New avenues for redox-active ligands: Non-classical reactivity with late transition metals facilitated by o-aminophenol derived architectures
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Chapter 5

The Generation of Transient Palladium Nitridyl Radicals by Redox-Active Ligands

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Chapter 5

5.1 Introduction

Transition metal oxo and nitrido complexes play important roles in many biological and industrial catalytic processes. To generate the most stable bonding situation with a transition metal, both ligands require three empty metal $d$-orbitals of suitable symmetry. Therefore, isolable metal oxo and nitrido complexes are mainly found with early transition metals. Ballhausen and Gray were the first to report the electronic structure of an octahedral vanadium oxo complex and describe the importance of ligand-to-metal $\pi$-bonding. $^1$ This seminal work resulted in the establishment of the “oxo wall”, which states that complexes with an octahedral geometry can have no more than 5 d-electrons and still retain some multiple character to the metal-oxo bond. In the absence of $\pi$-bonding to the metal, the oxo fragment/ligand will be extremely basic and unstable with respect to reactions with electrophiles (including protonation). Achieving the low $d$-electron count necessary for M-O multiple bonding becomes increasingly difficult with metals on the far-right of the transition series, $^2$ and the “oxo wall” is ‘established’ between the metals of Groups 8 and 9 of the periodic table. As nitrido ligands require the same bonding criteria as oxo ligands, the same limitations exist for multiple bonding in metal nitrido complexes. The inherent instability of oxo and nitrido complexes with late transition (platinum group) metals makes these reactive species interesting targets in synthetic and computational inorganic chemistry to gain understanding in how these entities behave.

An unsubstituted nitrogen ligand can coordinate to a transition metal in three different modes depending on the oxidation state at nitrogen (Figure 1). $^3$ One-electron reduction of the monoanionic nitrenido ligand results in a dianionic nitridyl radical, which upon another one-electron reduction gives the trianionic nitrido ligand.

![Figure 1. Lewis structures and nomenclature of the three possible binding modes of an unsubstituted nitrogen ligand.](image)

A commonly encountered strategy to prepare nitrido complexes with metals beyond Group 8 is to reduce the coordination number and enforce a non-octahedral geometry, in order to generate vacant orbitals that can engage in ligand-to-metal $\pi$-bonding. This approach does not violate (or break) the nitrido wall formalism, which only holds for octahedral complexes. There is much current interest to develop synthetic protocols toward (late) transition metal nitrido species to investigate their electronic structure and to establish fundamental reactivity, as this may aid the development of new methodologies for C-H activation, N$_2$ fixation and NH$_3$ oxidation. $^4$ Common pathways to obtain metal
nitrido complexes are by thermal, photolytic or oxidative decomposition of metal azides. Notably, in some examples redox-processes at a redox-active ligand appear to facilitate or stabilize the formation of a nitrido or nitridyl radical ligand.\textsuperscript{4b,f,g} This intrigued us to investigate the azido complexes 1 and 2PF\textsubscript{6} (Scheme 1) described in Chapter 3 towards controlled azide decomposition. In this Chapter we describe how the redox-active NNO ligand (introduced in Chapter 2) might enable the formation of nitridyl radicals by an intramolecular electron transfer process.

\textbf{Scheme 1.} The azido complexes 1 and 2PF\textsubscript{6} described in Chapter 3, bearing the redox-active NNO ligand.

\section*{5.2 Results and Discussion}

\textbf{Oxidative decomposition of complex 1}

Photolysis by high intensity UV irradiation or thermolysis of complex 1, either as a solid or in solution, resulted in the disappearance of the characteristic azide stretch at \(\nu 2035\ \text{cm}^{-1}\) in the IR spectrum. However, both methodologies are plagued by formation of a metallic precipitate and a mixture of unidentified species. Similar to the chloride analogue described in Chapter 2, complex 1 undergoes fully reversible one-electron oxidation and reduction at accessible potentials (\(E_{ox}^{\text{red}} = +0.07\ \text{V},\ E_{red}^{\text{ox}} = -0.97\ \text{V vs. Fe/Fe}^+\)), according to cyclic voltammetry. Treatment of complex 1 with one equivalent of the one-electron oxidant acetylferrocenium tetrafluoroborate resulted in a shift of the azide stretch to \(\nu 2024\ \text{cm}^{-1}\) in the IR spectrum, likely belonging to the corresponding \([\text{Pd(N}_3\text{)(NNO)}]^+\) species. However, in time a new strong azide stretch appears in the IR spectrum at \(\nu 2076\ \text{cm}^{-1}\), inherent to the formation of the previously described dinuclear diradical cation 2\textsuperscript{+} (see Chapter 3). Although the complex has a different counterion (BF\textsubscript{4} vs. PF\textsubscript{6}), identical IR, NMR and CSI-MS data were obtained. When the reaction was performed in a closed system, a clear pressure build-up was observed, which is indicative of dinitrogen evolution. Full conversion of complex 1 could also be achieved with half an equivalent of the oxidant.
Scheme 2. Reaction upon treatment of complex 1 with a one-electron oxidant resulting in the formation of complex 2BF₄, with proposed intermediacy of species 1⁺. Reagents and conditions: (i) acetylferrocenium tetrafluoroborate, CDCl₃, rt.

Based on these observations and intrigued by the formation of complex 2BF₄ from 1 upon one-electron oxidation, we were interested to understand the mechanism behind the formation of this dinuclear diradical. A potential mechanism, depicted in Scheme 3, involves oxidation of 1 to 1⁺ and subsequent loss of N₂, resulting in the formation of intermediate A, which can exist in three resonance structures: nitrenido 1A⁺, nitrido 1A⁺⁺ or nitridyl radical 1A⁺⁺⁺. Reductive coupling of two nitridyl radicals results in the formation of intermediate 1B⁺ that upon loss of dinitrogen from 1B⁺⁺ forms C, which is trapped by the second equivalent of 1 to form 2BF₄ as described in Chapter 3. Mechanisms involving loss of N₂ upon one-electron oxidation⁴e of azido complexes with follow-up reductive coupling of transient nitridyl radicals have been proposed by de Bruin and Schneider for Rh and Ir systems with neutral and monoanionic pincer ligands.⁴a,e,g

To support the radical coupling of two palladium nitridyl radicals, we prepared the ¹⁵N-labeled isotopomer of complex 1 by using Na¹⁵N¹⁴N₂ in its synthesis, yielding a 1:1 mixture of Pd¹⁵N¹⁴N₂ and Pd¹⁴N¹⁴N¹⁵N showing azide stretches at ν 2013 and 2025 cm⁻¹ in the IR spectrum, respectively. Upon oxidation with acetylferrocenium tetrafluoroborate, these signals instantly shift to 2006 and 2019 cm⁻¹ for 1⁺ and subsequently to 2057 and 2073 cm⁻¹ for 2⁺. Performing the reaction under a strict argon atmosphere allowed for gas analysis of the headspace by mass spectrometry, which revealed formation of both ¹⁵N≡¹⁵N and ¹⁵N≡¹⁴N, in agreement with a reductive coupling of two palladium nitridyl radicals. To confirm the presence of a reactive radical intermediate, the oxidation of 1 was performed in the presence of excess 1,4-cyclohexadiene (CHD) as H-atom donor, which led to several unidentified products and minor amounts of 2BF₄. Moreover, benzene formation was observed by ¹H NMR spectroscopy and ESI-MS analysis of the reaction mixture showed [NNOPd-NH₃]⁺ fragments at m/z 461.1822 that were not observed in the absence of CHD.
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Scheme 3. Possible mechanism for the formation of $2\text{BF}_4$ upon one-electron oxidation of $1$.

To understand the facile loss of dinitrogen at room temperature of $1^+$ compared to $1$, we used DFT calculations to gain insight into the thermal azide decomposition of both compounds. We calculated the barrier for loss of $N_2$ and the corresponding palladium nitrido complexes on the closed-shell singlet (CSS), open-shell singlet (OSS) and triplet surfaces for $1^+$ and on the doublet surface for $1$. The calculated energy profiles, depicted in Figure 2, show high barriers for both $1$ and $1^+$. The found closed-shell singlet (CSS) for $1^+$ is 14 kcal mol$^{-1}$ lower in energy than the optimized triplet state. The lowest barrier for loss of $N_2$ is on the open-shell singlet (OSS) surface, requiring 43 kcal mol$^{-1}$, which is lower by 4 and 8 kcal mol$^{-1}$ compared to the CSS and triplet state, respectively. Notably, for the cationic palladium nitrido species ($1A^+$) the triplet state is lowest in energy by 10 and 25 kcal mol$^{-1}$ compared to the OSS and CSS states, respectively. The barrier for $N_2$ loss from $1$ to form $1A$ is 53 kcal mol$^{-1}$, which is only 10 kcal mol$^{-1}$ higher in energy than the lowest barrier for $1^+$. This small difference does not explain the experimentally observed difference between the two compounds, as both barriers are still too high to occur at room temperature. An explanation might be that the loss of $N_2$ from $1^+$ is solvent or anion assisted. Alternatively, formation of $2\text{BF}_4$ proceeds via a different and currently unidentified mechanism that may involve an additional molecule of $1$ or $1^+$ to activate the azido-fragment. We have calculated spin density plots of $1A$ and $1A^+$, which show significant nitridyl radical (see experimental section). However, as the intermediacy of such intermediates (from direct loss of $N_2$) is unlikely, we refrain from further discussion here.
Photolysis of the dinuclear azido bridged palladium complex

A more facile route to prepare the dinuclear azido bridged complex that does not rely on oxidative decomposition of 1 is the treatment of an equimolar solution of 1 and the chlorido analogue with one equivalent of TIPF₆ to form 2PF₆ (see Chapter 3). The observed elongation of the Nα-Nβ bond and contraction of the Nβ-Nγ bond of the bridging azido ligand in the solid state structure of 2PF₆ suggests that facile loss of N₂ might be possible. Upon irradiation of complex 2PF₆ in benzene with a high intensity UV light source (300-600 nm, 150W), the characteristic azide stretch at 2076 cm⁻¹ in the IR spectrum disappeared within minutes and a new complex (3) was obtained in 67% yield, which was formulated as [{Pd(NNOISQ)}(μ-NH₂){Pd(NNOISQ)}]PF₆ (Scheme 4) based on spectroscopic and X-ray structural characterization. Broad signals were observed from 19 to -4 ppm in the ¹H NMR spectrum, comparable to the starting material 2PF₆ (see experimental section). CSI-MS studies showed a clear signal with m/z 906.3025 [M]+, corresponding to loss of N₂ and the addition of two H atoms (Figure 3).

Scheme 4 Synthesis of complex 3 by photolysis of complex 2PF₆. Conditions: hν, C₆H₆, reflux.
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Figure 3. CSI-MS spectra of 2PF₆ (top) and 3 (bottom).

Dark-brown single crystals of 3 suitable for X-ray diffraction were obtained by slow diffusion of pentane into a chloroform solution. The molecular structure (Figure 4) shows two slightly distorted square planar geometries around the Pd atoms and a single bridging amido ligand. The bond lengths in the two redox-active ligands are identical to each other, as the bridging nitrogen atom (N3) is found on a site of twofold axial symmetry. Analysis of the metric parameters revealed characteristic bond lengths for the iminosemiquinonato oxidation state of the ligands⁵ (metrical oxidation state (MOS)⁶ = -0.98 ± 0.05), which are nearly identical to those of complex 2PF₆. In the solid state, a clear H-F bonding interaction is observed between the protons of the µ-NH₂ ligand and the hexafluorophosphate anion, which is disordered over two orientations. The Pd-Pd distance of 3.1773(7) Å is significantly shorter than the distance in 2PF₆ (3.6843(3) Å). Moreover, it is also shorter than the sum of the van der Waals radii (3.26 Å), which implies an intramolecular d⁸-d⁸ interaction comparable to the µ-Cl analogue described in Chapter 3. The Pd-N-Pd angle also decreases from 127.32° to 102.74°. The DFT optimized geometry for 3 is in excellent agreement with the experimentally found geometry.

Similar to the chlorido analogue described in Chapter 3, a filled bonding and antibonding orbital inherent to the intramolecular d⁸-d⁸ interaction between the Pd centers was found upon analysis of the molecular orbitals.

To provide insight into the source of the H-atoms in 3, the photolysis was performed in both benzene and benzene-d₆. Both reactions yielded identical products and no deuterium incorporation was observed by CSI-MS. To exclude that H-atom abstraction occurs upon crystallization from chloroform, the crude product was recrystallized using both CHCl₃ and CDCl₃. Again identical products were obtained and no deuterium incorporation was detected by CSI-MS. Performing the photolysis in benzene-d₆ in the presence of 1,4-cyclohexadiene as a H-atom donor generated 3 with
<table>
<thead>
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</tr>
<tr>
<td>Pd1-Pd1</td>
<td>3.1773(7)</td>
<td>3.170</td>
</tr>
</tbody>
</table>

MOS: -0.97 ± 0.05

Figure 4. Left: Table showing relevant bond lengths (Å) and metrical oxidation state (MOS) of the solid state structure of complex 3. Relevant angle: Pd1-N3-Pd1’: 102.7(3)°. Right: Displacement ellipsoid plot (50% probability level) of complex 3. Most hydrogen atoms are omitted and tert-butyl groups are depicted as wireframe for clarity.

concomitant formation of benzene, showing that 1,4-cyclohexadiene can serve as a source of H-atoms. However, a 1,4-cyclohexadiene adduct, which likely results from nitrene insertion into the double bond, was also observed by CSI-MS. Similarly, CSI-MS analysis of the reaction mixture after photolysis in the presence of 2,6-di-tert-butylphenol showed formation of a 2,6-di-tert-butylphenol adduct. Using D₂O-saturated C₆H₆ as the solvent resulted in quantitative incorporation of two D atoms, as evidenced in the ESI-MS spectrum. When the crude product of the photolysis in C₆H₆ was re-dissolved in D₂O-saturated C₆H₆ and irradiated with high intensity UV light, only marginal deuterium incorporation was observed. Adventitious water itself is an unlikely source of H-atoms as the bond dissociation energy (BDE) of an O-H bond of water is slightly larger than that of a C-H bond of benzene (117.6 vs. 113.5 kcal mol⁻¹). However, coordination of water to a Lewis acid can result in a decrease of the BDE to 49.8 kcal mol⁻¹. Considering the labile nature of the monoatom-bridged species (see Chapter 3), it is conceivable that the harsh photolysis conditions can create an accessible coordination site on an NNOPd fragment for temporary coordination of an adventitious water molecule, thereby lowering the O-H BDE. How the resulting species in such a scenario will regenerate 2 or proceed towards 3 is unclear.

A proposed pathway for the formation of complex 3 is depicted in Scheme 5. Irradiation of 2⁺ results in loss of dinitrogen to form the intermediate bridged nitride 2A. Transfer of an electron from one of the redox-active ligands results in the formation of nitridyl radical 2A⁺, which can abstract an H-atom to form 2B. Upon a second H-atom transfer (HAT) process, the latter is converted to complex 3⁺. DFT
calculations (b3-lyp-d3, def2-TZVP) were performed to gain insight into the relative energies of the proposed intermediates. For $2^+$ and $3^+$, the OSS and triplet state energies are very close ($E_{\text{OSS}} - E_{\text{triplet}} = -0.35 \text{ kcal mol}^{-1}$ for both). For intermediate $2A$ the triplet state is higher in energy by 2.1 kcal mol$^{-1}$ than the OSS state. Similarly, the doublet and quartet spin states of intermediate $2B$ lie very close in energy ($E_{\text{doublet}} - E_{\text{quartet}} = -0.9 \text{ kcal mol}^{-1}$), with the lower spin state being more favorable. The experimental metric parameters and MOS values of complex $2^+$ were well-reproduced in the calculated structures, with exception of the Pd-Pd distance, which was ~0.3 Å shorter \textit{in silico}. Notably, the spin density plot of intermediate $2A$ (Figure 5) shows a significant localization on the nitrido nitrogen atom (1.1 e) and a decrease of spin density on the redox-active ligands relative to $2^+$. Moreover, a decrease in the MOS value of the redox-active ligands (from -0.95 ± 0.05 in $2^+$ to -0.64 ± 0.05 in $2A$) and a contraction of the NNOPd-N bonds compared to $2^+$ ($\Delta d = -0.16$ Å for both bonds) is observed, suggestive of intramolecular one-electron reduction ($\frac{1}{2}$ electron from each NNO ligand) of the bridging nitrenido ligand. As such, the resonance structure of $2A'$ in Scheme 5 is deemed to be the best description for the intermediate nitridyl radical. The doublet state of $2B$, with a high $S^2$ value of 1.70, is proposed to show a significant contribution of the quartet state. The calculated small energy difference ($E_{\text{doublet}} - E_{\text{quartet}} = -0.9 \text{ kcal mol}^{-1}$) and the characteristics of the spin density plot, which shows two unpaired electrons on the redox-active NNO ligands and one on the nitrido nitrogen, are in agreement with this proposal. As such, intermediate $2B$ is best described as a triradical with antiferromagnetic coupling of an iminosemiquinonato radical with an imidyl radical. The significant radical character of the bridging nitrogen atom in both intermediates $2A$ and $2B$ explains the H-atom abstraction to form complex $3$. Interestingly, the presence of the redox-active NNO ligands appears to play an essential role in the generation of the nitridyl radical $2A$ by intramolecular ligand-to-nitrido electron transfer.

Scheme 5 Proposed mechanism for the formation of compound 3.
In an attempt to observe an intermediate nitridyl or imidyl radical, low-temperature photolysis experiments were performed. The EPR spectrum of $\text{2PF}_6$ (Figure 6) in toluene glass at 20 K revealed a strong anisotropic signal at $g = 2.0048$ and a weak triplet signal, including a ($\Delta m_s = 2$) half-field triplet signal. Irradiation of the sample within the EPR cavity resulted in a decrease of the signal intensity and disappearance of the triplet signals. Upon removal of the (initially yellow) sample from the EPR cavity, the sample had turned dark-blue, but this color rapidly faded upon thawing of the sample, restoring the initial yellow color. Refreezing the sample in liquid nitrogen did not lead to any further color change and the EPR spectrum of the refrozen sample revealed a very similar spectrum to that of $\text{2PF}_6$, including the half-field signal. The disappearance of the $\Delta m_s = 2$ half-field triplet signal in the observed intermediate suggests that there is no accessible triplet state at 20K. This would be in agreement with formation of $\text{2A}$ as an intermediate, as it has a significantly higher calculated singlet-triplet energy gap than $\text{2}^+$ and $\text{3}^+$. This higher singlet-triplet gap would also account for the observed decrease in signal intensity due to partial antiferromagnetic coupling, which is conceivable based on the spin density plot of $\text{2A}$.
Figure 6. Stacked EPR spectra in toluene glass at 20 K of 2PF₆ before (top), and after irradiation (center) at 20 K and upon warming to r.t. and refreezing (bottom). The inset shows a zoom that visualizes the triplet signals.

5.3 Conclusion

In summary, oxidative decomposition of mononuclear azide 1 using a mild oxidant results in the formation of dinuclear diradical 2BF₄ featuring a μ-azido ligand. The mechanism involves loss of N₂, and a reactive radical intermediate that reacts with an H-atom donor. Upon irradiation with a high intensity UV light source in benzene, 2PF₆ loses dinitrogen to form diradical 3 with a bridging amido ligand. Low temperature photolysis within the EPR cavity allows for the observation of an intermediate, which could be a transient nitridyl radical as DFT calculations suggest that irradiation of 2PF₆ results in the formation of a bridging nitridyl radical facilitated by overall one-electron oxidation of the redox-active NNO ligands. The source of the H-atoms appears to be adventitious water. Most extraordinarily, the redox-active NNO ligand appears to facilitate the generation of transient palladium nitridyl radicals through intramolecular ligand-to-nitrido electron transfer. Future research is required to gain insight into the exact mechanism of the decomposition of these azido complexes. Nonetheless, the ability of the redox-active NNO ligand to generate reactive nitridyl and imidyl species hints towards opportunities for the use of redox-active ligands in dinitrogen activation and ammonia oxidation.
5.4 Experimental

All reactions were carried out in an N₂ filled glovebox. Complex 1 and 2PF₆ were prepared according to the procedures described in Chapter 3. Acetylferrocenium tetrafluoroborate was prepared according to literature. With exception of the compounds given below, all reagents were purchased from commercial suppliers and used without further purification. THF, pentane, hexane, and diethyl ether were distilled from sodium benzenophene ketyl. CH₂Cl₂ and methanol were distilled from CaH₂, and toluene was distilled from sodium under nitrogen. NMR spectra (¹³P, ¹H 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 an HP-Agilent GC-MS or JEOL AccuTOF GCv4G GC- HRMS. EPR spectra were recorded on a Bruker EMP Plus spectrometer. High resolution mass spectra were recorded on a JEOL AccuTOFC-plus JMS-T100LP or JEOL JMS SX/SX102A four-sector mass spectrometer; for FAB-MS, 3-nitrobenzyl alcohol was used as a matrix. Irradiation experiments were performed using a bluepoint 4 ecocure UV point source from Hönle UV technology containing a 150 W mercury lamp without any filter.

Oxidative decomposition of complex 1

A solution of complex 1 (24.9 mg, 0.05 mmol) in 1 mL CDCl₃ was added to a stirred suspension of acetylferrocenium tetrafluoroborate (8.7 mg, 0.025 mmol) in 1 mL CDCl₃. After stirring for 18 hours the mixture was concentrated to ~1 mL, whereafter pentane (10 mL) was added. The precipitate was collected and dissolved in CDCl₃ (1 mL) and pentane (10 mL) was added. The precipitate was collected and dried in vacuo, affording 2BF₄ as a light-green solid (24 mg, 92%). ¹H NMR (300 MHz, CDCl₃, ppm) δ 17.5 (bs), 11.3 (bs), 10.4 (bs), 5.3 (bs) 1.7 (bs), 0.4 (bs), -2.0 (bs). ¹H NMR (300 MHz, THF-d₈, ppm) δ 16.9 (bs), 11.4 (bs), 10.4 (bs), 5.3 (bs), 1.7 (bs), 0.38 (1H), -1.8 (bs). ¹⁹F NMR (282 MHz, CDCl₃, ppm) δ -150.9 (s). IR (ATR, cm⁻¹): ν 2960 (m Car-H), 2869 (w Calk-H), 1259 (m), 1012 (s), 840 (s PF₆⁻), 793 (s). CSI-MS (m/z) calcd for C₄₄H₆₀N₇O₂Pd₂: 932.28, found 932.32 [M⁺].

Photolytic decomposition of 2PF₆

A suspension of 2PF₆ (10 mg, 0.01 mmol) in benzene (6 mL) divided over two Schlenk cuvets containing a stirring bar. The stirred suspensions were irradiated four times for 120 seconds with one minute intervals, as depicted in Figure 7. The dark solutions were allowed to cool to ambient temperature, whereafter the fractions were combined and filtered through a Teflon syringe filter. All volatiles were evaporated in vacuo and the residue was dissolved in THF (0.6 mL). Slow diffusion of pentane afforded 3 as a dark solid (6.6 mg, 67%). ¹H NMR (300 MHz, THF-d₈, ppm) δ 14.5 (bs), 11.4 (bs), 11.0 (bs), 10.4 (bs), 8.4 (s) 5.3 (s), 4.6 (s), 3.7 (bs), -0.69 (bs). ¹³P NMR (121 MHz, THF-d₈, ppm) δ -143.9 (sept, Jₚ-F = 709 Hz). ¹⁹F NMR (282 MHz, THF-d₈, ppm) δ -72.7 (d, Jₚ-F = 709 Hz). IR (ATR, cm⁻¹): 2960 (m Cₛ=H), 2869 (w Cₛ=H), 1259 (m), 1012 (s), 840 (s PF₆⁻), 793 (s). CSI-MS (m/z) calcd for C₄₄H₆₂N₅O₂Pd₂: 906.2977, found 906.3025 [M⁺].
Figure 7. Experimental setup for the photolysis of $2\text{PF}_6$.

Figure 8. $^1\text{H}$ NMR spectra of $2\text{PF}_6$ (top) and complex 3 in THF-$d_8$. 
Single crystal X-ray crystallography

All reflection intensities were measured at 110(2) K using a SuperNova diffractometer (equipped with Atlas detector) with Cu Kα radiation (λ = 1.54178 Å) under the program CrysAlisPro (Version 1.171.36.32 Agilent Technologies, 2013). The same program was used to refine the cell dimensions and for data reduction. The structure was solved with the program SHELXS-2013 (Sheldrick, 2008) and was refined on $F^2$ with SHELXL-2013. Analytical numeric absorption correction based on a multifaceted crystal model was applied using CrysAlisPro. The temperature of the data collection was controlled using the system Cryojet (manufactured by Oxford Instruments). The H atoms were placed at calculated positions (unless otherwise specified) using the instructions AFIX 43 or AFIX 137 with isotropic displacement parameters having values 1.2 or 1.5 $U_{eq}$ of the attached C atoms.

Complex 3: The H atom (H3A) attached to N3 was found difference Fourier maps, and its coordinates and isotropic temperature factor were refined freely. The other H atom attached to N3 is symmetrically generated via a twofold axis (as N3 is found at sites of twofold axial symmetry). The asymmetric unit contains ½ Pd dimer complex + ½ PF$_6^-$ counterion as both moieties are found at sites of twofold axial symmetry. The counterion is found to be disordered over two orientations, and its occupancy factor was constrained to be 0.5. The crystal lattice contains some amount of very disordered solvent molecules, whose contribution has been taken out in the final refinement (SQUEEZE details are provided in the CIF file). The absolute structure configuration was established by anomalous-dispersion effects in diffraction measurements on the crystal. The Flack and Hooft parameters refine to 0.017(13) and 0.024(4), respectively.

3: Moiety formula: C$_{44}$H$_{62}$N$_5$O$_2$Pd$_2$.F$_6$P, Fw = 1050.75, red plate, 0.35 × 0.05 × 0.04 mm$^3$, Tetragonal, $P4_2_1c$ (no. 114), $a = 12.97123(14)$, $c = 28.4281(6)$ Å, $V = 4783.11(14)$ Å$^3$, $Z = 4$, $D_x = 1.459$ g cm$^{-3}$, $\mu = 6.92$ mm$^{-1}$, $T_{\text{min}}$−$T_{\text{max}}$: 0.261–0.846. 30162 Reflections were measured up to a resolution of $(\sin \theta / \lambda)_{\text{max}} = 0.616$ Å$^{-1}$. 4687 Reflections were unique $(R_{\text{int}} = 0.0551)$, of which 4571 were observed [$I > 2\sigma(I)$]. 316 Parameters were refined using 165 restraints. $R_1$/$wR_2$ [$I > 2\sigma(I)$]: 0.0316/0.0818. $R_1$/$wR_2$ [all refl.]: 0.0325/0.0823. S = 1.162. Residual electron density found between −0.56 and 0.78 e Å$^{-3}$.

DFT calculations

Geometry optimizations were carried out using TURBOMOLE$^{12}$ coupled with the PQS Baker Optimizer$^{13}$ via the BOpt package$^{14}$ at the DFT level using the b3-lyp functional and the def2-TZVP basis set. The corrected broken symmetry energies $\varepsilon_{BS}$ of the open-shell singlets ($S = 0$) were estimated from the energy $\varepsilon_S$ of the optimized single-determinant broken symmetry solution and the energy $\varepsilon_{S+1}$ from a separate unrestricted triplet calculation at the same level, using the approximate correction formula:$^{15}$

$$\varepsilon_{BS} \approx \frac{S_{S+1}^2 \varepsilon_S - S_S^2 \varepsilon_{S+1}}{S_{S+1}^2 - S_S^2}$$
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All minima (no imaginary frequencies) and transition states (one imaginary frequency) were characterized by numerically calculating the Hessian matrix. In the mononuclear systems the tert-butyl groups on the aminophenolate moiety were replaced by methyl groups for the calculated energy profile to decrease computation-time.

**Analysis of the electronic structure of 1A and 1A⁺**

The spin density plots of the DFT calculated nitrido intermediates show significant spin density on the nitrido nitrogen for the OSS and triplet states of 1A⁺ as well as for its one-electron reduced analogue in the doublet state (Figure 9). For the triplet state of 1A⁺ the spin density of the two unpaired electrons is localized for 95% on the nitrido nitrogen. Comparison of the NNOPd-N distances in 1⁺ and 1A⁺ in the triplet and OSS state shows little difference (Δ = 0.04 and 0.07 Å, respectively). Moreover, the bond distances in the redox-active ring are characteristic for the NNO¹SO oxidation state for both spin states of 1A⁺ (MOS₃triplet = 0.01 ± 0.06; MOS₃OSS = 0.08 ± 0.06). In combination with the spin localization observed in the spin density plots, intermediate 1A⁺ is best described as a NNO¹SO-Pd nitrenido triplet diradical. A very similar distribution of the spin density is observed for the OSS state of 1A⁺. The high S² value of 1.64 for the doublet state of 1A suggest significant contribution of a quartet state. The small energy difference between the two spin states (E₃doublet – E₄quartet = -3.8 kcal mol⁻¹) and the spin density plot, which shows two unpaired electrons on the nitrido nitrogen and one unpaired electron on the redox-active ligand, confirms this. The doublet state can be explained by antiferromagnetic coupling of the NNO²SQ ligand radical with one of the unpaired electrons on the nitrido nitrogen. Comparison of the NNOPd-N distances in 1 and 1A shows a contraction of the Pd-N bond by 0.17. In combination with characteristic bond lengths for the NNO²SQ oxidation state (MOS = 0.87 ± 0.07), 1A is best described as NNO²SQ-Pd nitridyl radical.

**Figure 9.** DFT (b3-lyp, def2-TZVP) calculated spin density plots of 1A⁺ (left: triplet; center: OSS) and 1A (right: doublet).
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5.6 References