Non-Innocent Ligands

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Exploiting Non-Innocent Ligands to Prepare Masked Palladium(0) Complexes**

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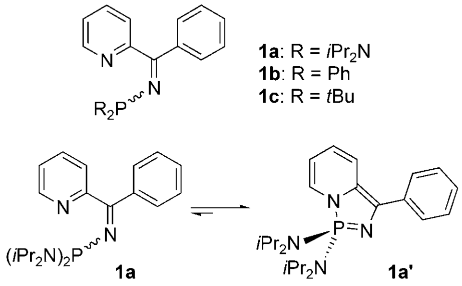
The last decade has shown an upsurge of interest in "non-innocent ligands" (NILs), a term originally coined by Jørgensen to describe metal scaffolds that are subject to redox changes at a site remote from the metal they support.[1] Such systems are well-established in biochemistry, being at the heart of many metalloproteins,[2] and are now found throughout coordination chemistry due to their diverse spectroscopic, magnetic, and electrochemical properties.[3,4] This versatility has extended the application of NILs to organometallic chemistry, where they have been used to enhance coordinated substrate reactivity.[5–8]

More recently, the term "NIL" has been expanded to include non-redox-active systems, where the metal's coordination sphere is perturbed through variation in ligand coordination mode and/or structure, which occurs in "response" to external stimuli.[9–12] These changes have been demonstrated to affect not only the rates of co-ligand dissociation, but also their intrinsic reactivity.[13,14]

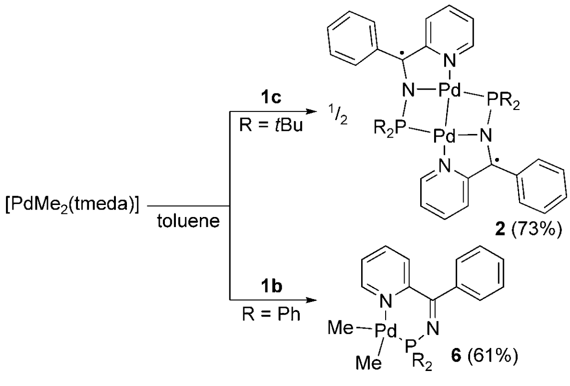
An unusual class of "responsive" NIL are the pyridyl-*N*-phosphinoimines **1**, with the "open" bis(diisopropylamino) derivative **1a** existing in tautomeric equilibrium with a "closed" anellated iminophosphorane form **1a'** (Scheme 1). As a result, **1a** has been shown to behave as either a κ^2-*PN* or a κ^1-*N* ligand depending on the nature of the partner metal, and to exhibit unusual redox behavior.[15,16] In contrast, the diphenyl analogue **1b** behaves only as a bidentate κ^2-PN_{Py} ligand and exhibits no tautomerism.[17]



Scheme 1. Pyridyl-*N*-phosphinoimines **1**.

Despite the importance of palladium catalysis in a variety of organic transformations,[17] there have been very few studies of Pd–NIL complexes.[13,19,20] This combination could help surmount the contradictory electronic and steric needs of the oxidative addition and reductive elimination steps key to many Pd-centered catalytic cycles through changes in NIL binding. To this end, we report here a study of the behavior of compounds **1** in the coordination sphere of palladium and the preparation of low-coordinate $\mathrm{Pd^0}$ complexes.

Since it is well-established that bulky ligands such as P*t*Bu$_3$ can promote the formation of unsaturated $\mathrm{Pd^0}$ species that show enhanced reactivity in Pd-catalyzed cross-coupling reactions, the P*t*Bu$_2$-substituted derivative **1c** (Scheme 2) was investigated.[21] Compound **1c** was prepared by modification of a known procedure and, as for **1b**, was found to exist purely in the "open" form.[17,22] Access to the target $\mathrm{Pd^0}$ complex was attempted through reaction of **1c** with equimolar quantities of [PdMe$_2$(tmeda)] (tmeda = *N*,*N*,*N'*,*N'*-tetramethylethylenediamine) using a variation on known methods.[23,24] The reaction proceeded to completion slowly over a



Scheme 2. Synthesis of complexes **2** and **6**.

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period of 7 d at room temperature, affording **2** as an intensely colored red/brown solid in 73 % yield (Scheme 2). Recrystallization from deuterobenzene afforded crystals of $\mathbf{2}\cdot 4\,C_6D_6$. X-ray diffraction revealed a centrosymmetric dimer structure in which a short Pd–Pd bond is supported by two P,N,N ligands each coordinated in a κ-NN,κ^1-P fashion (Figure 1).[22,25–27]

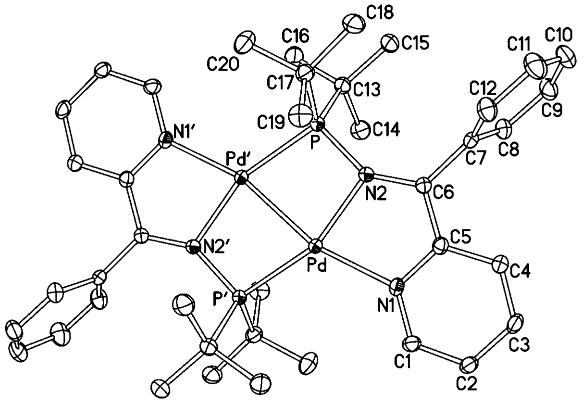
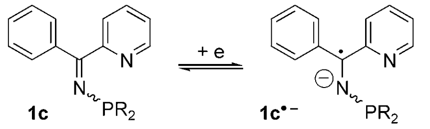


Figure 1. X-ray structure of $\mathbf{2}\cdot 4\,C_6D_6$ (50 % probability thermal ellipsoids, H atoms and solvate C_6D_6 molecules are omitted).[22,25] Primed atoms are generated by the inversion centre. Bond lengths (Å; calculated values in brackets[22]): Pd–Pd′ 2.4565(3) [2.511], Pd–P 2.8577(5) [2.922], Pd–P′ 2.2533(5) [2.300], Pd–N(1) 2.1376(15) [2.162], Pd–N(2) 2.0614(16) [2.100], P–N(2) 1.6795(16), N(2)–C(6) 1.348(2) [1.357], N(1)–C(5) 1.383(2) [1.395], C(5)–C(6) 1.433(2) [1.438]; angles [°]: Pd′-Pd-P′ 74.57(1) [74.7], Pd′-Pd-N(2) 84.94(4) [84.8], N(1)-Pd-P′ 121.21(5) [121.4], N(1)-Pd-N(2) 79.26(6) [79.0], N(2)-P-Pd′ 101.38(6) [101.3], Pd-N(2)-P 99.11(8) [99.1].

The Pd–Pd′ distance of **2** is at the lowest end of the range typically found for σ-bonds between square planar palladium centers (2.42–2.84 Å),[28] with few examples below 2.48 Å having been reported.[29–31]

The Pd atoms and two PN bridges of **2** are coplanar within experimental error, with the pyridine and phenyl rings being inclined to this plane by 3° and 84°, respectively; both C6 and N2 are planar (Σang = 360.00 and 359.75°). The geometry of the Pd′-P-N2-Pd bridge is dictated by an acute Pd-N2-P angle of 99.11(8)°, similar to that found in $[Cp_2Zr\{\kappa^2\text{-}PN\text{-}N(tBu)PEt_2\}IrH(Cp^*)]$.[32] Although **2** displays a long Pd–P contact of 2.8577(5) Å reminiscent of semi-bridging phosphine coordination,[33,34] here this palladium–phosphorus interaction is a consequence of geometric constraints imposed by the four-membered metallacycle, rather than a formal bonding interaction.

The N2–C6 bond of **2** (1.348(2) Å) is longer than in the related Pd^{II} complex $[PdCl_2(\kappa^2\text{-}PN\text{-}\mathbf{1b})]$ (1.278(2) Å) in which **1b** acts as a neutral PN-chelate, and is accompanied by a shortening of the C5–C6 bond (Δ = 0.08 Å).[17] These data reflect ligand **1c** having undergone a one-electron reduction, behaving as an open-shell monoanion $\mathbf{1c}^{\bullet-}$ rather than as a neutral P,N ligand **1c** (Scheme 3).[35] Thus **2** is best described as possessing a Pd^{I}–Pd^{I} core bearing a reduced organic scaffold.



Scheme 3. Two possible redox states for ligand **1c**.

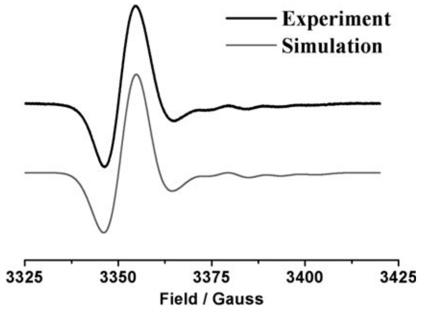


Figure 2. X-Band second derivative EPR (9.4 GHz, power = 0.02 mW, 293 K) spectrum of **2** (powder).

The formulation of **2** as $[\{Pd^{I}(\kappa^2\text{-}NN,\kappa^1\text{-}P\text{-}\mathbf{1c}^{\bullet-})\}_2]$ is supported by its solid-state EPR spectrum (Figure 2), which presents a 1:2:3:2:1 pattern consistent with an isolated ligand-centered unpaired electron coupling with two ^{14}N centers (splitting 8.80 G).[22] Any phosphorus contribution to the EPR pattern is assumed to be lost due to the large linewidths encountered. In conjunction with the experimentally determined g_{axial} values ($g_{(xy)} = 2.0062$; $g_{(z)} = 1.9894$), these data are consistent with an unpaired electron being localized on each of the P,N,N ligands. As a result, the distance between the two radical centers of **2** is significant (ca. 7 Å), which accounts for the absence of a half-field EPR signal, even at S-band frequency, where the relative intensity of this signal versus the main signal would be expected to be greatest.[22]

In agreement with the proposed diradical character, an effective magnetic moment (μ_{eff}) of 2.75 μ_B was obtained from a benzene solution of **2** using Evans' method. This value is intermediate between that expected for a broken symmetry (BS) biradical singlet (2.45 μ_B) and a high-spin (HS) triplet state (2.82 μ_B).[22,36] Despite repeated attempts, reliable values of μ_{eff} for **2** in the solid state were unforthcoming due to very low signal intensity. However, a broad, contact-shifted resonance centered at $\delta = -338.2$ ($\nu_{1/2} = 3880$ Hz) ppm was obtained for **2** by solid-state MAS ^{31}P NMR spectroscopy, consistent with its paramagnetic character.

The bonding situation in **2** was explored computationally using a combined extended Hückel theory (EHT)/density functional theory (DFT) study.[22,37] Complex **2** may be regarded as comprising two 15-electron T-shaped $[PdL_3]^+$ fragments bound through a single metal–metal bond, each of which possesses five occupied d-type frontier orbitals (FO) and a vacant orbital that has significant ligand character (Figure 3).[38] Interaction of the FOs of the two PdL_3 fragments leads to a set of ten metallic molecular orbitals (MO) and two ligand MOs. One metallic MO is strongly antibonding and destabilized in such a way that it becomes empty after interaction (LUMO+1). Consequently, Pd–Pd bonding occurs through a filled σ-type M–M bonding (HOMO−1) and a vacant σ*-type antibonding combination, implying that

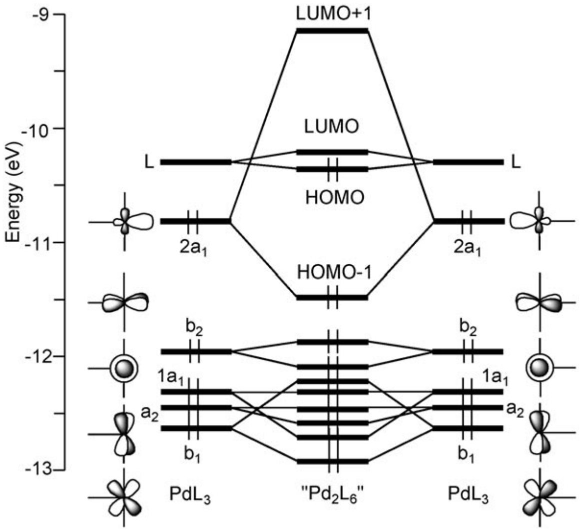


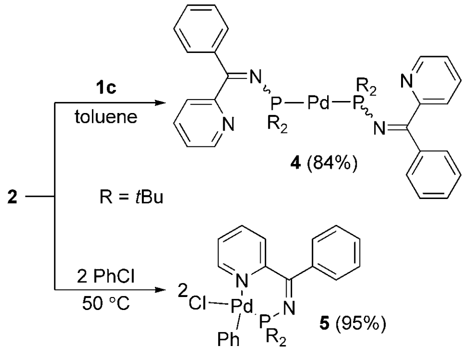
Figure 3. Qualitative EHT MO interaction diagram for **2** with C_{2v} symmetry.

two electrons are located on the ligand (HOMO). This is consistent with two 15-electron $[\mathrm{PdL_3}]^+$ fragments bound to each other through a single metal–metal bond giving rise to the expected 16-valence electron count.

This situation is fully supported by DFT calculations, with optimized bond distances and angles computed for **2** comparing well with the experimentally determined values. The HOMO and LUMO are close in energy and have a significant contribution localized on the ligand across the NCCN fragment (Figure 3).[22] Geometry optimization of both the HS triplet and the BS biradical singlet magnetic states of **2** reveals that they are close in energy (0.05 eV in favor of the BS state, although this value is probably somewhat overestimated by this functional), in agreement with the experimentally determined magnetic moment. The computed spin density is mostly localized on the nitrogen atoms and on one carbon atom over two of the ligands (0.13, 0.17, 0.18, 0.08, 0.33 electrons on N_1/N_1', N_2/N_2', C_2/C_2', C_4/C_4', C_6/C_6', respectively, for the triplet state).

The intriguing electronic structure and unusual synthesis of **2** prompted us to explore its chemistry in greater detail, in particular whether disruption of the bridging κ^1-*P* interaction (potentially important in supporting the Pd–Pd bond) would result in a change in structure. This was indeed the case with the addition of two equivalents of $\mathrm{PPh_3}$ to a [D$_6$]benzene solution of **2** leading to the quantitative formation of [Pd^0(PPh$_3$)(**1c**)] (**3**) according to ^{31}P NMR spectroscopy [AX spin system: $\delta(^{31}\mathrm{P}) = +26.7$ (d), $+106.6$ ppm (d) $\{^2J_{\mathrm{PP}} = 140$ Hz$\}$].[22] Further characterization and isolation of complex **3** was precluded by its facile decomposition affording "Pd black" within 1 h either in the solid state or in solution.

In an attempt to counter this problem and to further probe the reversibility of the **1c**/**1c**$^{\cdot-}$ interconversion, a toluene solution of **2** was treated with two equivalents of **1c**. This gave cleanly the stable, diamagnetic Pd^0 complex [Pd(κ^1-*P*-**1c**)$_2$] (**4**) [$\delta(^{31}\mathrm{P}) = +97.5$ ppm; cf. $\delta = 81.2$ ppm for **1c**], which was isolated in 84% yield (Scheme 4). The absence of pyridyl coordination is apparent from ^{1}H and ^{13}C NMR spectroscopic analysis since no characteristic high frequency coordination chemical shifts for the NCH resonances of the pyridyl moiety of **1c** are observed (cf. **5**).[17] Although crystals of **4** suitable for X-ray analysis were not forthcoming, a DFT study revealed that the most stable structure is indeed a 14-electron near-linear P-Pd-P complex.[22,37] Here, κ^1-*P* rather than κ^2-*P,N* coordination of **1c** is presumed to be favored due to the "soft" character of the Pd^0 center, something observed previously for a related P,N-scaffold.[39]



Scheme 4. Reactions of complex **2**.

Since it was apparent that displacement of the bridging κ^1-*P* motif of **2** by neutral donor ligands led to oxidation of **1c**$^{\cdot-}$ and metal reduction, other reactions leading to dimer cleavage were explored. A common transformation of L$_n$Pd–PdL$_n$ dimers is binuclear oxidative addition of organohalides RX to afford equimolar amounts of L$_n$Pd-X and L$_n$Pd-R.[27,40,41] Hence, **2** was treated with neat chlorobenzene at 50 °C for 2 h, which gave [PdCl(Ph)(κ^2-*PN*-**1c**)] (**5**) in 95% yield as a single regioisomer [$\delta(^{31}\mathrm{P}) = +97.3$ ppm] (Scheme 4). Complex **5** is structurally analogous to the methyl derivative [PdCl(Me)(κ^2-*PN*-**1b**)] reported previously.[17] The conversion of complex **2** into **5** in which both the organo- and halo-fragments are incorporated at the same Pd centre, is suggestive of a combined redox/κ^1-*P* dissociation process generating a low-coordinate Pd^0 intermediate, followed by two-electron oxidative addition, and not a binuclear process. Hence, complex **2** may be regarded as a "masked" form of Pd^0 in terms of its reactivity.

In contrast to the behavior of **1c**, reaction of P-diphenyl-substituted **1b** with [PdMe$_2$(tmeda)] under conditions identical to those used for the preparation of **2** rapidly afforded the dimethyl complex [PdMe$_2$(κ^2-*PN*-**1b**)] (**6**) [$\delta(^{31}\mathrm{P}) = +64.3$ ppm] as the only product; **6** was isolated in 61% yield and fully characterized in solution and the solid state (Scheme 2).[22] In contrast to the reactivity associated with **1c**, attempts to isolate the corresponding Pd^0 species were unsuccessful. Although reductive elimination of ethane from **6** was apparent [^{1}H NMR: $\delta = 0.78$ ppm (s)], over a period of 3 h the precipitation of "Pd black" occurred, with no tractable phosphorus-containing products being isolable.

Despite repeated attempts, no reaction was found to take place between the bis(diisopropylamino)-substituted derivative **1a**/**1a′** and [PdMe$_2$(tmeda)]. Contrastingly, **1a**/**1a′** reacts smoothly with an isoelectronic Rh$^{\mathrm{I}}$ complex [{RhCl(CO)$_2$}$_2$], to afford the P,N-chelated derivative [RhCl(CO)(κ^2-*PN*-**1a**)] in high yield.[15] This lack of reactivity has tentatively been ascribed to the significantly weaker Lewis basicity of the diamino phosphine moiety, which cannot displace the chelating tmeda.

In summary, it has been established that pyridyl-*N*-phosphino imine **1c** acts as an unusual type of non-innocent ligand in combination with Pd^0, behaving as both a "classical" redox-active as well as a "structurally responsive" NIL. Both theoretical and experimental investigations of complex **2** confirm its ligand-based biradical character over a range of temperatures in solution and the solid state. Significantly, perturbation of the palladium's coordination sphere in **2** by other donor ligands induces both a reversible electronic (ligand oxidation) and structural (κ^2-*NN*,κ^1-*P* to κ^2-*PN* to κ^1-*P*) reorganization, generating a palladium species that acts as a "masked" source of Pd^0 complex. Once again, this study highlights how slight modifications of the phosphorus substituents can substantially affect the chemical behavior of organophosphorus compounds. The catalytic utility of **2** is currently under investigation.

Experimental Section

All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk/glovebox techniques.

2: [$PdMe_2$(tmeda)] (173 mg, 0.69 mmol) and **1c** (224 mg, 0.69 mmol) were dissolved in C_6H_6 (10 mL) and allowed to react for 7 d. The crystals that formed were isolated, washed with benzene (3 × 2 mL), and dried in vacuum (24 h), giving **2**·4 C_6D_6 as a dark red/brown material (217 mg, 73 %). Elemental analysis, found: C 63.70, H 8.37, N 4.79 %; calcd: C 63.94, H 8.55, N 4.66 %.

3: To a C_6D_6 (0.8 mL) solution of **2** (10 mg, 0.01 mmol) was added PPh_3 (6 mg, 0.02 mmol). Following heating at 50 °C for 0.5 h a brown solution containing **3** was obtained. $^{31}P\{^1H\}$ NMR (161.91 MHz, C_6D_6): $\delta = 26.7$ (1 P, d, $^2J_{PP} = 140$), 106.6 ppm (1 P, d, $^2J_{PP} = 140$).

4: A toluene (5 mL) solution of **2** (80 mg, 0.09 mmol) was added to **1c** (60 mg, 0.18 mmol) in toluene (5 mL) and stirred for 4 d. Removal of volatile components in vacuum gave **4** as a red solid (117 mg, 84 %). Elemental analysis, found: C 63.09, H 7.11, N 7.43 %; calcd: C 63.28, H 7.17, N 7.38 %.

5: A chlorobenzene solution of **2** (18 mg, 0.02 mmol) was heated at 50 °C for 2 h. MS (FAB^+) *m*/*z*: 509 $[M-Cl]^+$, MS (EI^+) *m*/*z*: 469 $[M-Ph]^+$.

6: [$PdMe_2$(tmeda)] (150 mg, 0.595 mmol) and **1b** (217 mg, 0.595 mmol) were each dissolved in toluene and the solutions combined, resulting in the precipitation of an orange solid (2 d). This was isolated by filtration, washed with cold (0 °C) toluene, and dried in vacuum, leaving **6** as an orange solid (305 mg, 61 %). Elemental analysis, found: C 61.92, H 5.06, N 5.49 %; calcd: C 62.10, H 5.01, N 5.57 %.

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