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Dioxygen Reduction by a Pd(0)−Hydroquinone Diphosphine Complex

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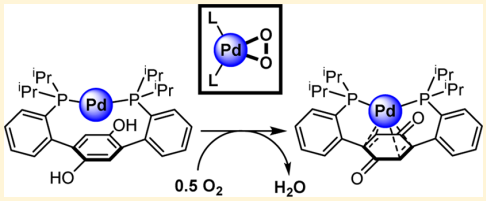
Supporting Information

ABSTRACT: A novel *p*-terphenyl diphosphine ligand was synthesized with a noninnocent hydroquinone moiety as the central arene (**1-H**). *Pseudo*-tetrahedral 4-coordinate Ni^0 and Pd^0−quinone (**2** and **3**, respectively) complexes proved accessible by metalating **1-H** with the corresponding $M(OAc)_2$ precursors. O_2 does not react with the Pd^0−quinone species (**3**) and protonation occurs at the quinone moiety indicating that the coordinated oxidized quinonoid moiety prevents reactivity at the metal. A 2-coordinate Pd^0−hydroquinone complex (**4-H**) was prepared using a one-pot metalation with Pd^{II} followed by reduction. The reduced quinonoid moiety in **4-H** shows metal-coupled reactivity with small molecules. **4-H** was capable of reducing a variety of substrates including dioxygen, nitric oxide, nitrous oxide, 1-azido adamantane, trimethylamine *n*-oxide, and 1,4-benzoquinone quantitatively producing **3** as the Pd-containing reaction product. Mechanistic investigations of dioxygen reduction revealed that the reaction proceeds through a η^2-peroxo intermediate (**Int1**) at low temperatures followed by subsequent ligand oxidation at higher temperatures in a reaction that consumed half an equivalent of O_2 and produced water as a final oxygenic byproduct. Control compounds with methyl protected phenolic moieties (**4-Me**), displaying a Ag^I center incapable of O_2 binding (**7-H**) or a cationic Pd−H motif (**6-H**) allowed for the independent examination of potential reaction pathways. The reaction of **4-Me** with dioxygen at low temperature produces a species (**8-Me**) analogous to **Int1** demonstrating that initial dioxygen activation is an inner sphere Pd-based process where the hydroquinone moiety only subsequently participates in the reduction of O_2, at higher temperatures, by H^+/e^- transfers.



INTRODUCTION

Dioxygen is commonly employed as an oxidant in biology where active site architecture regulates the delivery of reducing equivalents and protons to the substrate.[1] Similar strategies for electron[2] or proton management[3] using noninnocent ligand frameworks have been developed in synthetic systems. However, ligands capable of both proton and electron transfers during small molecule activation remain uncommon.[3b,4] Aerobic oxidation chemistry using Pd[5] has seen many advances recently due to the appeal of employing dioxygen as a stoichiometric oxidant similar to biological oxidase catalysts. Pd-catalyzed aerobic oxidations utilizing the reversible two proton-two electron couple of 1,4-benzoquinone as an additive has important applications in organic methodology.[6] The use of 1,4-benzoquinone and its substituted analogs as stoichiometric or catalytic oxidants in their own right has also recently been reviewed.[7] Recent mechanistic studies have highlighted the complicated reaction pathways available in the combination of redox active metal (Pd), redox active organic additive that can also act as ligand (1,4-benzoquinone), and O_2.[6a,8] Although in catalysis with Pd, 1,4-benzoquinone is used as a direct oxidant, we are particularly interested in the reactivity of the reduced counterpart, as a venue for providing protons and electrons for substrate activation in the presence of a reactive metal site. At the same time, the effect of the nature of the quinonoid fragment (reduced vs oxidized) on the chemistry of Pd with O_2 is particularly relevant to organic methodology. To that end, proximity to the reactive metal site is instrumental. Efforts to directly incorporate quinonoid moieties into ligand frameworks for Pd have been reported.[9] Although the interconversion of the hydroquinone and quinone forms of these ligands has been observed in some instances, the reduction of dioxygen with these Pd systems has not been reported. The use of π-bound quinonoid moieties as ligands has seen a several applications.[10]

Our group has reported the use of bis- and trisphosphinoarylbenzene ligands as scaffolds for mono- and multinuclear, π-bound transition metal complexes.[11] Noninnocence of the central arene moiety has been observed with cationic Ni—H complexes with respect to H-migration as well as with dinuclear Fe and Co carbonyl complexes with respect to partial reduction of the ring.[11e,g] The incorporation of a catechol moiety into the ligand scaffold capable of transferring multiple electrons and protons or other electrophiles during dioxygen reduction has also been recently reported for a Mo complex.[11c] In that case, there is no evidence that the metal center undergoes inner sphere chemistry with O_2, although electronic coupling with the quinonoid moiety and transfer of electrophile from catechol is

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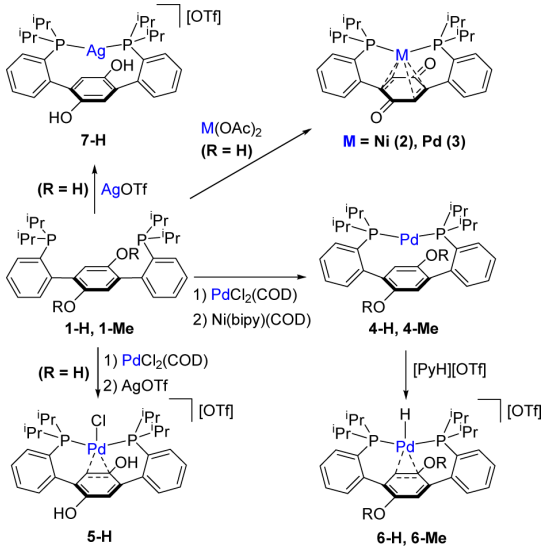
instrumental for reactivity. With its established inner sphere chemistry with O_2, Pd provides an ideal case study for the effect of a pendant noninnocent group capable of transferring both electrons and protons. Moreover, given the utilization of Pd, hydroquinone, and O_2 in catalysis the present studies have implications to organic methodology. We report the synthesis of a *p*-terphenyldiphosphine ligand containing a 1,4-hydroquinone moiety and the cooperative small molecule activation observed in a Pd^0 complex.

RESULTS AND DISCUSSION

Synthesis of Hydroquinone and Quinone Diphosphine-Supported Metal Complexes. The desired ligand, **1-H** (Scheme 1), was readily synthesized in five steps from commercially

Scheme 1. Synthesis of Reported Metal Complexes



available starting materials (see the Supporting Information (SI) for detailed ligand synthesis). Pd complexes supported by both the hydroquinone and quinone forms of compound **1-H** were targeted; a Ni complex was also synthesized for comparison. Metalations with either Ni or Pd diacetate proceeded in tetrahydrofuran (THF), though elevated temperatures were required for Ni. Both reactions yielded the corresponding M^0-quinone complexes **2** and **3** (~60% yield) as green and purple solids, respectively (Scheme 1).

The quinone assignment for the central arene was corroborated by strong ν_{CO} infrared (IR) absorptions at 1597 and 1603 cm^{-1} for complex **2** and **3**, respectively. While the quinone form of **1-H** could not be isolated, likely due to reactivity at the phosphine moieties, a shift to lower ν_{CO} stretching frequencies relative to 2,5-diphenyl-1,4-benzoquinone (1640 cm^{-1})[12] is consistent with data reported for other π-bound Ni and Pd quinone complexes.[13] Solution NMR data in CD_2Cl_2 for **2** and **3** are indicative of either C_2 structures or a fast process on the NMR time scale that exchanges the front and back of the molecules (as drawn). Both complexes show sharp singlets (**2**: 6.13 ppm, **3**: 6.10 ppm) corresponding to the central quinone protons and two distinct methine resonances (**2**: 2.52, 2.24 ppm, **3**: 2.46, 2.33 ppm) in the ^1H NMR spectra. By $^{31}P\{^1H\}$ NMR, single resonances are observed at 54.30 and 55.02 ppm for **2** and **3**, respectively. By UV−vis spectroscopy, absorptions are observed at ε_{389} = 5000 M^{-1} cm^{-1}, ε_{456} = 1700 M^{-1} cm^{-1}, ε_{623} = 650 M^{-1} cm^{-1} (**2**), and ε_{316} = 8300 M^{-1} cm^{-1}, ε_{375} = 6200 M^{-1} cm^{-1}, ε_{544} = 2400 M^{-1} cm^{-1} (**3**) (Figures S47 and S48).[14] Formally, these metalations result in the two proton/two electron oxidation of the hydroquinone moiety with the acetates and the M^{II} center serving as the proton and electron acceptors, respectively.

Single crystal X-ray diffraction (XRD) studies of **2** and **3** (Figure 1) confirm short C—O distances (**2**: 1.246(1) Å; **3**: 1.243(4) 1.242(5) Å) consistent with the quinone assignment for the central arene. Both complexes **2** and **3** bind the quinone moiety in an η^4 fashion similar to previously reported metal−quinone complexes.[13a−c,15] While η^4 binding has precedent for Pd, it should be noted that the majority Pd−quinone structures show η^2 coordination.[13c−e,15b,16] Both complex **2** and **3** display a distorted tetrahedral geometry with similar τ_4' values of 0.54 and 0.55 respectively using the two phosphine donors and the centroids of the bound C—C double bonds as the ligand contacts. Strong metal−arene interactions are evident from short average M—C distances of 2.16 and 2.32 Å for **2** and **3**, respectively. Substantial back bonding into the quinone C—C double bonds is also evident from the elongated C—C distances of 1.402(2) Å for **2** and 1.400(5) and 1.408(5) Å for **3**. A deplanarization of the quinone moiety is also observed with a C1—(C2—C3—C5—C6 centroid)—C4 angle of 162.2° for **3**.

Cyclic voltammetry (CV) studies of **3** in THF were also pursued to establish the redox chemistry of π-bound quinone moiety. Free quinone in DMSO shows two reductions to the corresponding radical anion and dianion at −0.91 V and −1.71 V versus Fc/Fc^+.[4c] Complex **3** shows a complicated CV data with two quasireversible reductions centered at −1.97 and −1.68 V and an irreversible oxidation at 0.54 v versus Fc/Fc^+ (Figure S53). However, additional oxidation events are observed at −1.09 and −0.4 V corresponding to the reduction events suggesting the formation of multiple species upon two electron reduction of **3**. Literature electrochemical data for Pd complexes with quinonoid moieties incorporated into the ligand scaffold show reductions at far milder potentials suggesting that the direct coordination of Pd to the quinone π-system results in significant changes in the electronic properties of the ligand.[9b,d,e]

The synthesis of Pd complexes with the hydroquinone form of **1-H** was pursued. Both Pd^0 (**4-H**) and Pd^{II} (**5-H**) species supported by **1-H** proved isolable (Scheme 1). **4-H** was synthesized as brown powder in 84% yield using a one-pot synthesis involving initial metalation with $PdCl_2$(COD) in THF followed by reduction with Ni(bipy) (COD) (bipy =2,2′-bipyridine). Treatment of **1-H** with $PdCl_2$(COD) followed by halide abstraction with silver triflate resulted in the formation of a cationic mono chloride species, **5-H**, which could be isolated as a dark red powder in 32% yield. Both **4-H** and **5-H** are stable as solids, but substantial decomposition to complicated mixtures of species in solution is observed over days.

Solution NMR spectra for both **4-H** (C_6D_6) and **5-H** (CD_3CN) show a sharp singlet (**4-H**: 6.94 ppm, **5-H**: 6.72 ppm) and a broad resonance (**4-H**: 4.14 ppm, **5-H**: 8.18 ppm) by ^1H NMR that correspond to the central hydroquinone CH and OH protons, respectively. One methine resonance at 1.88 and 3.12 ppm by ^1H NMR and a sharp singlet at 33.85 and a broad resonance at 34.22 ppm by $^{31}P\{^1H\}$ NMR are observed for **4-H** and **5-H**, respectively. These data are consistent with pseudo-C_2 symmetry or fast exchange processes on the NMR

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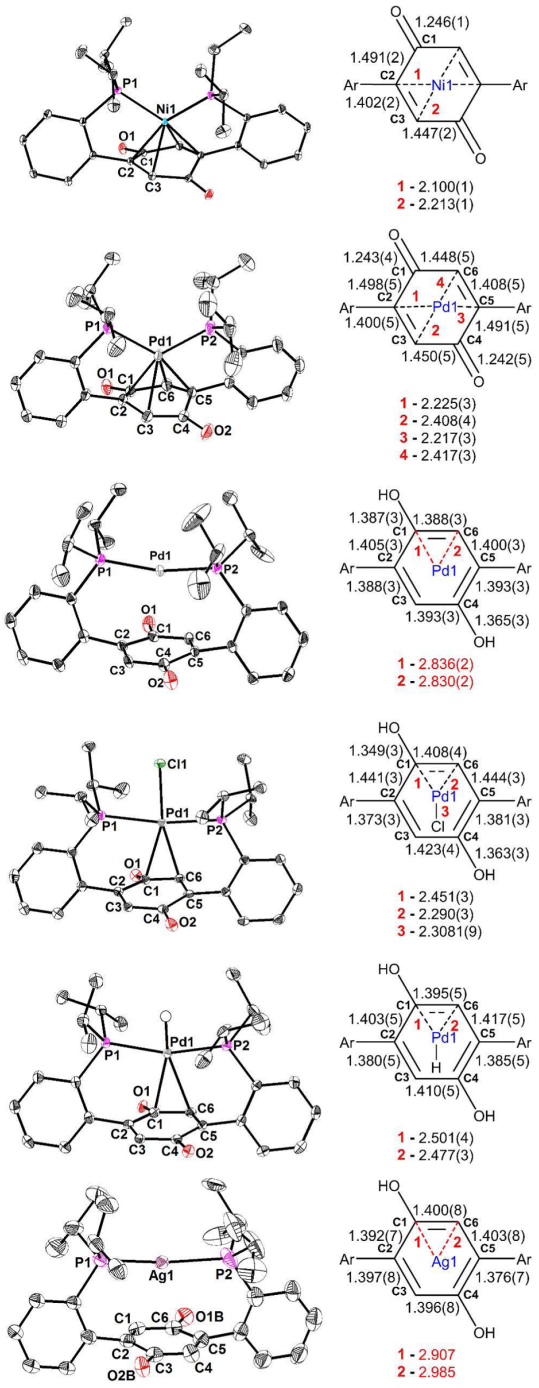

Figure 1. Solid-state structures and selected bond distances for complexes **2**, **3**, **4-H**, **5-H**, **6-H**, and **7-H** (top to bottom). Cocrystallized solvent, counteranions, and most hydrogen atoms omitted for clarity. Disorder of the hydroquinone oxygen positions has been omitted for clarity for complexes **6-H** and **7-H**.

time scale. Single crystals suitable for XRD analysis were obtained for **4-H** and **5-H** (Figure 1). Complex **4-H** was found to cocrystallize with a decomposition product presumably the result of extended time in solution during crystallization. Formation of this species suggests that decomposition of **4-H** in solution may occur via a metal-mediated isomerization of the hydroquinone moiety. The hydroquinone assignment for the central arene of **4-H** is supported by C—O distances of 1.387(3) and 1.365(3) Å, which are consistent with single bonds. The Pd center in **4-H** is two coordinate as long Pd1—C1 and Pd1—C6 distances of 2.836(2) and 2.830(2) Å, respectively, represent negligible metal−arene interactions. Consistent with this assignment, all the C—C bond distances of the central hydroquinone moiety do not vary substantially, ranging between 1.388(3) and 1.405(3) Å and are in line with structures of reported 2,5-diphenyl-1,4-hydroquinone moieties.[17] The P1—Pd1—P2 angle of 165.08(2)° also supports this assignment and is also likely enforced by the trans-spanning nature of the rigid *para*-terphenyl framework. These data indicate no disruption of aromaticity is occurring as would be expected upon metal coordination, making the best description of **4-H** a 14 e^-, two-coordinate Pd complex with a spectator hydroquinone moiety.

In complex **5-H**, the C—O bond lengths of 1.349(3) and 1.363(3) Å are comparable to **4-H** and consistent with the hydroquinone assignment for the central arene. Furthermore, complex **5-H** crystallizes with a clear hydrogen bonding interaction between a hydroquinone OH moiety and a neighboring triflate (SI). The Pd center shows an η^2 interaction with the central arene trans to the Cl ligand with Pd1—C1 and Pd1—C6 distances of 2.451(3) and 2.290(3) Å, respectively. Disrupted aromaticity in the hydroquinone moiety is evident from the alternating shorter (C1—C6, C2—C3, C4—C5) and longer (C1—C2, C3—C4, C5—C6) C—C bond lengths which indicate partially localized olefinic character resulting from Pd coordination. The geometry about Pd is square planar with a τ_4' value of 0.10 using the two phosphines, the chloride, and centroid of the C1—C6 bond as metal contacts. Complexes **3**, **4-H**, and **5-H** demonstrate the flexible nature of the Pd−central arene coordination (η^0, η^2, η^4) and how Pd oxidation state (**4-H** to **5-H**) and hydroquinone/quinone interconversion can influence preferred binding modes.

Small Molecule Activation by 4-H and Synthesis of Control Compounds. The hydroquinone−Pd^0 complex (**4-H**) was investigated for reactivity with small molecules toward utilization of protons and electrons stored in the central arene. In NMR experiments, the clean oxidation of **4-H** to **3** was observed with a variety of gaseous oxidants including dioxygen, nitric oxide, nitrous oxide, which were all confirmed to produce water as a reaction byproduct by ^{1}H NMR spectroscopy when reaction volatiles were transferred between J-Young tubes (S29−S31), although the nitrogen-containing byproducts were not identified. While rapid and clean conversion to **3** was observed with dioxygen and nitric oxide, the reaction of **4-H** with nitrous oxide was sufficiently slow that partial decomposition of the starting material was observed, which is observed to occur with **4-H** in solution over time in separate experiments. 1-Azido adamantane was also found to effect the transformation with the formation of 1-amino adamantane confirmed by gas chromatography−mass spectrometry (GC-MS). Additionally, trimethylamine *n*-oxide, 1,4-benzoquinone, and 2,4,6-tri*tert*butylphenoxyl radical were also found to react with **4-H** to form **3**. With all the substrates surveyed above, no further oxidation of **3** was observed.

A more detailed mechanistic understanding of the rapid reactivity of **4-H** with dioxygen was pursued. The reactions of Pd and Pt complexes with molecular dioxygen have been

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recently reviewed.[18] The direct activation of dioxygen by low-coordinate Pd^0 complexes has been reported and typically yields an η^2-peroxo.[16a,19] However, a bis(η^1-superoxo)[20] and a terminal η^1-superoxo[21] have been reported. Therefore, it is possible that initial dioxygen activation can occur at the Pd^0 center prior to subsequent activation of the hydroquinone moiety. The direct reaction of Pd hydrides with dioxygen to yield hydroperoxo complexes has also been reported though the reaction mechanism varies with different supporting ligands.[6a,8,22] Therefore, the possibility of proton transfer to the Pd center from the hydroquinone moiety prior to dioxygen activation must also be considered. The autoxidation of some hydroquinones by dioxygen in the absence of catalyst has been reported, most notably in the anthraquinone process which is the primary means of industrial hydrogen peroxide production.[23] As a net change in Pd oxidation state does not occur in the conversion of **4-H** to **3**, it is possible that the reaction with dioxygen is entirely mediated by the ligand without involvement of the metal center. Previous studies with a related catechol diphosphine ligand have shown that dioxygen activation likely occurs by an initial outer sphere electron transfer step offering another mechanistic proposal.[11c] Cooperative activation of dioxygen by both Pd center and the ligand in a concerted process is also plausible.

In order to address the aforementioned mechanistic possibilities, suitable complexes to investigate different reactivity patterns were synthesized. To test for Pd-only initial dioxygen activation, a Pd^0 complex supported by a previously reported diphosphine ligand with a para-dimethoxy substituted central arene was synthesized (**4-Me**) using the same synthetic route as **4-H** with the product obtained as an orange solid in 98% yield (Scheme 1). Solution NMR data (C_6D_6) are consistent with pseudo-C_2 symmetry or fast exchange processes on the NMR time scale with chemical shifts comparable to **4-H**. Sharp singlets are observed for the central arene CH and OMe proton resonances at 6.86 and 3.49 ppm, respectively. One methine resonance at 1.96 ppm by ^{1}H NMR and a sharp singlet at 33.81 by $^{31}P\{^1H\}$ NMR are also seen.

To test for the potential reactivity of Pd—H species, complex **4-H** and **4-Me** were protonated with one equivalent of pyridinium triflate to yield **6-H** and **6-Me**, respectively (Scheme 1). Solution NMR data for both species (CD_3CN) are quite similar and consistent with pseudo-C_2 symmetry or fast a exchange processes on the NMR time scale. Reminiscent of **5-H**, the central arene CH proton resonances appear as sharp singlets at 6.79 and 6.99 ppm for **6-H** and **6-Me**, respectively. The OH and OMe protons appear as a broad resonance at 7.42 and a sharp singlet at 3.73 ppm, respectively. A single methine proton resonance is observed (**6-H**: 2.46 ppm; **6-Me:** 2.48 ppm). Both complexes coincidentally show the Pd—H resonances as triplets (**6-H**: J_{PH} = 8.5 Hz, **6-Me**: J_{PH} = 9.0 Hz) at −16.33 ppm, while the $^{31}P\{^1H\}$ NMR shows a doublet centered at 41.57 ppm for **6-H** and a broadened singlet at 41.93 ppm for **6-Me**.

Single crystals suitable for XRD analysis were obtained for **6-H** (Figure 1). The hydroquinone oxygens were nearly equivalently disordered across the C1/C4 and C3/C6 positions, only the majority species has been shown in Figure 1 for clarity. While this disorder precludes assessment of the C—O bond lengths, the central arene bond distances show an alternation of long and short distances analogous to **5-H** suggestive of disrupted aromaticity in a hydroquinone moiety rather than a quinone assignment. The Pd-center shows η^2 coordination to C1—C6 akin to **5-H** though the Pd1—C1 and Pd1—C6 distances are longer at 2.501(4) and 2.477(3) Å respectively. **6-H** and **6-Me** are cationic and therefore represent a Pd—H that could potentially arise from intermolecular proton transfer between equivalents of **4-H**. These complexes can provide insight into the behavior of Pd—H species on the current ligand platforms and probe how the noninnocence of the hydroquinone moiety affects reactivity. An alternative Pd—H accessible from **4-H** could be neutral, corresponding to (formal) intramolecular proton transfer from the hydroquinone moiety to the Pd center. Such a compound has not been observed or isolated to date.

To probe for ligand-only reactivity, a Ag^I complex, **7-H**, was synthesized by metalation of **1-H** with silver triflate in THF. The product was isolated as colorless needles in 68% yield following recrystallization. Solution NMR data (CD_3CN) is consistent with pseudo-C_2 symmetry or fast exchange process on the NMR time scale. The central hydroquinone OH and CH proton resonances appear as a broad singlet at 6.98 ppm and a sharp singlet at 6.85 ppm, respectively. Additionally, a single methine resonance at 2.52 ppm is observed. The $^{31}P\{^1H\}$ NMR shows two pairs of doublets centered at 28.33 with J_{PAg} values of 559.7 and 484.9 Hz owing to coupling to ^{107}Ag (52% abundance) and ^{109}Ag (48% abundance) nuclei.

Single crystals of **7-H** suitable for XRD analysis were obtained. Like **6-H**, nearly equivalent disorder of the hydroquinone oxygens is present precluding detailed analysis of the C—O bond lengths. Ag1—C1 and Ag1—C6 distances are in excess of 2.9 Å, consistent with a negligible metal-arene interaction as for **4-H**. C—C bond lengths in the hydroquinone moiety do not show an alternation of longer and shorter bond distances. This structural information indicates that **7-H** serves as a suitable electronic and structural control for dioxygen reactivity with the hydroquinone moiety, as no substantial metal−arene interaction perturbs the reactivity of the central arene moiety as seen in **4-H**.

Studies of Initial Dioxygen Activation. The reactivity of dioxygen with all control compounds was pursued (Scheme 2). At room temperature **4-Me** was found to rapidly react with dioxygen to form a complicated mixture of species. This reactivity differs from that of previously reported bis(phosphine) Pd^0 complexes which are known to form (η^2-peroxo) complexes stable enough to be structurally characterized.[19a,b,f,l,q] Compound **7-H** showed no reaction for multiple weeks at room temperature when exposed to 1 atm of dioxygen (Scheme 2). This indicates that direct oxidation of the hydroquinone moiety of the ligand by dioxygen is not a facile reaction pathway, and it likely does not occur in the reaction of **4-H**. Compound **6-H** showed a color change upon mixing to generate a bright pink species that shows a peak at λ_{max} = 520 nm. By $^{31}P\{^1H\}$ and ^{1}H spectroscopy, the starting material is consumed within 6 h, resulting in the formation of a new major species, **3(H)**$^+$. No peaks are observed upfield of 0 ppm, suggesting the lack of a Pd—H moiety. An identical UV/vis spectrum was obtained upon addition of one equivalent of pyridinium triflate to **3** in THF leading to the assignment of this product as the protonated quinone species. **6-Me** showed reaction with dioxygen upon mixing at room temperature to generate a complicated mixture of species. To test for the direct oxidation of the hydroquinone moiety in **6-H** by dioxygen, **5-H** was treated with O_2, since dioxygen activation across Pd^{II}—Cl bond has not been reported to the best of our knowledge. No reaction with dioxygen was observed for complex **5-H**. Similar to **7-H**, these results suggest that oxidation of the

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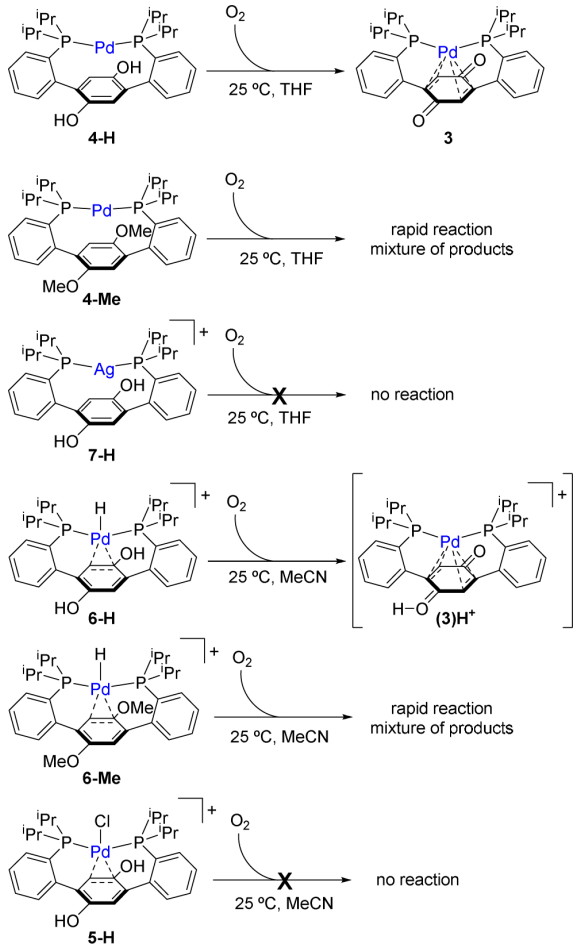
Scheme 2. Summary of Room Temperature Reactivity

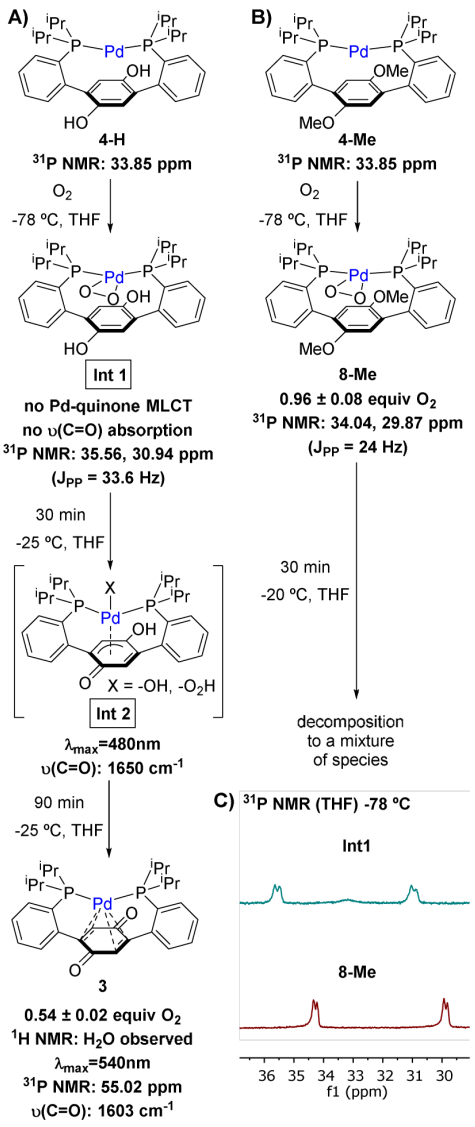


hydroquinone moiety to the corresponding quinone is likely metal-mediated as no evidence for direct ligand chemistry has been seen.

Studies of dioxygen reactivity at lower temperatures were pursued to detect intermediates for mechanistic insight. Dioxygen addition to **4-H** at −78 °C resulted in the formation of a new species (**Int1**, Scheme 3, a) by $^{31}P\{^{1}H\}$ NMR (THF). **Int1** shows two coupling doublets at 35.38 and 30.77 ppm (J_{PP} = 32 Hz) consistent with an asymmetric species in solution (Scheme 3, c). Low temperature solution IR data showed no absorptions consistent with a C—O double bond, indicating that no conversion of the hydroquinone moiety to a quinone or semiquinone form had occurred. While observed to be stable at −78 °C for up to an hour, **Int1** was found to be quite thermally sensitive with 80% conversion to **3** occurring at −50 °C over an hour. These data suggest that a Pd-only binding and activation of dioxygen is occurring at lower temperatures without any participation of the hydroquinone.

To test if the hydroquinone moiety was necessary for initial activation, dioxygen was added to a solution of **4-Me** at −78 °C, in which the phenolic moieties are protected with methyl groups. The formation of a new species, **8-Me**, was observed upon mixing by NMR (d_8-THF) (Scheme 3, b). Similar to **Int1**, $^{31}P\{^{1}H\}$ NMR shows two coupling doublets at

Scheme 3. Proposed Dioxygen Activation Mechanism for 4-H and 4-Me



34.04 and 29.87 ppm (J_{PP} = 24.0 Hz) again consistent with an asymmetric species suggesting the formation of a very similar species by NMR. By ^{1}H NMR, two signals for the central arene CH (6.87 and 6.66 ppm) and OMe (3.56 and 3.47 ppm) protons are observed. Three distinct methine proton signals that integrate 1:1:2 appear at 3.67, 3.59, and 1.98 ppm). Unlike **Int1**, **8-Me** was found to be stable for over 4 weeks at −78 °C in THF and for over multiple hours at −40 °C with no sign of decomposition. This information further supports the assignment of direct dioxygen binding at the Pd center without involvement of the hydroquinone moiety. Furthermore, the increased stability of **8-Me** suggests that the hydroquinone moiety, when present, facilitates further reactivity with the Pd-coordinated O_2 moiety.

No reaction of **6-H** or **6-Me** with dioxygen was observed at −30 °C by $^{31}P\{^{1}H\}$ NMR (CD_3CN), suggesting that the activation of dioxygen by **4-H** likely does not occur via a

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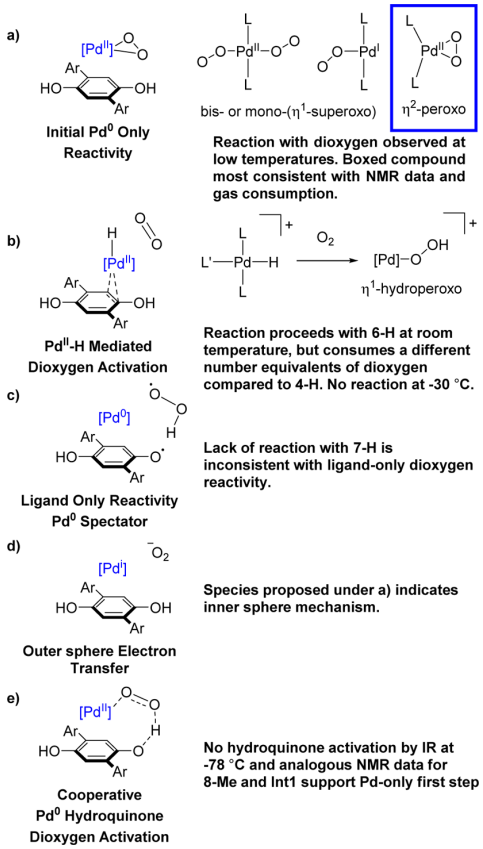
cationic Pd—H species. However, reactivity from a neutral complex generated by intramolecular protonation to form a Pd—H moiety and deprotonated hydroquinone cannot be ruled out. The similarity of **Int1** and **8-Me** by NMR further suggests that the activation of dioxygen by **4-H** does not occur via a Pd—H species, given that the precursor to **8-Me** does not have acidic protons. Gas quantification experiments using a Toepler pump were used to determine the equivalents of dioxygen consumed by each reaction (Table S1). At 25 °C, **4-H** and **6-H** were found to consume 0.54 ± 0.02 and 0.95 ± 0.04 equiv of dioxygen, respectively. This difference in dioxygen equivalents consumed may result from a different activation mechanism or hydrogen peroxide disproportionation by **4-H** or its intermediates. Oxygen addition to **4-Me** at −78 °C showed consumption of 0.96 ± 0.08 equiv of dioxygen. During the freeze−pump−thaw cycles of **Int1** during Toepler pump experiments a noticeable purple hue developed in the reaction vessel indicating the partial formation of **3** regardless of attempts to keep reaction mixtures from warming up substantially. These experiments with **4-H** were likely unsuccessful due to the decreased thermal stability of **Int1** compared to **8-Me** as seen in NMR experiments.

The binding of a single equivalent of dioxygen to **4-Me** at low temperatures rules out the formation of a bis(η^1-superoxo) (Scheme 4, a). The literature example of a η^1-(superoxo) complex was observed to convert to the corresponding η^2-peroxo over 80 min at temperatures above −82 °C.[21] Therefore, the most plausible assignment for **8-Me** and, due to similarities by $^{31}P\{^1H\}$ NMR, **Int1**, is an η^2-peroxo species (Scheme 4, a).[24] Furthermore, η^1-(superoxo) would be expected to bind the oxygenic ligand in a position trans to the central arene moiety as seen in the case of **5-Cl** resulting in equivalent phosphine donors on the NMR time scale. Differences in reaction rates at low temperature and the amount of dioxygen consumed make reactivity derived from a Pd—H species less likely (Scheme 4, b). The absence of oxidation of **7-H** rules out hydroquinone oxidation akin to that of the anthraquinone process (Scheme 4, c).[23] It is also noteworthy that the reactivity appears to proceed through an initial inner sphere intermediate unlike previous reports on molybdenum carbonyl complexes (Scheme 4d).[11c] Finally, cooperative activation of dioxygen between the Pd center and hydroquinone ligand is also ruled out as no evidence for hydroquinone oxidation by IR was observed for **Int1**. Additionally, the same type of intermediate can be accessed with **4-Me** which does not have the ability to transfer protons/H atoms (Scheme 4e).

Scheme 4. Possible Dioxygen Activation Mechanisms



As both **4-H** and **4-Me** activate dioxygen at low temperatures to likely form η^2-peroxo species, the electrophilic or nucleophilic character of the oxygenic moiety of **8-Me** was tested with external substrates. As a test for electrophilic character, **8-Me** was mixed with cyclohexene, 2,4,6-tri*tert*butylphenol, methyl *para*-tolyl sulfide, or triphenylphosphine.[25] No formation of cyclohexanone or sulfoxide product was observed by GC or GC-MS spectroscopy. No formation of 2,4,6-tri*tert*butylphenoxyl radical was observed by UV/vis spectroscopy suggesting that an H atom abstraction pathway is not occurring (BDFE (kcal mol^{-1}) in DMSO: 2,4,6-tri*tert*butylphenol =80.6, 1,4-hydroquinone =80.0).[4c] The formation of triphenylphosphine oxide was detected by GC-MS. However, low temperature NMR experiments show this reaction to proceed by initial triphenylphosphine substitution of **1-Me** to form $(PPh_3)_2Pd(\eta^2\text{-}O_2)$ by comparison to literature $^{31}P\{^1H\}$ chemical shifts[18a] and independent synthesis from $Pd(PPh_3)_4$ and dioxygen (Figure S54). Subsequent phosphine oxidation therefore likely does not involve terphenyl diphosphine. As a test for nucleophilic character, cyclohexane carboxyaldehyde or *para*-trifluoromethyl benzylalcohol were added to **8-Me**.[25a,b] In both cases, oxidation products, cyclohexene, and the corresponding benzaldehyde, were observed by GC and GC-MS analysis respectively, suggesting nucleophilic character for **8-Me**. These data taken together with the control reactions indicate that dioxygen activation at **4-H** occurs through a Pd-only mediated formation of a (η^2-peroxo) species with nucleophilic character. Hydroquinone activation occurs subsequently through an inter- or intramolecular proton transfer.

Low temperature NMR experiments were run to probe whether intermolecular proton transfer occurs. First, intermolecular proton transfer was tested by studying the reaction of dioxygen with a mixture of **4-Me** and the Ag^I complex, **7-H**. At −78 in THF, **8-Me** was formed in the presence of **7-H** upon the addition of dioxygen. Warming the reaction mixture to −40 °C did not result in any detectable reaction over more than 30 min suggesting intermolecular proton transfer is not occurring at these temperatures. In contrast, **Int1** shows significant conversion over 30 min, even at −50 °C. The dioxygen reactivity of **4-H** in the presence of **7-H** was also tested. As with **4-Me**, oxygen addition at −78 °C in THF resulted in the formation of **Int1** in the presence of **7-H**. Warming the reaction to −40 °C showed near quantitative conversion of **Int1** to form **3** within 10 min without any detectable consumption with **7-H**. While these experiments do not rule out intermolecular proton

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transfer during conversion of **Int1**, they do suggest that such proton transfer to the analogous (η^2-peroxo) species supported by **4-Me** without a pendant hydroquinone moiety either does not occur or is not sufficient for subsequent reactivity of the O_2 moiety.

The reaction of **4-H** with O_2 was monitored by UV−vis spectroscopy. Oxygen addition at −78 °C to a THF solution of **4-H** resulted in a color change from yellow/brown to orange/brown within 30 seconds consistent with the rapid formation of **Int1** (Figure 2A). Warming the solution of **Int1** to −25 °C

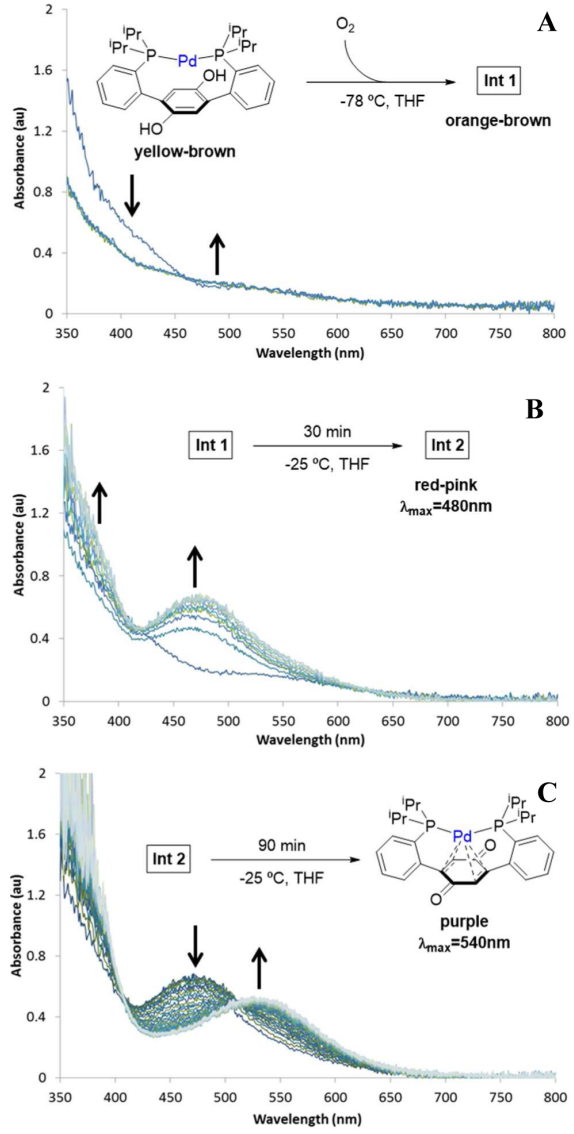

Figure 2. Low temperature UV/vis data obtained for the reaction of dioxygen with **4-H** in THF. (A) Conversion of **4-H** to **Int1** at −78 °C. (B) Conversion of **Int1** into **Int2** over 30 min at −25 °C. (C) Conversion of **Int2** into **3** over 90 min at −25 °C.

resulted in the conversion to a new intermediate (Figure 2B), in contrast to the NMR experiments, with a λ_{max} of 480 nm over the course of approximately 30 min. This suggests that at lower concentrations, the rates of steps following the formation of **Int1** (and **Int2**) are slowed enough to allow the observation of an additional intermediate. Low temperature solution IR data at −35 °C showed the appearance of an absorption at 1601 cm^{-1} attributable to the formation of a substantial quantity of **3**. However, a small absorption at 1650 cm^{-1} (Figure S45) was also observed that may be attributed to the transient formation of **Int2**, which suggests stepwise activation of the hydroquinone moiety. **Int2** was observed to gradually convert to **3**, the final reaction product, over the course of 90 min at −25 °C (Figure 2C). Cooling the solution of **Int2** to −78 °C could not arrest the conversion to **3**, although the reaction was slower. The formation of **Int2** and **3** both occur with isosbestic points indicating that these transformations correspond to the clean interconversion of these species. These data show that **Int2** possesses an activated hydroquinone with at least partial quinone character by IR spectroscopy. The UV−vis spectra of **Int2** is inconsistent with a Pd^0 protonated quinone, as such structure is assigned to be the product of **6-H** with dioxygen, which can be prepared independently, and shows a peak at λ_{max} = 520 nm. Therefore, it is proposed that **Int2** is a Pd^{II} species with the metal center coordinated to a semiquinone moiety (Scheme 3a). An anionic oxygenic fragment could be released or still remain coordinated to the metal center in a distorted geometry. If the oxygenic fragment is released, then **Int2** would formally correspond to $(\mathbf{3})\mathbf{H}^+$ which is inconsistent with the spectroscopic data. Therefore, it is proposed that an oxygenic moiety remains coordinated, and because of coordination trans to the central arene, a second proton transfer is slow, allowing observation of this intermediate. As one equivalent of dioxygen is assigned to be bound in **Int1** while only half an equivalent is consumed by the net reaction to 3, a dioxygen release must occur during the conversion of **Int1** to **3** via an intermolecular disproportionation process. If the oxygen release has already occurred by the time formation of **Int2**, then the proposed anionic oxygenic fragment may be a hydroxide ligand. However, if dioxygen release occurs in the conversion of **Int2** to **3**, then the bound oxygenic fragment may be a hydroperoxo species. Unfortunately, the instability of these intermediates and fluorescence from the ligand prevented detailed IR or resonance Raman spectroscopy to further characterize the identity of the reaction intermediates. As intermediate **Int2** is not observed at the higher concentrations of the NMR experiments, the steps following the formation of **Int2** must be slower than its generation. The concentration effect could be a consequence of the intermolecular reaction required for the proposed disproportionation.

In catalytic Pd-meditated organic transformations that utilize benzoquinone as a stoichiometric oxidant, the regeneration of $Pd^{II}X_2$ species required for substrate oxidation relies on the transfer of reducing equivalents from Pd^0 to the quinone moiety.[6] Compound **3** allows investigation of the propensity of a Pd^0 center coordinated to the π-system of the quinone to undergo oxidation or protonation. As supported by CV data and air stability, the oxidation of **3** to form a Pd^{II}−quinone complex requires strong oxidant. Excess (5 equiv) aqueous hydrogen peroxide was found to slowly bleach the characteristic UV/vis features of **3** (88% conversion over 12 h) at room temperature; however well-defined reaction products could not be isolated. The present reactivity suggests that loss of the benzoquinone ligand might be necessary prior to (or in concert with) oxidation of Pd^0, for example with O_2.[6a] In the present system, **4-H** undergoes facile reaction with O_2, showing that upon removal of hydroquinone coordination, oxidation of Pd^0

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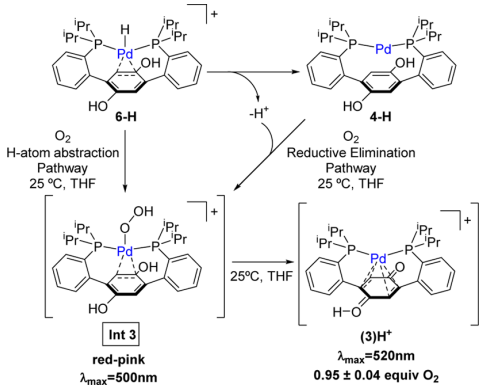
occurs readily. As Pd—H species are known intermediates in benzoquinone mediated chemistry, further studies were performed with **6-H**.[6a]

By UV−vis spectroscopy, **6-H** was found to convert to a pink compound with λ_{max} of 500 nm over several hours following oxygen addition at room temperature (Figure S49). The subsequent conversion to the final product that has a λ_{max} of 520 nm (Figure S50) requires greater than 16 h for completion as judged by the slowly shifting λ_{max} in the UV−vis spectrum. Toepler pump experiments indicate the overall reaction consumes a single equivalent of dioxygen. On the basis of literature precedence, this reaction may proceed via the initial formation of a hydroperoxo species in a geometry akin to **5-H** where the central hydroquinone moiety is trans to the oxygenic ligand. Whether this transformation occurs via a reductive elimination/deprotonation route or a hydrogen-atom abstraction pathway as proposed in the literature is unknown at this point (Scheme 5).[22b,c] Subsequent deprotonation of the hydroquinone

Scheme 5. Proposed Dioxygen Activation Mechanism of 6-H



moiety by the hydroperoxide results in release of H_2O_2 and formal reduction of the metal center by the pendant hydroquinone.[26] Given the difference in rate of oxidation between **6-H** and **4-H**, a cationic Pd—H is not an intermediate consistent with the fast reaction of **4-H** with O_2. Previously, benzoquinone has been reported to promote reductive elimination of carboxylic acid from Pd—H complexes.[6a] The final product $(\mathbf{3(H)}^+)$ in the reaction of **6-H** with O_2, lacking diagnostic Pd—H peaks by ^{1}H NMR spectroscopy, indicates that formation of such hydridic species by formal oxidation via protonation at the metal is unfavorable. The π-acidic benzoquinone moiety bound to Pd^0 makes the metal center electron deficient and stabilizes the lower oxidation state.

CONCLUSIONS

A novel noninnocent ligand platform capable of cooperatively mediating the multiproton-multielectron reduction of multiple substrates at a Pd^0 center has been synthesized based on a hydroquinone−diphosphine moiety. Reduction of O_2 was studied in detail. The reaction occurs by an initial Pd-mediated step which involves binding of one equivalent of dioxygen to form a nucleophilic η^2-peroxo species assigned by comparison to complex **8-Me**, displaying a dimethylated hydroquinone moiety. Subsequent activation of the hydroquinone moiety occurs at higher temperatures with a second intermediate observable by UV−vis spectroscopy at low concentrations. The reported reactivity represents an overall transformation that requires both the redox active metal capable of binding O_2 as well as the noninnocent pendant hydroquinone within the same molecule. A related Pd^0 complex (**4-Me**), lacking the hydroquinone moiety, or Ag^I-hydroquinone complex (**7-H**), lacking a metal center capable of binding O_2, do not reproduce the reactivity independently or even in combination. Overall, the described results highlight the potential for the reduction of small molecule substrates by utilizing auxiliary redox-active and acid−base noninnocent moieties to store reducing equivalents. From the perspective of oxidation organic methodology utilizing the Pd−benzoquinone combination, O_2 does not react with the isolated Pd^0−benzoquinone species and protonation occurs at the quinone moiety indicating that the oxidized quinonoid moiety prevents reactivity at the coordinated metal.

ASSOCIATED CONTENT

Supporting Information

This material available free of charge via the Internet at The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b12928.

Crystallographic details (CIF) (TXT)
Characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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(24) Resonance Raman experiments in 2-methyl tetrahydrofuran using wavelengths accessible to an Ar ion laser were attempted for Int1 and 8-Me. Depending on the excitation wavelength no signals from compound were detected of fluorescence from the ligand precluded the observation of bands corresponding to the O—O stretch in the peroxo species.

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