

## Redox-Active Ligands

## Redox-Active Ligand-Induced Homolytic Bond Activation\*\*

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

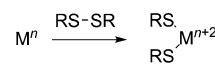
**Abstract:** Coordination of the novel redox-active phosphine-appended aminophenol pincer ligand (PNO<sup>H2</sup>) to Pd<sup>II</sup> generates a paramagnetic complex with a persistent ligand-centered radical. The complex undergoes fully reversible single-electron oxidation and reduction. Homolytic 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.<sup>[1]</sup> 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.<sup>[2]</sup> 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.<sup>[3]</sup> The majority of redox-active frameworks are based on nitrogen or oxygen donors,<sup>[4]</sup> with aminophenol-based *N,O* ligands as archetypical redox-active systems that can span three oxidation states.<sup>[5]</sup> In contrast and at odds with the relevance of phosphorus ligands in homogeneous catalysis, few phosphine-containing redox-active ligands exist.<sup>[6,7]</sup> Thomas and co-workers recently described an (*o*-anilino)phenylphosphine ligand that is susceptible to oxidation in the coordination sphere of Cu<sup>I</sup>, but radical P–P coupling precluded the use of

this scaffold as a reversible redox-active ligand.<sup>[8]</sup> 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.<sup>[9,10]</sup>

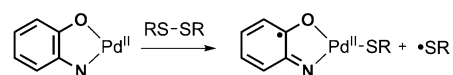
Bond homolysis is a very useful reaction to probe for accessible ligand-based reactivity. Established ligand-mediated bond activation (and formation) reactions classify overall as two-electron processes.<sup>[11–14]</sup> Metal-mediated one-electron homolysis is much rarer,<sup>[15]</sup> while reductive 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.<sup>[16]</sup>

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



M = noble metal

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<sup>II</sup> platform.<sup>[17]</sup> 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<sup>II</sup>. This system, which displays a markedly lower reduction potential than the Pd complex with our previously reported NNO system,<sup>[17]</sup> 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<sup>H2</sup> (<sup>31</sup>P NMR  $\delta$  = –20.25) was prepared as an air-sensitive

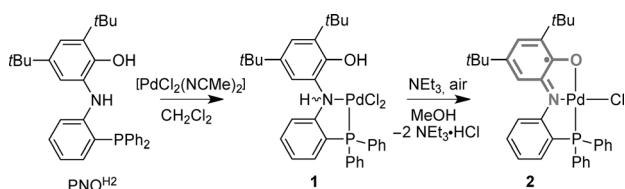
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[\*\*] Research funded by the European Research Council (ERC Starting Grant 279097 to J.I.v.d.V.). We thank Ed Zuidinga for assistance with ESI-MS measurements.

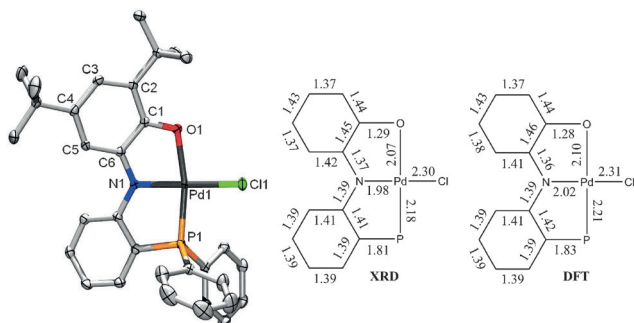


Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201410048>.



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

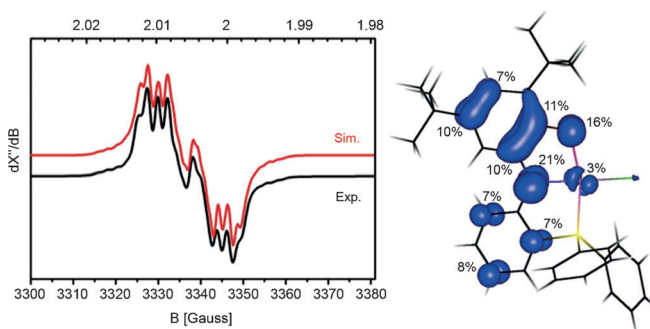
white solid in 58 % overall yield through a two-step procedure from commercially available *o*-iodoaniline and 3,5-di-*tert*-butylcatechol.<sup>[18]</sup> Reaction with  $[\text{PdCl}_2(\text{MeCN})_2]$  gave complex **1** as an orange solid in 67 % yield ( $^{31}\text{P}$  NMR  $\delta = 43.98$ ). Addition 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 ( $\mu_{\text{eff}}$ ) of  $1.81 \mu_{\text{B}}$ , thus indicating an  $S = \frac{1}{2}$  ground state. Hence, this species is best formulated as  $[\text{PdCl}(\text{PNO}^{\text{ISO}})]$ , 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 **2** at 110(2) K. b) Relevant experimental (XRD) and computed (DFT) metric parameters support the  $\text{PNO}^{\text{ISO}}$  state in **2**. Selected bond lengths [Å]:  $\text{N}_1\text{-Pd}_1\text{-Cl}_1$  2.30(5);  $\text{P}_1\text{-Pd}_1\text{-O}_1$  1.67(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).

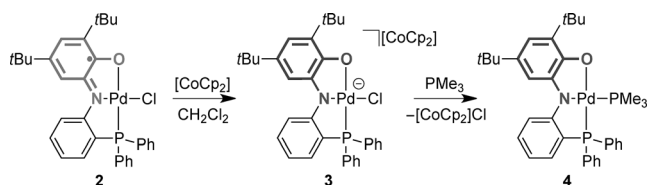
Complex **2** shows a slightly distorted square-planar geometry with an acute  $\angle\text{N}1\text{-Pd}1\text{-O}1$  angle of  $81.16(6)^\circ$ . Palladium–ligand bond lengths and angles in **2** compare well with  $\text{PdCl}$  complexes bearing redox-innocent monoanionic PNO pinners.<sup>[19]</sup> The metric parameters found for the amidophenolate fragment support the ISQ oxidation state of the ligand<sup>[20]</sup> and these data are reproduced by DFT (b3-lyp/def2-TZVP) optimized geometric parameters for the doublet  $\text{PNO}^{\text{ISO}}$  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  $^1\text{H}$  nuclei (see Table S1 in the Supporting Information). The  $g_{\text{iso}}$  value of 2.0052 suggests coordination of a  $\text{PNO}^{\text{ISO}}$  ligand radical to  $\text{Pd}^{\text{II}}$ .<sup>[21]</sup> 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  $\text{CH}_2\text{Cl}_2$  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):  $g_{\text{iso}}$  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**.

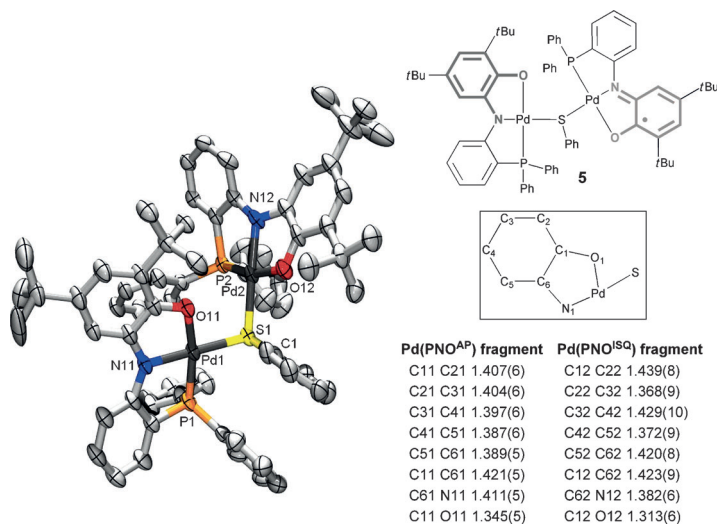
+0.07 V and –0.75 V vs.  $\text{Fc}/\text{Fc}^+$ , respectively. Reversible ligand-based redox chemistry was also observed by UV/Vis spectroelectrochemistry in an optically transparent thin-layer electrolysis (OTTLE) cell (see the Supporting Information for details of the redox chemistry). Chemical reduction of **2** with  $[\text{CoCp}_2]$  in  $\text{CH}_2\text{Cl}_2$  furnished air-sensitive diamagnetic complex **3**, formulated as  $[\text{CoCp}_2][\text{PdCl}(\text{PNO}^{\text{AP}})]$  ( $^{31}\text{P}$  NMR  $\delta = 36.56$ ; AP = amidophenolato). To assess the steric constraint imposed on the Pd center by the flanking phosphine donor, complex **3** was exposed to exogenous phosphines. No reaction was observed with  $\text{PPh}_3$  but coordination of  $\text{PMe}_3$  rapidly produced complex **4** ( $^{31}\text{P}$  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.<sup>[22]</sup> Given the demonstrated reversible one-electron chemistry of species **3** at a mild potential, we sought to investigate its reactivity toward disulfides. Addition of  $\text{TIPF}_6$  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 ( $\mu_{\text{eff}}$ ) of  $1.90 \mu_{\text{B}}$ , thus indicating an  $S = \frac{1}{2}$  ground state. This observation implies one-electron oxidation of  $\text{PNO}^{\text{AP}}$  to  $\text{PNO}^{\text{ISQ}}$ . CSI-MS studies in benzene indicate the presence of a dinuclear species in solution at  $m/z$  1279.28  $[\text{M}]^+$ , formulated as  $[\text{Pd}_2(\mu\text{-$

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

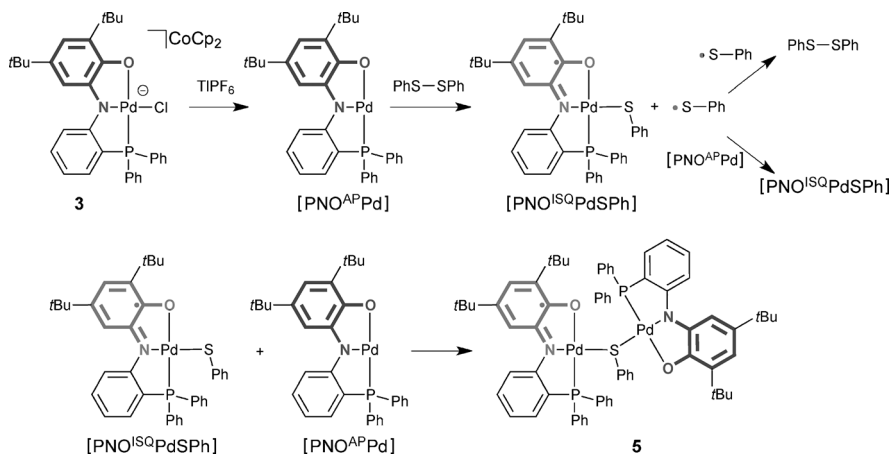


**Figure 4.** a) Displacement ellipsoid plot (50% probability level) of complex **5** at 110(2) K. Disorder in the 3,5-*t*Bu<sub>2</sub>Ph ring at Pd<sub>2</sub> and disordered solvent omitted for clarity. b) metric parameters for the PNO<sup>ISO</sup> and PNO<sup>AP</sup> fragments in **5**. Selected 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<sup>II</sup>(PNO) centers. This bridging monothiolate motif, although not unique, is rather uncommon, particularly with Pd.<sup>[23]</sup> 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<sup>AP</sup> and the PNO<sup>ISO</sup> 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.<sup>[24]</sup> For homodinuclear reaction centers, the mixed valency is typically metal-centered or shared between the metal and (bridging) ligand.<sup>[25]</sup> 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.<sup>[26]</sup> 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.<sup>[26]</sup> 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.<sup>[27]</sup> Using di(*tert*-butyl)disulfide instead of PhSSPh allowed observation of the corresponding Pd–disulfide adduct by NMR spectroscopy. The <sup>31</sup>P 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 <sup>1</sup>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 [PNO<sup>ISO</sup>PdSPh] and release of a PhS<sup>•</sup> radical. This thiyl radical can either undergo self-recombination or react with a ‘vacant’ [PNO<sup>AP</sup>Pd] complex, thus forming PhSSPh or a second equivalent of [PNO<sup>ISO</sup>PdSPh], respectively. The final step is the formation of the mixed-valent [(PNO<sup>ISO</sup>)Pd( $\mu$ -SPh)Pd-(PNO<sup>AP</sup>)] (**5**), through coordination of a sulfur lone pair in [PNO<sup>ISO</sup>PdSPh] to free [PNO<sup>AP</sup>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-(<sup>•</sup>SPh) adducts,<sup>[28]</sup> 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<sup>•</sup> with the solvent benzene. Using a mixture of PhSSPh and di(*p*-tolyl)disulfide



**Scheme 3.** Proposed mechanism for the formation of dinuclear [(PNO<sup>ISO</sup>)Pd( $\mu$ -SPh)Pd(PNO<sup>AP</sup>)] (**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<sup>H2</sup> pincer ligand can coordinate to Pd<sup>II</sup> 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<sup>ISO</sup> and one PNO<sup>AP</sup> 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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