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Redox-Active Ligands

Redox-Active Ligand-Induced Homolytic Bond Activation**

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Abstract: Coordination of the novel redox-active phosphine-appended aminophenol pincer ligand (PNO\(_{2}^{\text{H}}\)) to Pd\(_{0}^{\text{II}}\) generates a paramagnetic complex with a persistent ligand-centered radical. The complex undergoes fully reversible single-electron oxidation and reduction. Homolytic bond activation of diphenyl disulfide by the single-electron reduced species leads to a ligand-based mixed-valent dinuclear palladium complex with a single bridging thiolate ligand. Mechanistic investigations support an unprecedented intramolecular ligand-to-disulfide single-electron transfer process to induce homolytic S–S cleavage, thereby releasing a thiol (sulfanyl) radical. This could be a new strategy for small-molecule bond activation.

Redox-active ligands are frequently encountered in important natural processes mediated by metalloenzymes.\(^{[1]}\) In inorganic chemistry, these systems have long been considered to be primarily a spectroscopic curiosity, with major focus on understanding the electronic structure and bonding within homoleptic systems.\(^{[2]}\) Recently, heteroleptic complexes have been shown to offer unique reactivity in stoichiometric activation reactions and in catalysis, since the redox-active nature of these ligands allows their use as an electron reservoir during (catalytic) turnover.\(^{[3]}\) The majority of redox-active systems are based on nitrogen or oxygen donors,\(^{[4]}\) with aminophenol-based N,O ligands as archetypical redox-active systems that can span three oxidation states.\(^{[5]}\) In contrast and at odds with the relevance of phosphorus ligands in homogeneous catalysis, few phosphine-containing redox-active ligands exist.\(^{[6,7]}\) Thomas and co-workers recently described an (o-anilino)phenylphosphine ligand that is susceptible to oxidation in the coordination sphere of Cu\(^{2+}\), but radical P–P coupling precluded the use of this scaffold as a reversible redox-active ligand.\(^{[8]}\) Installment as a redox-innocent entity adjacent to a redox-active framework is less likely to affect the coordinative properties at phosphorus, but relatively few of these ligands have been developed.\(^{[9,10]}\)

Bond homolysis is a very useful reaction to probe for accessible ligand-based reactivity. Established ligand-mediated bond activation (and formation) reactions classify overall as two-electron processes.\(^{[11–14]}\) Metal-mediated one-electron homolysis is much rarer,\(^{[15]}\) while reductive homolytic bond fission originating from ligand-based overall single-electron transfer is, to the best of our knowledge, unknown (Figure 1). Methodologies that facilitate odd-electron transfer processes will allow the controlled generation of reactive substrate radicals for synthetic chemistry.\(^{[16]}\)

Figure 1. a) Typical reactivity concerning bond homolysis by noble metal complexes. b) Unprecedented reductive single-electron transfer from a redox-active ligand to a disulfide substrate, generating a thiolate and a thyl radical.

Recently, we reported a tridentate redox-active NNO ligand that accommodates radical-type C–H amination reactivity on a Pd\(^{2+}\) platform.\(^{[17]}\) In order to arrive at a redox-active phosphine ligand, we sought to merge the redox-active aminophenol framework with a flanking diphenylphosphine group. Addition of this (sterically encumbered) donor should impact the redox properties of the N,O moiety upon coordination to a transition metal, relative to the previous NNO scaffold. We herein describe the facile synthesis and electronic structure of a phosphorus ligand that is ‘redox active’ when coordinated to Pd\(^{2+}\). This system, which displays a markedly lower reduction potential than the Pd complex with our previously reported NNO system,\(^{[17]}\) is able to facilitate radical-type homolytic bond activation of disulfides, with formation of a well-defined ligand-based mixed-valent dinuclear complex.

The novel aminophenolphosphine ligand PNO\(^{12}^{\text{H}}\) (\(^{31}\)P NMR \(\delta = -20.25\)) was prepared as an air-sensitive
white solid in 58% overall yield through a two-step procedure from commercially available o-iodoaniline and 3,5-di-tert-butylcatechol.\textsuperscript{[18]} Reaction with [PdCl(MeCN)\textsubscript{2}] gave complex \textbf{1} as an orange solid in 67% yield (\textsuperscript{31}P NMR \(\delta = 43.98\)). Addition of triethylamine resulted in a rapid color change to green, and subsequent exposure to air afforded the dark-red paramagnetic species \textbf{2} in 78% yield (Scheme 1). Magnetic susceptibility measurements (Evans/C\textsubscript{29} method) showed an effective magnetic moment (\(\mu\text{eff}\)) of 1.81 \(\mu\text{B}\), thus indicating an \(S = \frac{1}{2}\) ground state. Hence, this species is best formulated as [PdCl(PNO\textsuperscript{iso})], and this assignment was confirmed by single-crystal X-ray diffraction (Figure 2; ISQ = iminosemiquinonato).

**Figure 2.** a) Displacement ellipsoid plot (50% probability level) of complex \textbf{2} at 110(2) K. b) Relevant experimental (XRD) and computed (DFT) metric parameters support the PNO\textsuperscript{iso} state in \textbf{2}. Selected bond angles (\(^{\circ}\)): N–Pd–Cl, 174.90(5); P–Pd–O, 167.43(4); P–Pd–Cl, 94.038(17); N–Pd–O, 81.16(6).

Complex \textbf{2} shows a slightly distorted square-planar geometry with an acute \(\sigma\text{N1–Pd}–\text{O1}\) angle of 81.16(6)\(^\circ\). Palladium–ligand bond lengths and angles in \textbf{2} compare well with PdCl complexes bearing redox-innocent monoanionic PNO pincers.\textsuperscript{[19]} The metric parameters found for the amidenophenolate fragment support the ISQ oxidation state of the ligand\textsuperscript{[20]} and these data are reproduced by DFT (b3-lyp/def2-TZVP) optimized geometric parameters for the doublet PNO\textsuperscript{iso} ground state. X-band EPR spectroscopy in toluene at 298 K revealed hyperfine couplings with \(^{105}\text{Pd}\), \(^{31}\text{P}\), \(^{14}\text{N}\), and three \(^{3}\text{H}\) nuclei (see Table S1 in the Supporting Information). The \(g\text{iso}\) value of 2.0052 suggests coordination of \(\text{PNO}\textsuperscript{iso}\) for details of the redox chemistry). Chemical reduction of \textbf{2} with [CoC\textsubscript{5}] in CH\textsubscript{2}Cl\textsubscript{2} furnished air-sensitive diamagnetic complex \textbf{3}, formulated as [CoC\textsubscript{5}][PdCl(PNO\textsuperscript{AP})] (\(^{31}\text{P}\) NMR \(\delta = 36.56\); AP = amidophenolato). To assess the steric constraint imposed on the Pd center by the flanking phosphine donor, complex \textbf{3} was exposed to exogenous phosphines. No reaction was observed with PPh\textsubscript{3} but coordination of PMe\textsubscript{3} rapidly produced complex \textbf{4} (\(^{31}\text{P}\) NMR \(\delta = 41.52\) (d) and \(-10.61\) (d); \(J_{P-P} 40.2\) Hz), formulated as [Pd(PMe\textsubscript{3})(PNO\textsuperscript{AP})] (Scheme 2).

Oxidative addition of a disulfide to low-valent Pd is usually a two-electron process.\textsuperscript{[21]} Given the demonstrated reversible one-electron chemistry of species \textbf{3} at a mild potential, we sought to investigate its reactivity toward disulfides. Addition of TIPF\textsubscript{4} to a suspension of \textbf{3} in benzene in the presence of an equimolar amount of diphenyl disulfide produced the soluble paramagnetic species \textbf{5}. Magnetic susceptibility measurements of \textbf{5} at 298 K using Evans’ method gave an effective magnetic moment (\(\mu\text{eff}\)) of 1.90 \(\mu\text{B}\), thus indicating an \(S = \frac{1}{2}\) ground state. This observation implies one-electron oxidation of PNO\textsuperscript{AP} to PNO\textsuperscript{iso}. CSI-MS studies in benzene indicate the presence of a dinuclear species in solution at \(m/z\ 1279.28\ [M]^+\), formulated as [Pd\(_4\) (PMe\textsubscript{3})\textsuperscript{2+} (PNO\textsuperscript{iso})\textsuperscript{2-} (PNO\textsuperscript{iso})\textsuperscript{2-}] (Scheme 3).

\textbf{Scheme 1.} Synthetic route to complexes \textbf{1} and \textbf{2}.

\textbf{Figure 3.} a) Experimental and simulated EPR spectrum of \textbf{2} (toluene, RT) Freq = 9.366829 GHz, \(T = 298\) K, Mod Ampl. = 1 Gauss, power = 20 mW. Simulated (DFT) g value and hyperfine couplings A (MHz): \(g\text{iso} = 2.0052 (2.0062); A^{\text{Pd}} = 10.70 (+8.61); A^{\text{Cl}} = -13.55 (-16.04); A^{\text{N}} = 16.45 (+11.0); A^{\text{P}} = -4.90 (-5.06); A^{\text{N}} = -7.18 (-5.66); A^{\text{Cl}} = (-2.15) NR = not resolved; DFT parameters: ORCA (b3-lyp, def2-TZVP). b) DFT (b3-lyp/def2-TZVP) calculated spin-density plot for \(\textbf{2}\). +0.07 V and \(-0.75\) V vs. Fe/Fe\textsuperscript{3+} respectively. Reversible ligand-based redox chemistry was also observed by UV/Vis spectroelectrochemistry in an optically transparent thin-layer electrolysis (OTTLE) cell (see the Supporting Information for details of the redox chemistry). Chemical reduction of \textbf{2} with [CoC\textsubscript{5}] in CH\textsubscript{2}Cl\textsubscript{2} resulted in [CoC\textsubscript{5}][PdCl(PNO\textsuperscript{AP})] (\(^{31}\text{P}\) NMR \(\delta = 36.56\); AP = amidophenolato). To assess the steric constraint imposed on the Pd center by the flanking phosphine donor, complex \textbf{3} was exposed to exogenous phosphines. No reaction was observed with PPh\textsubscript{3} but coordination of PMe\textsubscript{3} rapidly produced complex \textbf{4} (\(^{31}\text{P}\) NMR \(\delta = 41.52\) (d) and \(-10.61\) (d); \(J_{P-P} 40.2\) Hz), formulated as [Pd(PMe\textsubscript{3})(PNO\textsuperscript{AP})] (Scheme 2).

\textbf{Scheme 2.} Synthetic route to complexes \textbf{3} and \textbf{4}.

**Figure 3.** a) Displacement ellipsoid plot (50% probability level) of complex \textbf{2} at 110(2) K. b) Relevant experimental (XRD) and computed (DFT) metric parameters support the PNO\textsuperscript{iso} state in \textbf{2}. Selected bond angles (\(^{\circ}\)): N–Pd–Cl, 174.90(5); P–Pd–O, 167.43(4); P–Pd–Cl, 94.038(17); N–Pd–O, 81.16(6).

Cyclic voltammetry of \textbf{2} in CH\textsubscript{2}Cl\textsubscript{2} solution shows fully reversible one-electron oxidation and reduction events at
SPh)(PNO)2]. UV/Vis spectroscopy shows characteristic absorption bands for both PNOAP and PNOSSO ligand fragments. X-band EPR spectroscopy of compound 5 in toluene at 298 K showed an isotropic signal with no resolved hyperfine couplings. The $g_{\text{iso}}$ value of 2.0041 supports the presence of a PNO ISQ ligand radical. This assignment was corroborated by X-ray diffraction (Figure 4).

The occurrence of outer-sphere electron transfer from 2 to PhSSPh is excluded on the basis of their relative redox potentials. The formation of species 5 (Scheme 3) is proposed to involve initial chloride dissociation and disulfide coordination. Dialkyl disulfides have a higher S–S bond dissociation energy than diaryl disulfides and are thus less prone to undergoing bond homolysis.

Using $\text{d}$(tert-butyldisulfide) instead of PhSSPh allowed observation of the corresponding Pd–disulfide adduct by NMR spectroscopy. The $^{31}$P NMR chemical shift of $\delta = 39.82$ is similar to that of neutral 4. The non-equivalent tert-buty1 groups of the substrate are shifted upfield in the $^1$H NMR spectrum, which otherwise resembles that of 4 (see the Supporting Information). Subsequent intramolecular ligand-to-substrate single-electron transfer results in homolytic S–S bond cleavage with formation of [PNOSSO(PdSPh)] and release of a PhS radical. This thyl radical can either undergo self-recombination or react with a ‘vacant’ [PNOAPd] complex, thus forming PhSSPh or a second equivalent of [PNOSSO(PdSPh)], respectively. The final step is the formation of the mixed-valent [(PNOSSO)Pd(μ-SPh)Pd(PNOAP)] (5), through coordination of a sulfur lone pair in [PNOSSO(PdSPh)] to free [PNOAPd]. Starting with a 4:1 ratio of 3/PhSSPh also leads to the clean production of complex 5, thus supporting this pathway. Detection of thyl radicals by EPR spectroscopy with DMPO ($\text{DMPO}$ = 5,5-dimethyl-1-pyrroline N-oxide) as a spin-trapping agent was unsuccessful, probably owing to a high recombination rate relative to the generation rate of these thyl radicals, the short lifetime of DMPO·(C₅SPh) adducts, and the competitive reaction of 3 with DMPO. However, GC–MS analysis of the reaction mixture confirmed the presence of diphenylsulfide, which is generated from the reaction of PhS with the solvent benzene. Using a mixture of PhSSPh and $\text{d}$(p-tolyldisulfide)
led to co-formation of phenyl(p-tolyl)disulfide, as detected by GC–MS, thus supporting the intermediary of thyl radicals created by this ligand-to-substrate electron transfer process.

In conclusion, the first example of a phosphine ligand appended to a redox-active aminophenol framework is reported. This PNO\textsubscript{SS} pincer ligand can coordinate to Pd\textsuperscript{II} as a neutral (1), radical monoanionic (2), or dianionic scaffold (3, 4), as supported by spectroscopic, X-ray crystallography, and computational data. Cyclic voltammetry and spectreroelectrochemistry demonstrate reversible single-electron redox events for complex 2. The bulky phosphine arm and rigid backbone enforce considerable steric crowding around the Pd center. One-electron reduction generates complex 3, which is a competent reagent for homolytic bond activation of disulfides through ligand-to-substrate single-electron transfer. The resulting dinuclear Pd species 5, featuring a mononiohila bridgehead, contains a unique mixed-valence ligand set, with one PNO\textsubscript{SS} and one PNO\textsubscript{AP} unit. The introduction of a flanking phosphine group could allow the expansion of the concept of ligand-induced electron transfer and radical-type reactivity to “softer” low-valent noble metals.

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The simulated spectrum and calculated hyperfine couplings correlate well with the experimental data, with the exception of some hyperfine interactions (see the Supporting Information).


Reduction potential vs. SCE: PhSSPh/Co 1.6 V; tBuSSBu/Co 2.71 V. Bond dissociation energy (BDE) of PhSSPh 55.0 kcal mol⁻¹; dialkyldisulfides 65 kcal mol⁻¹; MeSSMe: 73.2 kcal mol⁻¹.