

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 preparations³ did not conclusively establish their monomeric nature, and subsequent reports⁴ strongly favored the trimeric formulation [Pd₃(CNR)₆]. These latter studies culminated in Francis’ structural determination of *triangulo*-[Pd(μ₂-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)₂C₆H₃), 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 Pd⁰L₂ complexes featuring strongly σ-donating phosphine⁶ (PR₃) or NHC^{7,8} ligands.

Access to orange Pd(CNAr^{Dipp2})₂ was achieved by Mg⁰ reduction of the dichloride PdCl₂(CNAr^{Dipp2})₂ in a 4:1 Et₂O/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(μ₂-CNR)(CNR)]₃ species.^{4d} Both the ¹H NMR (C₆D₆) 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 (∠(C1–Pd–C2) = 169.8(2)°, Figure 1a). Isocyanide bending is observed for one CNAr^{Dipp2} ligand (∠C1–N1–C3 = 163.6(4)°, while the other remains comparatively unperturbed (∠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 PdCl₂(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 PdCl₂(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 ¹H NMR spectroscopy, Pd(CNAr^{Dipp2})₂ does not decompose in C₆D₆ 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 ¹H NMR and

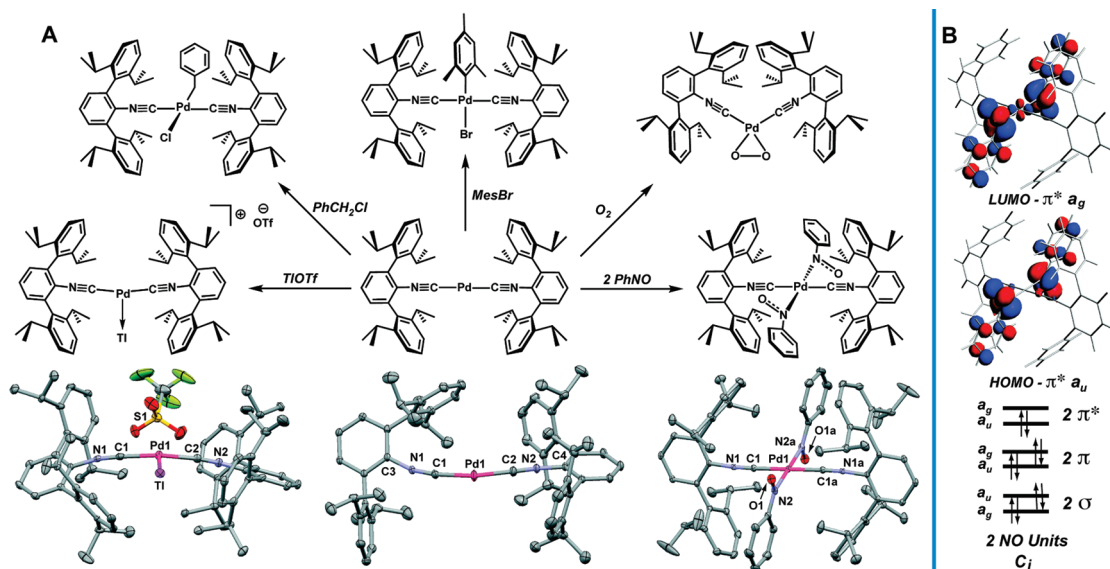


Figure 1. (A) Reaction pinwheel for Pd(CNAr^{Dipp2})₂ and molecular structures of [TIPd(CNAr^{Dipp2})₂][OTf] (left), Pd(CNAr^{Dipp2})₂ (center), and Pd(κ¹-N-PhNO)₂(CNAr^{Dipp2})₂ (right). (B) HOMO, LUMO, and qualitative MO diagram for Pd(κ¹-N-PhNO)₂(CNAr^{Dipp2})₂ based on restricted *S* = 0 DFT calculations.

FTIR spectroscopies, addition of another equivalent of $\text{CNAr}^{\text{Dipp2}}$ to $\text{Pd}(\text{CNAr}^{\text{Dipp2}})_2$ 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 ^1H NMR time scale down to -80°C .

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

The resistance of $\text{PdBr}(\text{Mes})(\text{CNAr}^{\text{Dipp2}})_2$ toward migratory insertion processes suggested that a $\text{CNAr}^{\text{Dipp2}}$ -supported Pd system may effect Suzuki–Miyaura C–C bond formation.¹⁰ Indeed, $\text{Pd}(0)$ complexes of the type $\text{Pd}(\text{PR}_3)_2$ and $\text{Pd}(\text{NHC})_2$ are well-known to be chemically competent for catalytic $\text{C}_{\text{aryl}}-\text{C}_{\text{aryl}}$ and $\text{C}_{\text{aryl}}-\text{N}$ 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 proposed⁶ 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 % $\text{Pd}(\text{CNAr}^{\text{Dipp2}})_2$ was found to readily cross-couple MesBr with phenyl boronic acid ($\text{PhB}(\text{OH})_2$) in 94% isolated yield in THF solution at room-temperature. Furthermore, the less hindered substrate, 2- $\text{MeC}_6\text{H}_4\text{Br}$, is similarly coupled with $\text{PhB}(\text{OH})_2$ in 95% isolated yield.

The low-coordinate, electron-rich nature of $\text{Pd}(\text{CNAr}^{\text{Dipp2}})_2$ renders it active toward Lewis acidic substrates. Thus, treatment of $\text{Pd}(\text{CNAr}^{\text{Dipp2}})_2$ with TiOTf forms the Lewis acid–base adduct $[\text{TiPd}(\text{CNAr}^{\text{Dipp2}})_2]\text{OTf}$, which contains a one-coordinate $\text{Ti}(\text{I})$ center directly bound to Pd (Figure 1a).¹² Interestingly, $\text{Ti}(\text{I})$ acetate is known¹³ to accelerate Pd-catalyzed C–C bond formation, and further investigations of $[\text{TiPd}(\text{CNAr}^{\text{Dipp2}})_2]\text{OTf}$ in conjunction with the coupling chemistry outlined above may potentially elucidate the elementary steps governing this process.

Bis-isocyanide $\text{Pd}(\text{CNAr}^{\text{Dipp2}})_2$ also reacts smoothly with electronically unsaturated substrates. Addition of 1 equiv of dioxygen to $\text{Pd}(\text{CNAr}^{\text{Dipp2}})_2$ proceeds smoothly to the peroxo complex $(\eta^2\text{-O}_2)\text{Pd}(\text{CNAr}^{\text{Dipp2}})_2$, which serves as a structurally characterized complement to $(\text{O}_2)\text{Pd}(\text{CN}t\text{-Bu})_2$ prepared by Otsuka (Figures 1a and S4.6).^{3c} Most remarkably however, $\text{Pd}(\text{CNAr}^{\text{Dipp2}})_2$ reacts with 2 equiv of nitrosobenzene (PhNO) to form the dark red, diamagnetic complex $\text{Pd}(\kappa^1\text{-N-PhNO})_2(\text{CNAr}^{\text{Dipp2}})_2$. 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 $d(\text{Pd}-\text{C}_{\text{iso}})$ of $2.004(2) \text{ \AA}$,¹⁴ which is markedly longer than those of $\text{Pd}(\text{CNAr}^{\text{Dipp2}})_2$, and near linear $\text{C}_{\text{iso}}-\text{N}-\text{C}_{\text{ipso}}$ angles ($174.6(2)^\circ$) reflective of decreased π -back-donation to the isocyanide ligands.¹⁵ Furthermore, the N–O bond length of $1.291(2) \text{ \AA}$ for $\text{Pd}(\kappa^1\text{-N-PhNO})_2(\text{CNAr}^{\text{Dipp2}})_2$ 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 $\text{PdCl}_2(\kappa^1\text{-N-PhNO})_2$ ($d(\text{NO}) = 1.209(3) \text{ \AA}$).¹⁷

It is tempting to suggest that ligation to $\text{Pd}(\text{CNAr}^{\text{Dipp2}})_2$ results in a one-electron reduction of each $\kappa^1\text{-N-PhNO}$ unit to its *O*-centered nitroxyl radical. Coupled with the observed diamagnetism of $\text{Pd}(\kappa^1\text{-N-PhNO})_2(\text{CNAr}^{\text{Dipp2}})_2$, such a valence bond picture suggests that a singlet diradical form¹⁸ 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 $\text{Pd}(\kappa^1\text{-N-PhNO})_2(\text{CNAr}^{\text{Dipp2}})_2$. Indeed, restricted DFT calculations on the $S = 0$ state of the model $\text{Pd}(\kappa^1\text{-N-PhNO})_2(\text{CNAr}^{\text{Ph2}})_2$ 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 $\kappa^1\text{-N-PhNO}$ ligand, which to our knowledge is unprecedented in the coordination chemistry of nitroso compounds.¹⁶ Accordingly, detailed investigations into $\text{Pd}(\kappa^1\text{-N-PhNO})_2(\text{CNAr}^{\text{Dipp2}})_2$ and the chemistry accessible to zerovalent $\text{Pd}(\text{CNAr}^{\text{Dipp2}})_2$ 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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