (Scheme 1).[8] Complex **2** has high stability as a solid (more than one year) and in MeOH and THF (several months). The complex is tolerant to moisture, but reacts quickly with atmospheric oxygen in solution and the solid state.



1 2

Scheme 1. Synthesis of the cationic low-valent binuclear hydride **2**.

Initial characterization of **2** was based on an X-ray crystal structure determination, which establishes the Pd/NHC connectivity and its monocationic status. ^{1}H NMR spectral data subsequently provided initial evidence of a hydride ligand, which was confirmed by mass spectrometry. The terminal hydride ligand has been established by a neutron crystal structure analysis (Figure 1).

The Pd–H bond length in **2** determined from the neutron structure analysis (1.58(3) Å) is typical, and is comparable to the μ-H–Pd^I distance in [(dipp)$_2$Pd$_2$(μ-H)(μ-CO)]$^+$ (1.531(11) and 1.540(10) Å; X-ray; dipp = 1,3-bis(diisopropylphosphino)propane).[9] A terminal hydride (1.53(5) Å) is known for

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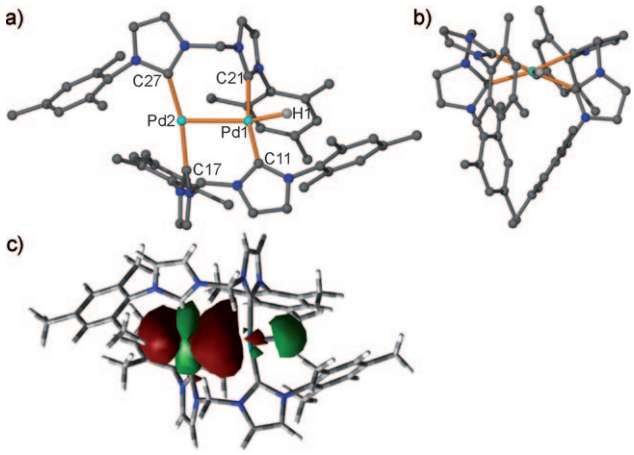

Figure 1. a,b) Neutron crystal structure of **2** (only hydride H atom shown, all atoms depicted with arbitrary atomic radii):[8] a) general view, b) viewed down the Pd1–Pd2 bond. Bond lengths [Å] and angles [°]: Pd1–H1 1.58(3); C11,21-Pd1-H1 84.2(10), 84.0(10), Pd2-Pd1-H1 168.5(11), Σ(C-Pd1,Pd2-C) 360.0, 357.2. X-ray data: Pd1–Pd2 2.7530(4), Pd1–C11,C21 2.035(3), 2.012(3), Pd2–C17,C27 2.008(3), 2.041(3); Pd2-Pd1-C11,C21 105.45(9), 85.01(8), Pd1-Pd2-C17,C27 85.66(9), 103.11(9), C-Pd1,Pd2-C 169.45(12), 168.96(12), Pd1-C11-N11,N12 126.4(2), 130.3(2), Pd1-C21-N21,N22 131.1(2), 124.8(2), Pd2-C17-N13,N14 121.9(2), 134.1(2), Pd1-C27-N23,N24 134.1(2), 123.7(2). c) Optimized structure (B3LYP/BS1) of **2** showing the Pipek–Mezy localized σ-bonding orbital between the palladium(I) centers; Pd1–Pd2 2.84, Pd1–H1 1.55; H1-Pd1-Pd2 169.8.

the Pd^{II} A-frame complex $[(\mu\text{-dppm})_2HPd(\mu\text{-Cl})PdMe]^+$,[10] (Pd···Pd 3.013(1) Å; dppm = bis(diphenylphosphino)methane). Pd/E bridged hydrides exist for $[LPd_2(\mu\text{-}HER_2)_2]^{n+}$ (E = Si, Ge, P).[11] Terminal Pd–H bond lengths in a bis(NHC)Pd^{II} benzoate[12] and two cationic (NHC)Pd^{II} species[13] are 1.54(2), 1.77(7), and 1.57(3) Å, respectively (all X-ray).

Complex **2** is a rare case of a CH_2-linked bis(NHC) supporting a M–M bond.[14] The Pd–Pd distance in **2** in three crystalline forms vary over 2.7530(4)–2.8757(6) Å, which is possibly linked with the frailty of this interaction (see DFT studies below).[8] This distance is in the longer range for binuclear palladium(I) complexes, which are subject to large ligand influences.[15] DFT calculations[16] show the bonding in the Pd_2H^+ core to occur between palladium(I) centers (d^9 configuration), as opposed to a plausible $Pd^0 \rightarrow (Pd^{II}H)^+$ donor–acceptor pair given the inequivalent metal coordination geometries.[17] A Pd–Pd σ bond (2.84 Å) is formed by overlap of the palladium(I) fragment molecular orbitals composed of Pd 4d,5s and H 1s atomic orbitals (Figure 1c).

^{1}H NMR spectroscopy of **2** revealed fluxional behavior. Above about −30 °C (to limit of study, 50 °C, [D_4]methanol), each NHC ring is equivalent, but mesityl group rotation is restricted (two *o*-Me singlets). Methylene resonances form an AX spin system and the hydride occurs at about −16.2 ppm. Around −30 °C the hydride signal broadens, and sharpens below this temperature to −16.5 ppm (to limit of study −70 °C).[12,13,18] NHC signals also undergo coalescences, which were only partly analyzed owing to signal overlap and poor solubility. Most apparent are eight *o*-Me resonances that are consistent with inequivalence of all four NHC rings and the cation symmetry seen in the solid state. The fluxional processes most likely relate to hydride ligand mobility (giving equivalence of palladium centers and thus each end of the NHC) and flipping of the twisted palladium coordination planes (41.78(7)° in the solid state (Figure 1b), giving equivalence of each NHC).[19,20]

The formation of the binuclear palladium(I) complex **2** from the palladium(II) precursor must proceed via several steps. No intermediates were observed by ^{1}H NMR spectroscopy and mass spectrometry (which gives **2** as the deuteride in CD_3OD). The reaction proceeds cleanly to the single product in apparent quantitative yield. Reaction at room temperature is greatly slowed, but again no intermediates are seen. β-H elimination from a Pd^{II}OMe species giving Pd^{II}–H is a likely early step, which is known for NHC Pd^{II}–OR (R = *i*Pr/Me) species and is exploited in aryl dehalogenation.[18] The proposed mechanism for formation of $[(dipp)_2Pd_2(\mu\text{-H})(\mu\text{-CO})]^+$ from [(dipp)Pd(Cl)Ph] in MeOH under basic/neutral conditions may be partly relevant here.[9] In our case, base is required and the bis(NHC)$PdBr_2$ precursor does not react. Further CH_2O involvement is not implied and reduction is likely to arise from MeOH elimination from a later Pd^{II}(H)OMe intermediate. The lack of participation of the NHC ligand at this stage is notable as 2-substituted imidazoliums are known to form by NHC involvement in reductive elimination with alkyls, acyls, and hydrides.[4a] In a study probing the mechanism of C_2H_4/CO alternating copolymerization using **1** as a precatalyst, the cationic Pd^{II}Me(NCMe) complex was also found to be stable towards such reactivity.[21] Finally, combination of Pd^{II}–H and Pd^0 species in some fashion would give **2**, as suggested for $[(dipp)_2Pd_2(\mu\text{-H})(\mu\text{-CO})]^+$.[9]

The stage at which the chelated[8b] to bridged bis(NHC) conversion occurs in the synthesis of **2** is currently unknown. Some evidence exists in tethered bis(NHC)Rh^{III}/Rh^I systems for chelation preference in the higher oxidation state.[22] If the same is true for palladium, it may be that chelated CH_2-linked bis(NHC)s cannot support palladium(I) or palladium(0), which has implications in homogeneous catalyzed C–C coupling reactions with this ligand class[8b,23] regarding the stability of mononuclear species. Indeed, various routes are known to inactive species for palladium(II)-chelated CH_2-linked bis(NHC) complexes even before consideration of such issues associated with low-valent states.[24] All attempts to isolate *N*-alkyl analogues of **2** gave palladium black, highlighting the subtle ligand effects in stabilizing low-valent palladium complexes with multidentate NHCs. A limited number of binuclear palladium(I) precatalysts for C-C/N coupling reactions have been reported, with some high activities being rationalized by disproportionation of the precatalysts to give active palladium(0) and/or palladium(II) species.[25] Thus, it remains to be demonstrated whether the Pd^I–Pd^I interaction has a useful role in this class of catalysis, which is in stark contrast to the topical role that Pd^{III}–Pd^{III} interactions play in some oxidative-addition-initiated catalytic processes.[26] Binuclear palladium(I) complexes supported by chelating P–P and P–N and bridging allyl ligands have been observed in situ during Pd^0/Pd^{II}-catalyzed allylic substitution reactions and discussed as both acting as

reservoirs for active palladium(0) species[27] and being intermediaries to polynuclear clusters leading to inactive metallic palladium.[28] We are unaware of any isolated low-valent Pd NHC complexes supporting similar mechanistic proposals in relation to C–C/N coupling reactions, though the concept is well-documented.[4]

In summary, we have isolated a binuclear Pd^{I} NHC complex in high yield under catalytically relevant reaction conditions. Various novel structural motifs are noted for palladium chemistry, in general, and NHC chemistry. Whilst the in situ observation of the palladium(I) complex has thus far not been achieved during catalysis, the scope of in-situ-formed low-valent Pd NHC species to be considered feasible in catalysis should be broadened. The observed chelating/bridging NHC binding change and the limited access to analogues, or other isolable low-valent species, with NHC variation highlight subtle influences on the in situ generation of active/inactive species under basic reducing conditions from palladium(II) precatalysts. We are pursuing mechanistic studies on the formation of **2** and its catalytic activity.

Experimental Section

$[\{(MesIm)_2CH_2\}_2Pd_2H][PF_6]$ (**2**): A methanol solution (20 mL) of $[\{(MesIm)_2CH_2\}Pd(NCMe)_2][PF_6]_2$ **1** (0.20 g, 0.23 mmol) and sodium carbonate (0.060 g, 0.57 mmol) was heated for two hours at 50 °C, giving a red solution. The solution was filtered to remove excess sodium carbonate and the solution concentrated in vacuo to about 10 mL, yielding red crystals of **2** upon slow cooling to −20 °C in an acetone bath. A mixture of red needles and prismatic crystals were isolated by removal of the methanolic mother liquor, which could be cropped for further product yield. The crystals were dried in vacuo and stored in the glove box (110 mg, 0.19 mmol, 84 %). The product could also be recrystallized from THF, giving red prismatic crystals as a THF solvate. ^{1}H NMR (300 MHz, CD_3OD, 298 K): $\delta = -16.21$ (s, 1 H; hydride) 1.48 (s, 12 H; *o*-Me), 1.64 (s, 12 H; *o*-Me), 2.41 (bs, 12 H; *p*-Me), 5.97 (d, ^2J(H,H) = 12.0 Hz, 2 H; CH_2), 6.82 (s, 4 H; CH(imidazolin-2-ylidene)), 6.87 (s, 4 H; *m*-CH(aryl)), 6.93 (s, 4 H; *m*-CH(aryl)) 7.48 (s, 8 H; CH(imidazolin-2-ylidene)), (s, 6 H; *o*-Me), 7.88 ppm (bd, ^2J(H,H) = 12.6 Hz, 2 H; CH_2). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_3OD, 298 K): $\delta = 16.8$ (*o*-Me), 17.4 (*o*-Me), 20.1 (*p*-Me), 64.1 (CH_2), 119.4 (CH(imidazolin-2-ylidene), 122.4 (CH(imidazolin-2-ylidene)), 128.5 (*m*-CH(aryl)), 129.0 (*m*-CH(aryl)), 134.83, 135.45, 137.1, 138.12 ppm (2 x *o*-CH(aryl), *p*-CH(aryl), carbene). LSI-MS: *m*/*z*: 983 $[\{(MesIm)_2CH_2\}_2Pd_2H]^+$. Elemental analysis (%) calcd ($C_{50}H_{57}N_8Pd_2PF_6$): C 53.25, H 5.09, N 9.94; found: C 52.78, H 5.17, N 9.55.

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