New avenues for redox-active ligands: Non-classical reactivity with late transition metals facilitated by o-aminophenol derived architectures

Broere, D.L.J.

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Chapter 6

Redox-Active Ligand-Induced Homolytic Bond Activation of Disulfides on a Pd(II) Platform*

* Part of this work has been published: D. L. J. Broere, L. L. Metz, B. de Bruin, J. N. H. Reek, M. A. Siegler, J. I. van der Vlugt, Angew. Chem. Int. Ed. 2015, 54, 1516.
6.1 Introduction

Redox-active ligands are frequently encountered in important natural processes mediated by metalloenzymes.\(^1\) In inorganic chemistry, these systems have long been considered 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, as the redox-active nature of these ligands allows for their use as electron-reservoir in (catalytic) chemical transformations.\(^3\) 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 coordinate in three different 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 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 reversible redox-active ligand.\(^8\) Installment of a phosphine donor as a redox-innocent entity adjacent to a redox-active framework is less likely to affect the coordinative properties at phosphorus but relatively few ligand classes are developed to date.\(^9,10\)

Bond homolysis is a useful reaction to probe for accessible ligand-based reactivity. Established ligand-mediated bond activation (and formation) reactions classify as overall two-electron processes.\(^11,12,13,14\) Metal-mediated one-electron homolysis is much rarer,\(^15\) while reductive homolytic bond fission originating from ligand-based overall single-electron transfer is unknown, to the best of our knowledge. Methodologies that facilitate odd-electron transfer processes will allow the controlled generation of reactive substrate radicals for synthetic chemistry.\(^16\)

![Common two electron oxidative addition:](image)

\[
\text{M}^n + \text{RS-SR} \rightarrow \text{RS} + \text{RS}^{m+2} \\
\text{M = noble metal}
\]

![Ligand-induced one-electron bond homolysis](image)

\[
\text{Pd}^{II} + \text{RS-SR} \rightarrow \text{Pd}^{II} \cdot \cdot \cdot \text{SR} + \cdot \text{SR}
\]

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

In order to arrive at a redox-active phosphine ligand, we sought to merge the redox-active o-aminophenol framework with a flanking diphenylphosphine group. Addition of this (sterically encumbering) donor should impact the redox-properties of the N,O-moieity upon coordination to a
transition metal, relative to the **NNO** scaffold utilized in Chapters 2-5. We herein describe the facile synthesis of a ‘redox-active’ phosphorus ligand and its coordination chemistry on PdII. This system displays a markedly lower reduction potential compared to the **NNO** analogue and is able to facilitate radical-type homolytic bond activation of disulfides, with formation of a well-defined ligand-based mixed-valent dinuclear palladium complex.

### 6.2 Results and Discussion

The novel aminophenolphosphate ligand **PNO**H2 (Scheme 1) was prepared via a two-step procedure from commercially available materials. A condensation reaction between o-iodoaniline and 3,5-di-tert-butylcatechol affords compound 1, which is subsequently reacted with diphenylphosphine in a palladium-catalyzed coupling reaction to give **PNO**H2 as an air-sensitive white solid in 58% overall yield (13P NMR: δ -20.25).17 Reaction with PdCl2(MeCN)2 gave complex 2 as an air-stable orange solid in 67% yield (31P NMR: δ 43.98).18 Addition of triethylamine resulted in a rapid color change to green, and subsequent exposure to air afforded dark-red paramagnetic species 3 in 78% yield. Magnetic susceptibility measurements (Evans’ method) showed an effective magnetic moment (μeff) of 1.81 μB, indicating an S = ½ ground state. Infrared spectroscopy confirmed the disappearance of the -NH and -OH stretching absorptions, and solely broad signals at 2.5, 7.2, 7.6 and 7.7 ppm were observed in the 1H NMR spectrum, in agreement with the formation of a paramagnetic species.

![Scheme 1. Synthetic route to PNOH2 and complexes 2 and 3. Reagents and conditions: (i) Xantphos, Pd2(dba)3, NEt3, 1,4-dioxane, 95 °C; (ii) PdCl2(MeCN)2, CH2Cl2, rt; (iii) NEt3, air, MeOH, rt.](image)

Dark brown single crystals suitable for X-ray structure determination of 3 were obtained by vapor diffusion of pentane into a chloroform solution. Complex 3 shows a distorted square planar geometry with a slightly bent ligand (torsion angle C8–C7–N1–C6 ≈ 26°) induced by a steric repulsion between the protons on C5 and C8 (Figure 2). Palladium-ligand bond lengths and angles in 3 compare well with PdCl-complexes bearing ‘redox-innocent’ monoanionic PNO-pincers.19 The metric parameters found for the amidophenolate fragment support the iminosemiquinonato (ISQ) oxidation state of the ligand (MOS = 0.92 ± 0.08)20 and these data are reproduced by DFT (b3-lyp, def2-TZVP) optimized geometric parameters for the doublet **PNO** ISQ ground state. Hence, species 3 is best described as PdCl(**PNO** ISQ).
# Chapter 6

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<td>-0.92 ± 0.08</td>
<td>-0.90 ± 0.09</td>
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**Figure 2.** Left: relevant experimental (XRD) and computed (DFT) metric parameters and MOS values supporting the PNO\textsuperscript{SQ} ligand oxidation state in \textit{3}. Selected bond angles (º): \(N_1\text{-}Pd_1\text{-}Cl_1\) 174.90(5); \(P_1\text{-}Pd_1\text{-}O_1\) 167.43(4); \(P_1\text{-}Pd_1\text{-}Cl_1\) 94.038(17); \(N_1\text{-}Pd_1\text{-}O_1\) 81.16(6). Right: Displacement ellipsoid plot (50% probability level) of complex \textit{3} at 110(2) K. Hydrogen atoms and solvent molecule omitted for clarity.

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 (Figure 3, left). The \(g_{\text{iso}}\) value of 2.0052 supports coordination of a PNO\textsuperscript{SQ} ligand radical to Pd\textsuperscript{II}. The simulated spectrum and calculated hyperfine couplings correlate well with the experimental data (see experimental section). The calculated spin-density for \textit{3} (Figure 3, right) predominantly resides on the ligand (97% total spin density, 21% on the iminosemiquinonato nitrogen), in agreement with EPR observations. Notably, in contrast with the NNO analogue described in Chapter 2 – where the spin-density is solely localized on the redox-active ring – the spin-density plot shows density on the \(\alpha\)-phosphinoaniline ring, similar to the system described in Chapter 4.

**Figure 3.** Left: Experimental and simulated EPR spectrum of \textit{3} (toluene, r.t.) Freq = 9.366829 GHz, \(T = 298\) K, Mod Ampl. = 1 Gauss, power = 20 mW. Right: DFT (b3-lyp, def2-TZVP) calculated spin-density plot for \textit{3}. 

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Cyclic voltammetry of 3 in CH₂Cl₂ solution shows fully reversible one-electron oxidation and reduction events at +0.07 V and -0.75 V vs. Fe/Fe⁺, respectively (Figure 4, insets). The observed redox potentials confirm the anticipated “electron poorer” nature of the ligand relative to the NNO analogue (oxidation and reduction potentials at -0.04 V and -1.1 V vs. Fe/Fe⁺). Fully reversible ligand-based redox-chemistry was also observed by UV-vis spectroelectrochemistry in an optically transparent thin-layer electrolysis (OTTLE) cell (Figure 4). Intra-ligand charge-transfer bands, characteristic for the coordination of a monoanionic NO₂SO radical (800, 900 and 1000 nm)²¹, clearly disappear upon both the one-electron reduction (Figure 4, left) and one-electron oxidation (Figure 4, right) of 3. Upon oxidation, the absorption band at 261 nm is red-shifted whereas a blue-shift is observed in the reduction towards 3⁻. In the oxidation from 3 to 3⁺ the absorption band at 360 nm decreases in intensity and two bands at 427 and 525 nm appear. In the reduction to 3⁻ no new absorption bands > 400 nm are observed, the band at 375 nm is slightly blue-shifted and a new absorption band appears at 332 nm appears.

In agreement with the fully reversible one-electron reduction observed with spectroelectrochemistry, chemical reduction of 3 with CoCp₂ in C₆H₆ furnished air-sensitive diamagnetic complex 4, formulated as [CoCp₂][PdCl(PNOAP)] (³¹P NMR: δ 36.56, Scheme 2). To assess the steric constraint imposed on the Pd center by the flanking phosphine donor, complex 4 was exposed to exogenous phosphines. In contrast to the NNO analogue described in Chapter 2, no reaction was observed upon the addition of PPh₃. However, addition of PMe₃ rapidly produced complex 5 (³¹P NMR: δ 41.52 (d) and -10.61 (d); Jₚ₋ₚ 40.2 Hz), formulated as Pd(PMe₃)(PNOAP) (Scheme 2). We ascribe this difference in reactivity to the more sterically demanding nature of the PNO ligand. Similar to the NNO analogue described in Chapter 2, complex 4 is also capable of facilitating the radical type intramolecular C-H
activation of 4-phenylbutyl azide to form the corresponding Boc-protected pyrrolidine. However, the use of toluene as solvent and a higher temperature (130 °C) are required to observe pyrrolidine formation.

Scheme 2. Synthetic route to complexes 4 and 5. Reagents and conditions: (i) CoCp₂, C₆H₆, rt; (ii) PMe₃, C₆H₆, rt.

Oxidative addition of a disulfide to low-valent Pd is usually a two-electron process. Given the demonstrated reversible one-electron chemistry of species 4 at mild potential, we sought to investigate its reactivity toward disulfides. Addition of TlPF₆ to a suspension of 4 in C₆H₆ in the presence of an equimolar amount of diphenyldisulfide produced soluble, paramagnetic and dark-colored species 6.

Scheme 3. Synthetic route to complex 6. Reagents and conditions: (i) PhS-SPh, TlPF₆, C₆H₆, rt.

Magnetic susceptibility measurements of 6 at 298 K using Evans’ method gave an effective magnetic moment (μₑffective) of 1.90 μ₀, indicating an S = ½ ground state. This observation implies one-electron oxidation of a single PNOAP to PNOISQ. CSI-MS spectra in C₆H₆ indicate the presence of a dinuclear species in benzene solution at m/z 1279.28 [M]⁺, formulated as Pd₂(μ-SPh)(PNO)₂. UV-vis spectroscopy shows both absorption bands at 315 nm and 512 nm, characteristic for the Pd(PNOAP) fragment, as well as intra-ligand charge-transfer bands at 790, 891 and 1033 nm characteristic for the presence of a Pd(PNOISQ) fragment. The X-band EPR spectrum of compound 6 in toluene at 298 K shows an isotropic signal with no resolved hyperfine couplings (Figure 6, left). The giso value of 2.0041 supports the presence of a PNOISQ ligand radical. Black single crystals suitable for X-ray structure determination were obtained by vapor diffusion of pentane into a benzene solution. The molecular structure contains one thiophenolate unit bridging two slightly distorted square planar Pd⁴(PNO) centers (Figure 5). This bridging monothiolate motif is rather uncommon, particularly for
Pd. Strikingly, the observed metric parameters indicate different ligand oxidation states for the two Pd(PNO) fragments present, i.e. the amidophenolato (Pd1(PNOAP)) and the iminosemiquinonato (Pd2(PNOISQ)) oxidation state (Figure 5). Similar to the NNOAP system described in Chapter 2, the metrical oxidation state for the Pd(PNOAP) fragment gives a non-integer value around -1.5, showing that not only high valent d⁰ metal complexes give non integer MOS values. It is common for mixed valence systems to give averaged structures due to facile intramolecular electron transfer. As a result of the stereogenic sulfur atom the two Pd(PNO) fragments are nonequivalent. In combination with poor electronic communication – as both fragments are perpendicular to each other – the unpaired electron is localized, indicative of a Robin Day Class II system.

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<td>Pd1-S1</td>
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MOS: -1.53 ± 0.15, -1.19 ± 0.13

Figure 5. Left: metric parameters and MOS values for the PNOISQ and PNOAP fragments in 6. Selected additional bond lengths (Å) and angles (°): Pd1-N1 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-S-Pd2 104.58(4); N11-Pd1-S1 178.45(10); N12-Pd2-S1 S1 175.5(4); N11-Pd1-O11 82.63(12); N12-Pd2-O12 81.5(3). Right: Displacement ellipsoid plot (50% probability level) of complex 6 at 110(2) K. Disorder in 3,5-tBu2Ph-ring at Pd2, hydrogen atoms and disordered solvent omitted for clarity.

To gain insight into the electron localization in solution, VT-EPR spectroscopy of complex 6 in toluene solution was performed over a temperature range of 201-270 K (Figure 6, right). Upon lowering the temperature the signal intensity increased but no hyperfine coupling could be discerned. In the range of 220-201 K, the signal exhibited some asymmetry, which can be caused by slow tumbling due to increased viscosity of the toluene solution at these temperatures. The hyperfine structure is most likely obscured by rapid electron exchange between the two ligands, similar to the ligand-based mixed valent systems described in Chapter 4. The observed line broadening when increasing the temperature is an indication for facile electron exchange in solution. The EPR spectrum in frozen toluene at 17 K also did not reveal any hyperfine structure.
We are not aware of similar examples of monobridged dinuclear complexes that show ligand-based mixed valence.\textsuperscript{27} For homodinuclear reaction centers, the mixed valency is typically metal-centered or shared between metal and (bridging) ligand.\textsuperscript{28} Systems with separated mixed valent ligand-based redox-centers are of interest to study intramolecular electron-transfer processes. Future endeavors could exploit the selective formation of analogues of 6 using different disulfides to study the effect of the nature of the monothiolate bridgehead on the intramolecular electron-transfer.

Formation of species 6 (Scheme 4) is proposed to involve initial chloride dissociation and disulfide coordination. Dialkyldisulfides have a higher S-S bond dissociation energy than diaryldisulfides and are thus less prone to undergo bond homolysis.\textsuperscript{29} Using di(tert-butyl)disulfide instead of PhSSPh allowed for observation of the corresponding \textit{PNOAP}Pd(disulfide) adduct by NMR spectroscopy. The \textsuperscript{31}P NMR chemical shift of $\delta$ 39.82 is similar to that of neutral 5. The nonequivalent tert-butyl groups of the substrate are shifted upfield in the $^1$H NMR spectrum ($\delta$ 1.09 and 0.96 ppm), which otherwise resembles that of the neutral phosphine stabilized complex 5. Subsequent intramolecular ligand-to-substrate single-electron transfer results in homolytic S-S bond cleavage with formation of \textit{PNOISO}PdSPh and release of a PhS• radical. This thyl-radical can either undergo self-recombination or react with a ‘vacant’ \textit{PNOAP}Pd complex, forming PhSSPh or a second equivalent of \textit{PNOISO}PdSPh, respectively. The occurrence of outer-sphere electron-transfer from 4 to PhSSPh is excluded on the basis of relative redox-potentials.\textsuperscript{30} The final step is the formation of the ligand mixed-valent complex 6, \textit{(PNOISO)Pd(µ-SPh)Pd(PNOAP)}, by coordination of a sulfur lone pair in \textit{PNOISO}PdSPh to free \textit{PNOAP}Pd. Starting with a 4:1 ratio of 4:PhSSPh also cleanly produced complex 6, supporting this pathway. Detection of thyl radicals by EPR spectroscopy using DMPO (DMPO = 5,5-dimethyl-1-pyrroline N-oxide) as spin trapping agent was unsuccessful, probably due to a high recombination rate relative to the generation rate of these thyl radicals, the short lifetime of DMPO(•SPh) adducts\textsuperscript{31} and the competitive reaction of complex 4 with DMPO. However, GC-MS
analysis of the reaction mixture confirmed the presence of diphenylsulfide (PhSPh), generated from reaction of PhS• with the solvent benzene. Using a mixture of PhSSPh and di(p-tolyl)disulfide led to co-formation of phenyl(p-tolyl)disulfide, as detected by GC-MS, supporting the intermediacy of thyl-radicals created via this ligand-to-substrate electron transfer process.

Scheme 4. Proposed mechanism for the formation of dinuclear compound 6 (PNO\textsuperscript{SO})Pd(µ-SPh)Pd(PNO\textsuperscript{AP}) with mixed valency in the two PNO scaffolds.

6.3 Conclusion

In conclusion, the first example of a phosphine ligand appended to an redox-active aminophenol framework is described. This PNO\textsuperscript{H2} pincer ligand can coordinate to Pd\textsuperscript{II} as neutral, radical monoanionic or dianionic scaffold, as supported by spectroscopic, X-ray crystallographic and computational data. Cyclic voltammetry and spectroelectrochemistry demonstrate reversible single electron redox-events for complex 3. The bulky phosphine arm and rigid backbone enforce considerable steric crowding around the Pd center. One-electron reduction generates complex 4, which is a competent reagent for homolytic bond activation of disulfides via ligand-to-substrate single-electron transfer. The resulting dinuclear Pd-species 6 with a monothiolate bridgehead contains a unique mixed valent ligand set, with one PNO\textsuperscript{SO} and one PNO\textsuperscript{AP} unit. The introduction of a flanking phosphine group could allow for expanding the concept of ligand-induced electron-transfer and radical-type reactivity to “softer” low-valent noble metals.
6.4 Experimental section

General methods
All reactions were carried out under an atmosphere of dry dinitrogen using standard Schlenk techniques unless noted otherwise. Reagents were purchased from commercial suppliers and used without further purification. THF, pentane, hexane, and diethyl ether were distilled from sodium benzophenone ketyl. CH₂Cl₂, and methanol were distilled from CaH₂, and toluene was distilled from sodium under nitrogen. NMR spectra (¹H, ³¹P and ¹³C{¹H}) were measured on a Bruker DRX 500, Bruker AMX 400, Bruker DRX 300 or on a Varian Mercury 300 spectrometer at r.t. unless noted otherwise. GC-MS measurements were performed on a HP-Agilent GC-MS or JEOL AccuTOF GCv4G GC-HRMS. EPR spectra were on a Bruker EMP Plus spectrometer. High resolution mass spectra were recorded on a JEOL AccuTOF-plus JMS-T100LP or JEOL JMS SX/SX102A four-sector mass spectrometer. Spectroelectrochemistry was performed in an optically transparent thin-layer (200 μm) electrochemical (OTTLE) cell equipped with CaF₂ optical windows and a platinum minigrid working electrode. Cyclic voltammograms were recorded using an Autolab PGSTAT302N electrochemical workstation, and an airtight three-electrode cell under dry N₂. The working electrode was a carefully polished Pt microdisc (diameter 0.5 mm). A coiled Pt wire was used as a counter electrode and a coiled Ag wire as the pseudo-reference electrode. All electrode potentials reported in this work are referenced versus the internal standard ferrocene/ferrocenium (Fc/Fc+) couple. Cyclic voltammetry measurements were performed in CH₂Cl₂ (1 × 10⁻³ M) containing N(n-Bu)₄PF₆ (0.1 M) at room temperature under an N₂ atmosphere using a glassy carbon electrode. All redox potentials are referenced to Fc/Fc⁺.

2-4-di-tert-butyliodoaniline (1)

2-Iodoaniline (1.261 g, 5.73 mmol) and 3,5-di-tert-butyliodoaniline (1.274 g, 5.73 mmol) were heated to 140 °C for 30 min. The resulting black liquid was cooled to room temperature and was purified by column chromatography (hexane or 18:1 hexane:EtOAc), affording the title compound as a brown solid (2.165 g, 89 % yield). Additional crystallization from pentane yields white crystals (44 %). ¹H NMR (300 MHz, CDCl₃) δ 7.75 (dd, J = 7.8, 1.6 Hz, 1H, Ar-H), 7.32 – 7.21 (m, 1H, ap-H), 7.19 – 7.07 (m, 1H, Ar-H), 7.01 (d, J = 2.4 Hz, 1H, ap-H), 6.59 (t, J = 7.6 Hz, 1H, Ar-H), 6.41 (dd, J = 8.1, 1.6 Hz, 1H, Ar-H), 6.27 (s, 1H, OH), 5.44 (bs, 1H, NH), 1.45 (d, J = 1.7 Hz, 9H, tBu), 1.28 (s, 9H, tBu). ¹³C-NMR (126 MHz, CDCl₃, ppm): δ 149.73 (C₂H₂), 146.95 (C₂H₂), 142.82 (C₂H₂), 139.24 (C₂H₂), 136.1 (C₂H₂), 129.76 (CH), 127.33 (C₂H₂), 122.82 (C₂H₂), 122.29 (C₂H₂), 121.38 (C₂H₂), 114.57 (C₂H₂), 86.62 (C₂H₂), 35.35 (C(CH₃)₂), 34.63 (C(CH₃)₂), 31.82 (C(CH₃)₂), 29.84 (C(CH₃)₂). IR (ATR, cm⁻¹): ν 3438 (m, N-H), 3332 (m, O-H), 3301 (w, C₂H₅-N), 2956, 2863 (m, C₂H₅-N), 1581, 1492 (s, C₂H₅-N), 749 (vs, C₂H₅-N). MS-EI (m/z) calcd for C₂₉H₃₁INO: 423.1059, found 423.0910 [M⁺].
2,4-di-tert-butyl-(2-diphenylphosphanylanilino)phenol (PNOH₂)

Triethylamine (2.3 ml, 16.6 mmol) dissolved in dioxane (60 mL) was added to a Schlenk flask containing 1 (5.8 g, 13.8 mmol), Xantphos (320 mg, 0.056 mmol, 4 mol%) and Pd₂(dba)₃ (260 mg, 0.028 mmol, 2 mol%) under an N₂ atmosphere. Diphenylphosphine (2.9 mL, 16.6 mmol) was added and the mixture was heated to 95 °C for 48 hours. Volatiles were evaporated in vacuo and the residue was partitioned between ethyl acetate (55 mL) and water (25 mL). The aqueous fraction was subsequently extracted with ethyl acetate (2 × 20 mL). The combined organic fractions were washed with water (10 mL), dried over Na₂SO₄ and concentrated in vacuo. The resulting crude product was impregnated onto SiO₂ and purified by column chromatography (12:2 hexane:ethyl acetate), affording PNOH₂ as a white solid (3.8 g, 58%). ³¹P NMR (162 MHz, CDCl₃, ppm): δ -20.32 (s). ¹H NMR (400 MHz, CD₂Cl₂, ppm): δ 7.40 (m, 10H, Ar-H), 7.29 – 7.13 (m, 2H, Ar-H + ap-H), 6.92 – 6.81 (m, 2H, Ar-H), 6.77 (dd, J = 7.5, 1.1 Hz, 1H, Ar-H), 6.39 (ddd, J = 8.2, 5.0, 1.1 Hz, 1H, Ar-H), 6.07 (s, 1H, O H/NH), 5.91 (d, J = 8.0 Hz, 1H, Ar-H), 1.38 (s, 9H, tBu), 1.23 (s, 9H, tBu). ¹³C-NMR (500 MHz, CDCl₃, ppm): δ 149.81 (d, J = 17.4 Hz, C(A)), 149.62 (C(A)), 34.96 (C(CH₃)₃), 142.2 (C(A)), 135.19 (C(A)), 134.83 (d, J = 7.3 Hz, C(A)), 134.03 (d, J = 3.9 Hz, C(A)), 133.75 (d, J = 19.2 Hz, C(A)), 130.6 (C(A)), 129.17 (C(A)), 128.83 (d, J = 7.3 Hz, C(A)), 127.4 (d, J = 1.5 Hz, C(A)), 122.23 (C(A)), 122.10 (C(A)), 121.46 (d, J = 8.8 Hz, C(A)), 119.85 (d, J = 2.4 Hz, C(A)), 113.86 (d, J = 1.9 Hz, C(A)), 34.37 (C(CH₃)₃), 31.61 (C(CH₃)₃), 29.5 (C(CH₃)₃). IR (ATR mode, cm⁻¹): ν 3416 (m, N-H), 3281 (m, O-H), 3052, 3000.50 m (C(A)-H stretch), 2952, 2865 (m, C(alk-H)), 1585, 1570 (s, C(A)-H), 694, 649 (vs, C(A)-H). MS-ESI⁺ (m/z) calcd for C₃₂H₃₆NOP: 481.2535, found 481.2474 [M]⁺.

Complex 2 (PdCl₂(κ²-P,N:PNOH₂))

Dichloromethane (3 mL) was added to a Schlenk flask containing PNOH₂ (44.7 mg, 0.092 mmol) and PdCl₂(MeCN)₂ (24.1 mg, 0.093 mmol). The mixture was stirred for 1 hour and then concentrated to ~1 mL. Pentane (10 mL) was added and an orange precipitate was collected by filtration. The solid was washed with pentane and dried in vacuo, affording complex 1 as an orange solid (44 mg, 67%). ³¹P NMR (162 MHz, CDCl₃, ppm): δ 43.98 (s). ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.95 (s, 1H, OH), 8.15 (dd, J = 7.7 Hz, J = 4.4 Hz, 2H, Ar-H), 7.50-7.64 (m, 10H, Ar-H + ap-H), 7.42 (m, 2H, Ar-H), 7.23 (m, 1H, Ar-H), 7.05 (d, J = 2.2 Hz, 1H, ap-H), 5.97 (s, 1H, NH), 1.43 (s, 9H, tBu), 0.79 (s, 9H, tBu). ¹³C NMR (126 MHz, CDCl₃, ppm): δ 152.64 (d, J = 17.3 Hz, C(A)), 145.69 (C(A)), 142.19 (C(A)), 134.93 (C(A)), 134.05 (d, J = 11.0 Hz, C(A)), 133.75 (d, J = 11.7 Hz, C(A)), 132.70 (C(A)), 132.32 (C(A)), 133.13 (C(A)), 129.91 (d, J = 12.8 Hz, C(A)), 129.69 (C(A)), 129.79 (C(A)), 129.84 (C(A)), 127.89 (d, J = 10.7 Hz, C(A)), 126.41 (C(A)), 125.98 (C(A)), 121.87 (C(A)), 35.37 (C(CH₃)₃), 34.24 (C(CH₃)₃), 30.94 (C(CH₃)₃), 30.06 (C(CH₃)₃). IR (ATR mode, cm⁻¹): ν 3415 (w, N-H), 3285 (w, O-H), 3053 (w, C(A)-H), 2866-2954 (m, C(alk-H)), 1570-1586 (m, C(A)-H), 649-693 (s, C(A)-H). MS-ESI⁺ (m/z) calcd for C₃₀H₃₆Cl₂NOPd: 656.1, found 656.2 [M]⁺.
Chapter 6

Complex 3 (PdCl(PNO\textsuperscript{3SQ}))

Triethylamine (0.189 mL, 1.34 mmol) was added dropwise to a solution of 2 (377 mg, 0.67 mmol) in MeOH (40 mL), resulting in a color change from yellow via green to brown. The brown mixture was stirred for 1 hour under an ambient atmosphere, whereafter the solution was concentrated by evaporation of volatiles in air. The crude product was dissolved in CHCl\textsubscript{3} (50 mL) and was washed with water (2 x 30 mL) and brine (30 mL). The organic fraction was dried over Na\textsubscript{2}SO\textsubscript{4} and then concentrated. Slow diffusion of pentane afforded complex 2 as paramagnetic dark brown crystals (326 mg, 78 %). \textsuperscript{1}H NMR (400 MHz, CD\textsubscript{2}Cl\textsubscript{2}, ppm): δ 7.78 (b), 7.65 (b), 7.26 (b), 2.55 (b). IR (ATR mode, cm\textsuperscript{-1}): ν 3100 (w, C Ar-H), 2958 (m, C Alk-H), 1416 (m, C Ar-H), 687-741 (s, C Ar-H). MS-CSI\textsuperscript{1} (m/z) calcd for C\textsubscript{32}H\textsubscript{34}ClNOPd: 620.1110, found 620.1132 [M]\textsuperscript{+}. Anal. Calcd for C\textsubscript{32}H\textsubscript{34}ClNOPd: C, 61.84 ; H, 5.51; N, 2.25. Found: C, 61.69; H, 5.59; N, 2.22.

Complex 4 ([CoC\textsubscript{p}$_{2}$][PdCl(PNO\textsuperscript{4P})])

A solution of CoC\textsubscript{p}$_{2}$ (19 mg, 0.1 mmol) in benzene (5 mL) was added dropwise to a stirred solution of 3 (62 mg, 0.1 mmol) in benzene (1 mL). After 30 minutes the fine green precipitate was collected by filtration. The residue was washed with benzene (4 mL) and pentane (2 mL) and dried in vacuo, affording 4 as a green solid (45 mg, 55 %)*. Complex 3 was sparingly soluble in benzene and decomposed in more polar solvents, precluding full spectroscopic analysis. NMR analysis was possible when a sample was freshly prepared in CD\textsubscript{2}Cl\textsubscript{2} inside an N\textsubscript{2}-filled glovebox.

* Complex 4 precipitates as an extremely fine powder, making it difficult to isolate in good yields by filtration techniques and is therefore preferably made in situ. Use of a centrifuge under inert atmosphere could facilitate isolation. \textsuperscript{31}P NMR (162 MHz, CD\textsubscript{2}Cl\textsubscript{2}, ppm): δ 36.56 (s). \textsuperscript{1}H NMR (400 MHz, CD\textsubscript{2}Cl\textsubscript{2}, ppm) δ 7.89 (m, 4H, Ar-H), 7.49 (m, 7H, Ar-H), 7.29 (d, J = 2.2 Hz, 1H, ap-H), 7.05 (dd, J = 7.7, 1.3 Hz, 1H, Ar-H), 6.87 (m, 1H, Ar-H), 6.63 (s, 1H, ap-H), 6.31 (dd, J = 7.3, 1.3 Hz, 1H, Ar-H), 1.49 (s, 9H, tBu), 1.22 (s, 9H, tBu). MS-CSI\textsuperscript{1} (m/z) calcd for C\textsubscript{32}H\textsubscript{34}ClINO\textsubscript{Pd}: 620.1110, found 620.1588 [M]\textsuperscript{+}.

Complex 5 (Pd(PMe\textsubscript{3})(PNO\textsuperscript{4P}))

A solution of PMe\textsubscript{3} in toluene (0.7 mL, 1 M, 0.7 mmol) was added to a stirred suspension of complex 4 (41 mg, 0.05 mmol) in C\textsubscript{6}H\textsubscript{6} (4 mL). After 1 hour the reaction mixture was filtered through a syringe filter, concentrated to a thick sludge to which pentane (4 mL) was added. The supernatant was syringed off and the brown precipitate was dried in vacuo, affording 5 as a brown solid (25 mg, 75%). \textsuperscript{31}P NMR (162 MHz, C\textsubscript{6}D\textsubscript{6}, ppm): δ 41.52 (d, J = 40.4 Hz, PPh$_{3}$), -10.61 (d, J = 40.4 Hz, PMe$_{3}$). \textsuperscript{1}H NMR (400 MHz, C\textsubscript{6}D\textsubscript{6}, ppm) δ 8.11 (dd, J = 8.6, 6.1 Hz, 1H, Ar-H), 7.85 (d, J = 2.2 Hz,
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1H, ap-H), 7.47 (ddd, J = 12.0, 8.3, 1.4 Hz, 4H, Ar-H), 7.23 (dd, J = 2.2, 1.0 Hz, 1H, Ar-H), 7.14 – 7.10 (m, 1H, Ar-H), 7.02 – 6.89 (m, 6H, Ar-H + ap-H), 6.72 (ddd, J = 12.9, 7.6, 1.6 Hz, 1H, Ar-H), 6.29 (ddd, J = 9.1, 6.9, 1.4 Hz, 1H, Ar-H), 1.94 (s, 9H, tBu), 1.51 (s, 9H, tBu), 0.77 (d, J = 10.3 Hz, 9H,P(C(H3)3)). 13C NMR (126 MHz, C6D6, ppm): δ 162.1 (b, CAr), 144.7 (CAr), 135.7 (CAr), 135.5 (CAr), 134.3 (CArH), 133.4 (d, J = 12 Hz, CArH), 131.5 (d, J = 50 Hz, CArH), 131.1 (CArH), 129.1 (d, J = 11 Hz, CArH), 128.3 (CArH), 122.5 (CAr), 119.2 (CAr), 115.0 (CArH), 114.8 (CArH), 113.0 (CArH), 111.7 (CArH), 35.7 ((CH3)3), 34.6 ((CH3)3), 32.7 ((CH3)3), 30.5 ((CH3)3), 14.4 (d, J = 29 Hz, P(CH3)3).

MS-CSI+ (m/z) calcd for C35H43NOP2Pd: 661.1855, found 661.1815 [M]+.

Complex 6 (Pd(PNOAP)(µ-SPh)Pd(PNOISQ))

TIPF₆ (35 mg, 0.1 mmol) was added to a suspension of 4 (81 mg, 0.1 mmol) and diphenyl disulfide (54.6 mg, 0.25 mmol) in C₆H₆ (8 mL). The mixture was stirred overnight, whereafter it was filtered through a Teflon syringe filter and concentrated. Vapour diffusion of pentane to a concentrated solution in C₆H₆ afforded 6 as black crystals (22 mg, 34%). 31P NMR (162 MHz, C₆D₆, ppm): δ silent. 1H NMR (400 MHz, C₆D₆, ppm) δ 8.77 (b), 7.49 (b), 6.95 (b), 6.82 (b), 6.55 (b), 2.56 (b). MS-CSI+ (m/z) calcd for C₇₀H₇₃N₂O₂P₂Pd₂S: 1279.2937, found 1279.2784 [M]+. Anal. Calcd for C₇₀H₇₃N₂O₂P₂PdS: C, 65.62; H, 5.74; N, 2.19. Found: C, 65.52; H, 5.97; N, 2.22.

Observation of di(tert-butyl)disulfide adduct of complex 4

TIPF₆ (3.5 mg, 0.01 mmol) was added to a suspension of 4 (8.1 mg, 0.01 mmol) and di(tert-butyl)disulfide (1.8 mg, 0.01 mmol) in C₆D₆ (0.8 mL). The resulting mixture was analyzed by NMR spectroscopy to reveal a diamagnetic intermediate. This intermediate shows two additional nonequivalent tert-butyl groups in the 1H NMR spectrum, which is in agreement with disulfide coordination. Signals for the ligand in both the 31P NMR and 1H NMR spectrum are very comparable to those of complex 5, which has a comparable coordination environment. In time, the signals weaken in intensity, with formation of the tert-butyl analogue of complex 5, as evidenced by mass spectrometry data.

EPR spectroscopy of complex 3

X-band EPR spectroscopy of complex 3 in toluene at 298 K revealed hyperfine couplings with 105Pd, 31P, 14N and three 1H nuclei. The simulated spectrum and calculated hyperfine couplings correlate well with the experimental data with exception of the hyperfine interaction with 14N and 105Pd. Using the ADF software package for the calculation of the hyperfine interaction resulted in better agreement for the value for 105Pd but decreased that for 14N. Moreover, three hyperfine interactions with three 1H
nuclei were not resolved in the experimental spectrum. The $g_{\text{iso}}$ value of 2.0052 supports an PNO$^{59}$ ligand radical coordinated to Pd$^{II}$.

**Table S1** Experimental$^{(a)}$ and DFT calculated$^{(b),(c)}$ EPR parameters of 3.

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<th>DFT $^{(b)}$</th>
<th>DFT $^{(c)}$</th>
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Parameters from spectral simulation. NR = not resolved.

(a) ADF, BP86, TZP.
(b) Orca, b3-lyp, def2-TZVP.
(c) HFIs in MHz, signs follow those from the DFT calculations.

**Computational details**

Geometry optimizations were carried out using TURBOMOLE$^{34}$ coupled with the PQS Baker optimizer$^{35}$ via the BOpt package$^{36}$ at the DFT level using the b3-lyp functional and the def2-TZVP basis set. All minima (no imaginary frequencies) characterized by numerically calculating the Hessian matrix. Calculated EPR spectra were obtained with ORCA$^{37}$ (DFT: b3-lyp, def2-TZVP) level, using Turbomole optimized geometries.

**6.5 Acknowledgements**

Lotte Metz is thanked for her contributions to the experimental work described in this chapter. Dr Maxime Siegler is thanked for X-ray diffraction studies. Prof. Bas de Bruin is thanked for help with EPR measurements, simulation of the spectra and fruitful discussions.
6.6 References


18 This step allows the use of partly oxidized (~90%) PNOH2 which is easily by trituration of the complex.


24 This phenomenon is also observed for the DFT optimized geometry of the monoanionic PNO⁻³PdCl fragment (b3-lYP, def2-TZVP).


29 Reduction potential vs. SCE: PhSSPh -1.6 V; ³BuSS³Bu -2.71 V. Bond dissociation energy (BDE) of PhSSPh 55.0 kcal mol⁻¹; dialkyl-disulfides ~65 kcal mol⁻¹; MeSSMe: 73.2 kcal mol⁻¹.


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