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Bond Activation, Substrate Addition and Catalysis by an Isolable Two-Coordinate Pd(0) Bis-Isocyanide Monomer

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In analogy to binary Pd(0) carbonyls,[1] monomeric homoleptic isocyanide complexes of Pd(0) have remained elusive species. Indeed, when studied in conjunction with isocyanides such as CNXyl, CN*t*-Bu, and CNCy (Cy = cyclohexyl), [Pd(CNR)$_n$] species are observed invariably to aggregate into higher nuclearity clusters.[2] With respect to purported bis-isocyanide "[Pd(CNR)$_2$]" species, early preparations[3] did not conclusively establish their monomeric nature, and subsequent reports[4] strongly favored the trimeric formulation [Pd$_3$(CNR)$_6$]. These latter studies culminated in Francis' structural determination of *triangulo*-[Pd(μ_2-CNCy)(CNCy)]$_3$, which was the first binary Pd(0) isocyanide complex to be definitively characterized.[5] Presumably, the proclivity of unencumbered isocyanides to bridge metal centers facilitates the aggregation of these reduced Pd species. Accordingly, herein we report that the encumbering *m*-terphenyl isocyanide, CNAr^{Dipp2} (Dipp = 2,6-(i-Pr)$_2$C$_6$H$_3$), can successfully stabilize the highly reactive two-coordinate bis-isocyanide monomer Pd(CNAr^{Dipp2})$_2$. Because of the strong π-acidic nature of the isocyanide function, Pd(CNAr^{Dipp2})$_2$ serves as an intriguing counterpoint to two-coordinate Pd^{0}L$_2$ complexes featuring strongly σ-donating phosphine[6] (PR$_3$) or NHC[7,8] ligands.

Access to orange Pd(CNAr^{Dipp2})$_2$ was achieved by Mg^0 reduction of the dichloride PdCl$_2$(CNAr^{Dipp2})$_2$ in a 4:1 Et$_2$O/THF mixture. Generation of Pd(CNAr^{Dipp2})$_2$ by straightforward reduction of a divalent precursor is notable in that similar protocols have been reported to yield exclusively trimeric [Pd(μ_2-CNR)(CNR)]$_3$ species.[4d] Both the ^{1}H NMR (C$_6$D$_6$) and FTIR (KBr) spectra of Pd(CNAr^{Dipp2})$_2$ are devoid of features characteristic of a hydride functionality, lending credence to its zerovalent formulation. Crystallographic characterization of Pd(CNAr^{Dipp2})$_2$ revealed a two-coordinate monomer which diverges slightly from an ideal linear geometry ($\angle$(C1−Pd−C2) = 169.8(2)°, Figure 1a). Isocyanide bending is observed for one CNAr^{Dipp2} ligand ($\angle$C1−N1−C3 = 163.6(4)°), while the other remains comparatively unperturbed ($\angle$C2−N2−C4 = 174.1(4)°). Whereas this lack of bending may be a reflection of only moderate π-back-donation to the isocyanide ligands, it is important to note that Pd(CNAr^{Dipp2})$_2$ gives rise to ν_{CN} stretches (2073 and 2011 cm^{-1}, KBr), that are considerably lower in energy than found for divalent PdCl$_2$(CNAr^{Dipp2})$_2$ (ν_{CN} = 2202 cm^{-1}, KBr). Furthermore, Pd(CNAr^{Dipp2})$_2$ exhibits average Pd−C$_{iso}$ bond distances which are shorter relative to those in PdCl$_2$(CNAr^{Dipp2})$_2$ (1.930(3) Å av vs 1.976(2) Å av, respectively). These structural data are consistent with appreciable π back-donation in Pd(CNAr^{Dipp2})$_2$, as zerovalent centers may be reasonably expected to exhibit longer M−L bond distances than their divalent counterparts when only σ-donor ligands are present. Significant π back-donation in Pd(CNAr^{Dipp2})$_2$ is also indicated by DFT calculations, which clearly reveal two orthogonal π-back-bonding interactions (see the Supporting Information).

The encumbering Ar^{Dipp2} units provide Pd(CNAr^{Dipp2})$_2$ with a substantial degree of thermal and kinetic stability in solution. As indicated by ^{1}H NMR spectroscopy, Pd(CNAr^{Dipp2})$_2$ does not decompose in C$_6$D$_6$ when heated to 80 °C for up to 5 d. Furthermore, while the CNAr^{Dipp2} ligands effectively stabilize a monomeric Pd(0) complex, they also enforce a homoleptic bis-isocyanide formulation. Thus, as assayed by both ^{1}H NMR and

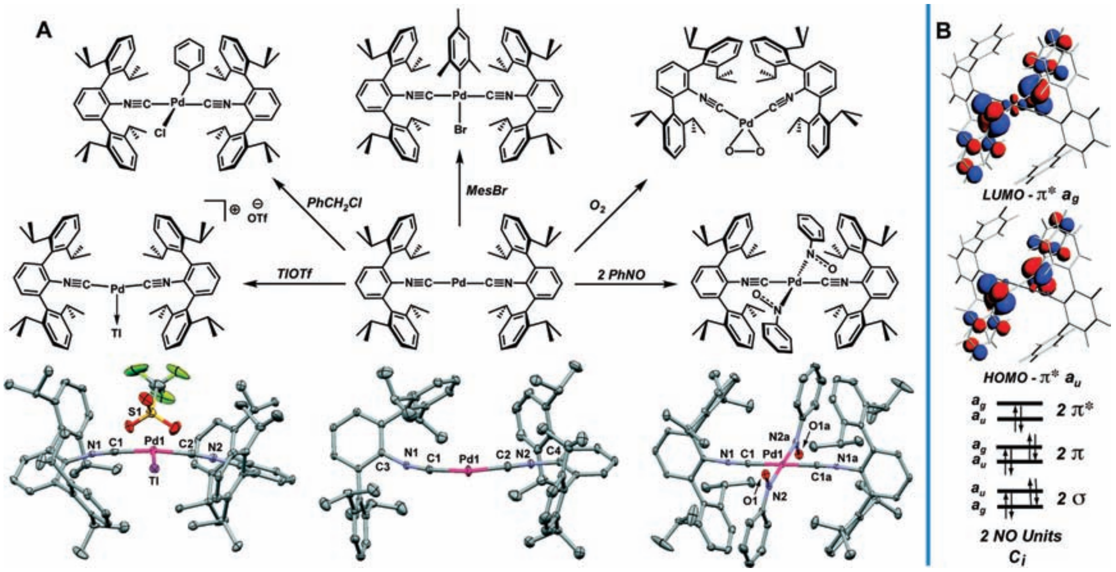

Figure 1. (A) Reaction pinwheel for Pd(CNAr^{Dipp2})$_2$ and molecular structures of [TlPd(CNAr^{Dipp2})$_2$]OTf (left), Pd(CNAr^{Dipp2})$_2$ (center), and Pd(κ^1-*N*-PhNO)$_2$(CNAr^{Dipp2})$_2$ (right). (B) HOMO, LUMO, and qualitative MO diagram for Pd(κ^1-*N*-PhNO)$_2$(CNAr^{Ph2})$_2$ based on restricted S = 0 DFT calculations.

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FTIR spectroscopies, addition of another equivalent of CNAr^{Dipp2} to Pd(CNAr^{Dipp2})$_2$ in C_6D_6 results in rapid isocyanide exchange rather than formation of a tris-isocyanide species. Variable temperature studies in toluene-d_8 indicate that isocyanide exchange remains fast on the ^{1}H NMR time scale down to -80 °C.

In accord with its reduced nature, Pd(CNAr^{Dipp2})$_2$ is competent for the oxidative addition of σ-bonds. For instance, Pd(CNAr^{Dipp2})$_2$ readily forms the benzyl chlorido complex PdCl(Bz)(CNAr^{Dipp2})$_2$ upon reaction with $PhCH_2Cl$. Similarly, Pd(CNAr^{Dipp2})$_2$ also adds across the carbon−bromine bond of mesityl bromide (MesBr) to generate PdBr(Mes)(CNAr^{Dipp2})$_2$ (Figure 1a). Remarkably, despite the additional presence of the encumbering Mes substituent, PdBr(Mes)(CNAr^{Dipp2})$_2$ retains its integrity in C_6D_6 solution at 80 °C for several days. Such behavior is notable since $L_nM(R)(CNR')$ species, especially those featuring sterically congested coordination environments, are well-known to form iminoacyl complexes (*i.e.*, $L_nM(C({=}NR')R)$) via migratory insertion.[9]

The resistance of PdBr(Mes)(CNAr^{Dipp2})$_2$ toward migratory insertion processes suggested that a CNAr^{Dipp2}-supported Pd system may effect Suzuki−Miyaura C−C bond formation.[10] Indeed, Pd(0) complexes of the type $Pd(PR_3)_2$ and $Pd(NHC)_2$ are well-known to be chemically competent for catalytic $C_{aryl}-C_{aryl}$ and $C_{aryl}-N$ bond coupling.[6,8,11] However, π-acidic ligands have received limited attention as ancillary groups in Pd-based cross-coupling chemistry. This is surprising given that electron-rich, monoligated Pd^0L species are proposed[6] as the catalytically active protagonists in cross-coupling schemes and may be further stabilized by a π-acidic ligand. Accordingly, in preliminary unoptimized screens, 5 mol % Pd(CNAr^{Dipp2})$_2$ was found to readily cross-couple MesBr with phenyl boronic acid ($PhB(OH)_2$) in 94% isolated yield in THF solution at room-temperature. Furthermore, the less hindered substrate, 2-MeC_6H_4Br, is similarly coupled with $PhB(OH)_2$ in 95% isolated yield.

The low-coordinate, electron-rich nature of Pd(CNAr^{Dipp2})$_2$ renders it active toward Lewis acidic substrates. Thus, treatment of Pd(CNAr^{Dipp2})$_2$ with TlOTf forms the Lewis acid−base adduct [TlPd(CNAr^{Dipp2})$_2$]OTf, which contains a one-coordinate Tl(I) center directly bound to Pd (Figure 1a).[12] Interestingly, Tl(I) acetate is known[13] to accelerate Pd-catalyzed C−C bond formation, and further investigations of [TlPd(CNAr^{Dipp2})$_2$]OTf in conjunction with the coupling chemistry outlined above may potentially elucidate the elementary steps governing this process.

Bis-isocyanide Pd(CNAr^{Dipp2})$_2$ also reacts smoothly with electronically unsaturated substrates. Addition of 1 equiv of dioxygen to Pd(CNAr^{Dipp2})$_2$ proceeds smoothly to the peroxo complex (η^2-O_2)Pd(CNAr^{Dipp2})$_2$, which serves as a structurally characterized complement to (O_2)Pd(CN*t*-Bu)$_2$ prepared by Otsuka (Figures 1a and S4.6).[3c] Most remarkably however, Pd(CNAr^{Dipp2})$_2$ reacts with 2 equiv of nitrosobenzene (PhNO) to form the dark red, diamagnetic complex Pd(κ^1-*N*-PhNO)$_2$(CNAr^{Dipp2})$_2$. Structural characterization of the latter revealed a distinctly square planar coordination geometry about Pd, thus strongly indicating the presence of a divalent metal center (Figure 1a). Metrical parameters supporting this claim include a $d(Pd-C_{iso})$ of 2.004(2) Å,[14] which is markedly longer than those of Pd(CNAr^{Dipp2})$_2$, and near linear $C_{iso}-N-C_{ipso}$ angles (174.6(2)°) reflective of decreased π-back-donation to the isocyanide ligands.[15] Furthermore, the N−O bond length of 1.291(2) Å for Pd(κ^1-*N*-PhNO)$_2$(CNAr^{Dipp2})$_2$ is longer than typically found in monomeric nitrosoarene compounds but shorter than standard N−O single bonds.[16] However, it is in fact considerably longer than the N−O bond length in divalent $PdCl_2$(κ^1-*N*-PhNO)$_2$ ($d(NO) = 1.209(3)$ Å).[17]

It is tempting to suggest that ligation to Pd(CNAr^{Dipp2})$_2$ results in a one-electron reduction of each κ^1-*N*-PhNO unit to its *O*-centered nitroxyl radical. Coupled with the observed diamagnetism of Pd(κ^1-*N*-PhNO)$_2$(CNAr^{Dipp2})$_2$, such a valence bond picture suggests that a singlet diradical form[18] may be a significant resonance contribution to its electronic structure. However, an alternative, MO description featuring a $(\sigma)^4(\pi)^4(\pi^*)^2$ singlet ground state with nondegenerate π^* components (a_g and a_u in C_i symmetry) may also accurately describe the electronic structure of the NO units in Pd(κ^1-*N*-PhNO)$_2$(CNAr^{Dipp2})$_2$. Indeed, restricted DFT calculations on the $S = 0$ state of the model Pd(κ^1-*N*-PhNO)$_2$(CNAr^{Ph2})$_2$ correspond well with this latter view (Figure 1b). Notably, both foregoing bonding descriptions correspond to a formal NO bond order of 1.5 for each κ^1-*N*-PhNO ligand, which to our knowledge is unprecedented in the coordination chemistry of nitroso compounds.[16] Accordingly, detailed investigations into Pd(κ^1-*N*-PhNO)$_2$(CNAr^{Dipp2})$_2$ and the chemistry accessible to zerovalent Pd(CNAr^{Dipp2})$_2$ are in progress.

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Supporting Information Available: Synthetic procedures, results of DFT, NMR, FTIR and crystallographic studies (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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