

Redox-Active Ligand-Induced Homolytic Bond Activation**

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Dedicated to Professor Thomas B. Rauchfuss on the occasion of his 65th birthday

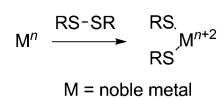
Abstract: Coordination of the novel redox-active phosphine-appended aminophenol pincer ligand (PNO^{H2}) to Pd^{II} generates a paramagnetic complex with a persistent ligand-centered radical. The complex undergoes fully reversible single-electron oxidation and reduction. Homolytic bond activation of diphenyldisulfide 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 thiyl (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 frameworks 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^I, 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]

Common: two-electron homolysis of e.g. disulfides



Unknown: ligand-induced reductive one-electron bond homolysis

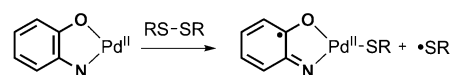


Figure 1. a) Typical reactivity concerning bond homolysis by noble metal complexes. b) Unprecedented reductive single-electron transfer from a redox-active ligand to a disulfide substrate, generating a thiolate and a thiyl radical.

Recently, we reported a tridentate redox-active NNO ligand that accommodates radical-type C–H amination reactivity on a Pd^{II} 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^{II}. 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.

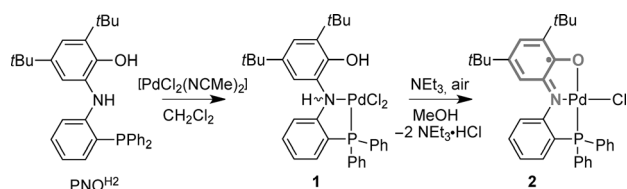
The novel aminophenolphosphine ligand PNO^{H2} (³¹P NMR $\delta = -20.25$) was prepared as an air-sensitive

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[**] Research funded by the European Research Council (ERC Starting Grant 279097 to J.I.v.d.V.). We thank Ed Zuidinga for assistance with ESI-MS measurements.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201410048>.



Scheme 1. Synthetic route to complexes **1** and **2**.

white solid in 58 % overall yield through a two-step procedure from commercially available *o*-iodoaniline and 3,5-di-*tert*-butylcatechol.^[18] Reaction with $[\text{PdCl}_2(\text{MeCN})_2]$ gave complex **1** as an orange solid in 67 % yield (^{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 **2** in 78 % yield (Scheme 1). Magnetic susceptibility measurements (Evans' method) showed an effective magnetic moment (μ_{eff}) of $1.81 \mu_{\text{B}}$, thus indicating an $S = 1/2$ ground state. Hence, this species is best formulated as $[\text{PdCl}(\text{PNO}^{\text{ISQ}})]$, and this assignment was confirmed by single-crystal X-ray diffraction (Figure 2; ISQ = iminosemiquinonato).

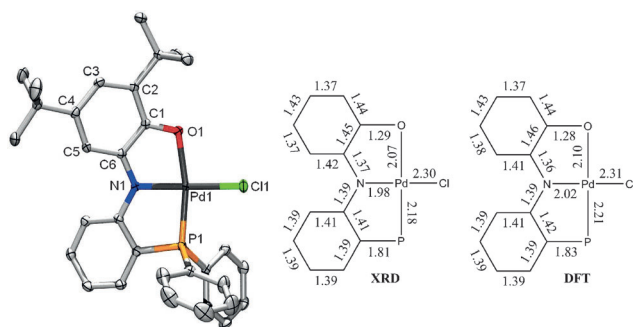


Figure 2. a) Displacement ellipsoid plot (50% probability level) of complex **2** at 110(2) K. b) Relevant experimental (XRD) and computed (DFT) metric parameters support the PNO^{ISQ} state in **2**. Selected bond angles [°]: $\text{N}_1\text{-Pd}_1\text{-Cl}_1$ 174.90(5); $\text{P}_1\text{-Pd}_1\text{-O}_1$ 167.43(4); $\text{P}_1\text{-Pd}_1\text{-Cl}_1$ 94.038(17); $\text{N}_1\text{-Pd}_1\text{-O}_1$ 81.16(6).

Complex **2** shows a slightly distorted square-planar geometry with an acute $\angle \text{N}_1\text{-Pd}_1\text{-O}_1$ angle of $81.16(6)^\circ$. Palladium–ligand bond lengths and angles in **2** compare well with PdCl complexes bearing redox-innocent monoanionic PNO pincers.^[19] The metric parameters found for the amidophenolate fragment support the ISQ oxidation state of the ligand^[20] and these data are reproduced by DFT (b3-lyp/def2-TZVP) optimized geometric parameters for the doublet PNO^{ISQ} ground state. X-band EPR spectroscopy in toluene at 298 K revealed hyperfine couplings with ^{105}Pd , ^{31}P , ^{14}N , and three ^1H nuclei (see Table S1 in the Supporting Information). The g_{iso} value of 2.0052 suggests coordination of a PNO^{ISQ} ligand radical to Pd^{II} .^[21] The calculated spin density for **2** predominantly resides on the ligand (97 % total spin density, 21 % on the iminosemiquinonato nitrogen), in agreement with EPR observations (Figure 3 and the Supporting Information).

Cyclic voltammetry of **2** in CH_2Cl_2 solution shows fully reversible one-electron oxidation and reduction events at

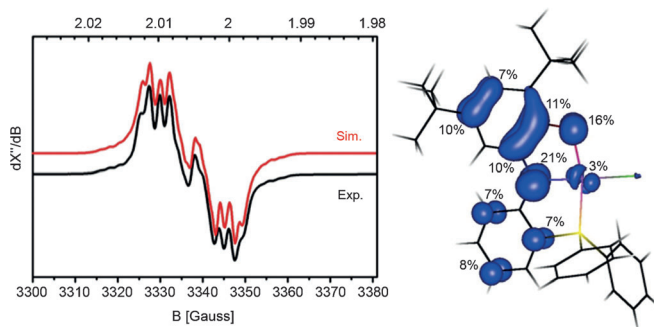
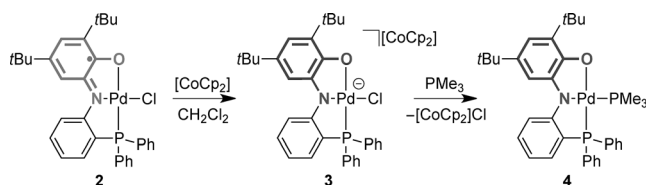


Figure 3. a) Experimental and simulated EPR spectrum of **2** (toluene, RT) Freq = 9.366829 GHz, $T = 298$ K, Mod Ampl. = 1 Gauss, power = 20 mW. Simulated (DFT) g value and hyperfine couplings A (MHz): g_{iso} 2.0052 (2.0062); $A_{\text{iso}}^{\text{Pd}}$ +10.70 (+8.61); $A_{\text{iso}}^{\text{P}}$ −13.55 (−16.04); $A_{\text{iso}}^{\text{N}}$ +16.45 (+11.0); $A_{\text{iso}}^{\text{H}^1}$ −4.90 (−5.06); $A_{\text{iso}}^{\text{H}^2}$ (NR) (−0.78); $A_{\text{iso}}^{\text{H}^3}$ −4.95 (−5.24); $A_{\text{iso}}^{\text{H}^4}$ (NR) (2.60); $A_{\text{iso}}^{\text{H}^5}$ −7.18 (−5.66); $A_{\text{iso}}^{\text{H}^6}$ (NR) (2.15) NR = not resolved; DFT parameters: ORCA (b3-lyp, def2-TZVP). b) DFT (b3-lyp/def2-TZVP) calculated spin-density plot for **2**.

+0.07 V and −0.75 V vs. Fc/Fc^+ , 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 **2** with $[\text{CoCp}_2]$ in CH_2Cl_2 furnished air-sensitive diamagnetic complex **3**, formulated as $[\text{CoCp}_2][\text{PdCl}(\text{PNO}^{\text{AP}})]$ (^{31}P NMR $\delta = 36.56$; AP = amidophenolato). To assess the steric constraint imposed on the Pd center by the flanking phosphine donor, complex **3** was exposed to exogenous phosphines. No reaction was observed with PPh_3 but coordination of PMe_3 rapidly produced complex **4** (^{31}P NMR $\delta = 41.52$ (d) and −10.61 (d); $J_{\text{P-P}}$ 40.2 Hz), formulated as $[\text{Pd}(\text{PMe}_3)(\text{PNO}^{\text{AP}})]$ (Scheme 2).



Scheme 2. Synthetic route to complexes **3** and **4**.

Oxidative addition of a disulfide to low-valent Pd is usually a two-electron process.^[22] Given the demonstrated reversible one-electron chemistry of species **3** at a mild potential, we sought to investigate its reactivity toward disulfides. Addition of TIPF_6 to a suspension of **3** in benzene in the presence of an equimolar amount of diphenyldisulfide produced the soluble paramagnetic species **5**. Magnetic susceptibility measurements of **5** at 298 K using Evans' method gave an effective magnetic moment (μ_{eff}) of $1.90 \mu_{\text{B}}$, thus indicating an $S = 1/2$ ground state. This observation implies one-electron oxidation of PNO^{AP} to PNO^{ISQ} . CSI-MS studies in benzene indicate the presence of a dinuclear species in solution at m/z 1279.28 $[M]^+$, formulated as $[\text{Pd}_2(\mu$

SPh)(PNO)₂]. UV/Vis spectroscopy shows characteristic absorption bands for both PNO^{AP} and PNO^{ISO} 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*_{iso} value of 2.0041 supports the presence of a PNO^{ISO} ligand radical. This assignment was corroborated by X-ray diffraction (Figure 4).

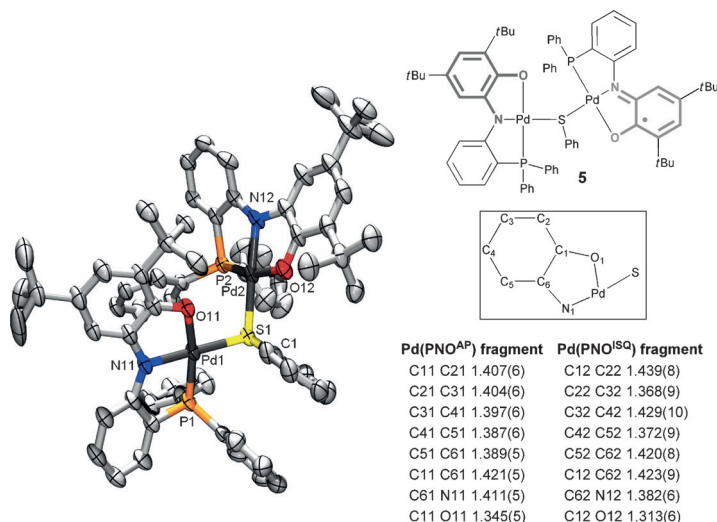
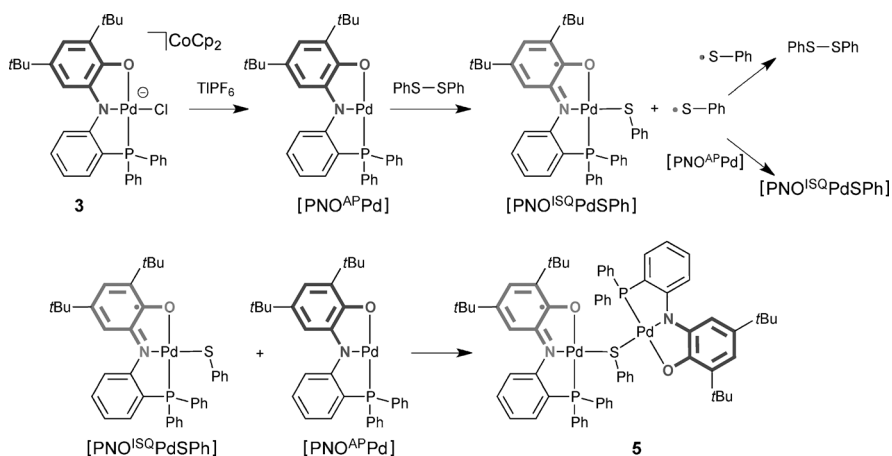


Figure 4. a) Displacement ellipsoid plot (50% probability level) of complex **5** at 110(2) K. Disorder in the 3,5-*t*Bu₂Ph ring at Pd₂ and disordered solvent omitted for clarity. b) metric parameters for the PNO^{ISO} and PNO^{AP} fragments in **5**. Selected additional bond lengths [Å] and angles [°]: Pd1–N11 1.990(3); Pd2–N12 2.011(3); Pd1–O11 2.041(3); Pd2–O12 2.063(3); Pd1–S1 2.3203(9); Pd2–S1 2.3012(10); Pd1–S1–Pd2 104.58(4); N11–Pd1–S1 178.45(10); N12–Pd2–S1 175.5(4); N11–Pd1–O11 82.63(12); N12–Pd2–O12 81.5(3). Atom numbering: first digit = atom number, second digit = ligand number.

The molecular structure contains one thiophenolate unit bridging two Pd^{II}(PNO) centers. This bridging monothiolate motif, although not unique, is rather uncommon, particularly with Pd.^[23] Strikingly, the observed metric parameters indicate different oxidation states for the two PNO ligands present, that is, the amidophenolato (N11–O11) and the iminosemiquinonato (N12–O12) forms. VT-EPR spectroscopic data indicate facile electron exchange between the PNO^{AP} and the PNO^{ISO} moieties of **5** in solution (see the Supporting Information). We are not aware of similar examples of monobridged dinuclear complexes that show ligand-based mixed valency.^[24] For homodinuclear reaction centers, the mixed valency is typically metal-centered or shared between the metal and (bridging) ligand.^[25] Systems with separated mixed-valent ligand-based redox centers could be of interest for studying intramolecular electron-transfer processes and potentially also for ligand-

assisted redox catalysis.^[26] Selective formation of such species through controllable synthetic procedures from stable monomeric precursors might allow the study of these electronic configurations.

The occurrence of outer-sphere electron transfer from **2** to PhSSPh is excluded on the basis of their relative redox potentials.^[26] 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.^[27] Using di(*tert*-butyl)disulfide instead of PhSSPh allowed observation of the corresponding Pd–disulfide adduct by NMR spectroscopy. The ³¹P NMR chemical shift of $\delta = 39.82$ is similar to that of neutral **4**. The non-equivalent *tert*-butyl groups of the substrate are shifted upfield in the ¹H 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 [PNO^{ISO}PdSPh] and release of a PhS[•] radical. This thiyl radical can either undergo self-recombination or react with a ‘vacant’ [PNO^{AP}Pd] complex, thus forming PhSSPh or a second equivalent of [PNO^{ISO}PdSPh], respectively. The final step is the formation of the mixed-valent [(PNO^{ISO})Pd(μ -SPh)Pd(PNO^{AP})] (**5**), through coordination of a sulfur lone pair in [PNO^{ISO}PdSPh] to free [PNO^{AP}Pd]. Starting with a 4:1 ratio of 3/PhSSPh also leads to the clean production of complex **5**, thus supporting this pathway. Detection of thiyl radicals by EPR spectroscopy with DMPO (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 thiyl radicals, the short lifetime of DMPO·(SPh) adducts,^[28] and the competitive reaction of complex **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 di(*p*-tolyl)disulfide



Scheme 3. Proposed mechanism for the formation of dinuclear [(PNO^{ISO})Pd(μ -SPh)Pd(PNO^{AP})] (**5**) with mixed valency in the two PNO scaffolds.

led to co-formation of phenyl(*p*-tolyl)disulfide, as detected by GC–MS, thus supporting the intermediacy of thiyl 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^{H2} pincer ligand can coordinate to Pd^{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 spectroelectrochemistry 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 monothiolate bridgehead, contains a unique mixed-valence ligand set, with one PNO^{ISO} and one PNO^{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.

Received: October 13, 2014

Revised: October 30, 2014

Published online: November 27, 2014

Keywords: bond activation · mixed valency · palladium · phosphane ligands · redox-active ligands

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