

Formation of the Palladium(IV) Complex $[(\text{Me}_3\text{tacn})\text{Pd}^{\text{IV}}\text{Me}_3]^+$ through Aerobic Oxidation of $(\text{Me}_3\text{tacn})\text{Pd}^{\text{II}}\text{Me}_2$ ($\text{Me}_3\text{tacn} = N,N',N''$ -Trimethyl-1,4,7-triazacyclononane)

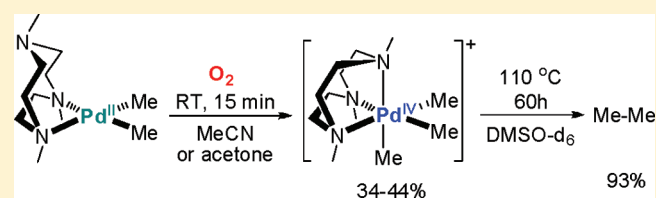
Julia R. Khusnutdinova,[†] Fengrui Qu,[†] Ying Zhang,[†] Nigam P. Rath,[‡] and Liviu M. Mirica^{*,†}

[†]Department of Chemistry, Washington University, One Brookings Drive, St. Louis, Missouri 63130-4899, United States

[‡]Department of Chemistry and Biochemistry, University of Missouri—St. Louis, One University Boulevard, St. Louis, Missouri 63121-4400, United States

Supporting Information

ABSTRACT: The dimethyl Pd^{II} complex $(\text{Me}_3\text{tacn})\text{Pd}^{\text{II}}\text{Me}_2$ ($\text{Me}_3\text{tacn} = N,N',N''$ -trimethyl-1,4,7-triazacyclononane) undergoes facile aerobic oxidation to yield the stable species $[(\text{Me}_3\text{tacn})\text{Pd}^{\text{IV}}\text{Me}_3]^+$. EPR, UV–vis, and ESI-MS studies suggest an inner-sphere mechanism for the oxidation of $(\text{Me}_3\text{tacn})\text{Pd}^{\text{II}}\text{Me}_2$ by O_2 and formation of Pd^{IV} species. In addition, the structurally characterized complex $[(\text{Me}_3\text{tacn})\text{Pd}^{\text{IV}}\text{Me}_3]^+$ undergoes selective elimination of ethane at elevated temperatures. Overall, this system represents one of the first examples of aerobic oxidation of a Pd^{II} organometallic precursor to yield a well-defined Pd^{IV} product, supporting the role of Pd^{IV} species as viable intermediates in Pd-mediated catalytic or stoichiometric aerobic oxidative transformations.

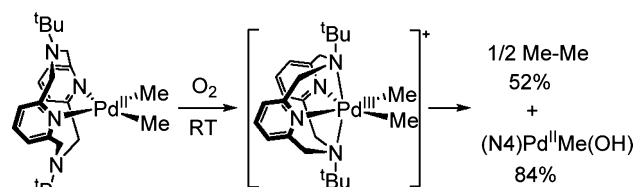


Aerobic transformations catalyzed by palladium complexes are among the most important synthetic tools in organic synthesis and provide a practical means of dioxygen utilization as an environmentally benign and inexpensive oxidant.¹ While the majority of Pd-catalyzed aerobic transformations have been proposed to involve the formation of Pd^0 complexes and their subsequent reoxidation by dioxygen,¹ the intermediacy of high-valent Pd^{IV} or Pd^{III} species has recently been proposed in some catalytic and stoichiometric aerobic transformations.^{2–4} In this context, there are only two reports on the aerobic oxidation of Pd^{II} complexes to generate spectroscopically detected Pd^{III} species.^{3b,4} However, the formation of Pd^{IV} complexes by aerobic oxidation of Pd^{II} precursors has not been documented, and their relevance to aerobic oxidation catalysis is often based on indirect evidence.² Importantly, the direct aerobic oxidation of Pd^{II} organometallic complexes to Pd^{IV} may not only provide alternate reactivity patterns to the commonly employed Pd^{II} / Pd^0 -mediated transformations but also avoid common problems associated with Pd black formation.^{1g}

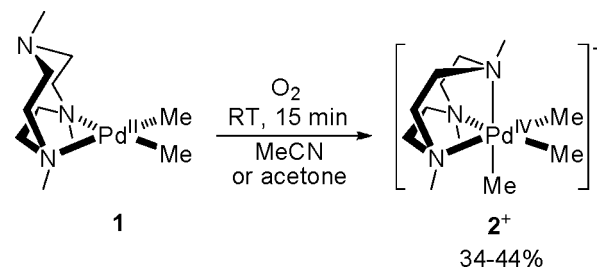
We have previously shown that a $\text{Pd}^{\text{II}}\text{Me}_2$ complex supported by the tetradentate ligand ${}^t\text{BuN}4$ (${}^t\text{BuN}4 = N,N'$ -di-*tert*-butyl-2,11-diaza[3.3](2,6)pyridinophane) undergoes facile inner-sphere oxidation by O_2 or peroxides to yield the Pd^{III} complex $[({}^t\text{BuN}4)\text{Pd}^{\text{III}}\text{Me}_2]^+$, which then undergoes elimination of ethane under ambient conditions (Scheme 1).⁴ Herein we report the aerobic oxidation of $(\text{Me}_3\text{tacn})\text{Pd}^{\text{II}}\text{Me}_2$ ($\text{Me}_3\text{tacn} = N,N',N''$ -trimethyl-1,4,7-triazacyclononane) to yield the stable complex $[(\text{Me}_3\text{tacn})\text{Pd}^{\text{IV}}\text{Me}_3]^+$ (Scheme 2), one of the first examples of formation of a well-defined Pd^{IV} species upon aerobic oxidation of a Pd^{II} precursor.⁵

The Pd^{II} complex $(\text{Me}_3\text{tacn})\text{Pd}^{\text{II}}\text{Me}_2$ (**1**) was obtained in 82% yield through the reaction of $(\text{COD})\text{PdMe}_2$ with

Scheme 1. Reported Aerobic Reactivity of $({}^t\text{BuN}4)\text{Pd}^{\text{II}}\text{Me}_2$ ⁴



Scheme 2. Aerobic Reactivity of $(\text{Me}_3\text{tacn})\text{Pd}^{\text{II}}\text{Me}_2$



Me_3tacn .⁶ X-ray analysis of **1** reveals a square-planar geometry of the Pd^{II} center, which is bound to two methyl ligands and two N atoms, while the third N atom of Me_3tacn points away from the metal center (Figure 1a), similar to the reported structure of $(\text{Me}_3\text{tacn})\text{Pd}^{\text{II}}\text{Cl}_2$.⁷ The Pd–Me distances are 2.032 and 2.034 Å, in line with those for other $\text{Pd}^{\text{II}}\text{Me}_2$ complexes supported by diamine ligands.⁸ The two methyl ligands of **1** give rise to a singlet at 0.37 ppm in the ${}^1\text{H}$ NMR

Received: May 17, 2012

Published: June 11, 2012

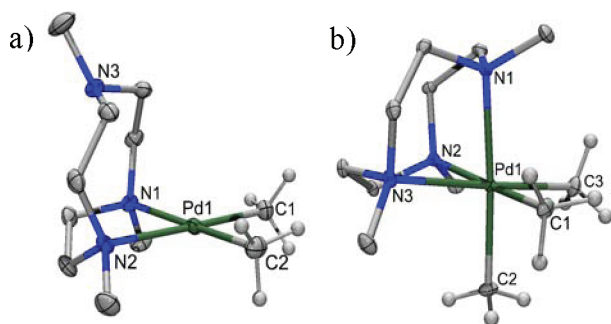


Figure 1. ORTEP representation of **1** (a) and the cation of **[2]I** (b). Selected bond lengths (Å) and angles (deg) are as follows. **1**: Pd1–C1, 2.032(2); Pd1–C2, 2.0339(19); Pd1–N1, 2.220(6); Pd1–N2, 2.249(4). **2⁺**: Pd1–C1, 2.0375(14); Pd1–C2, 2.0380(14); Pd1–C3, 2.0384(14); Pd1–N1, 2.2180(11); Pd1–N2, 2.2192(11); Pd1–N3, 2.2193(11); C1–Pd1–C2, 87.18(6); C1–Pd1–C3, 86.79(6); C2–Pd1–C3, 86.06(7).

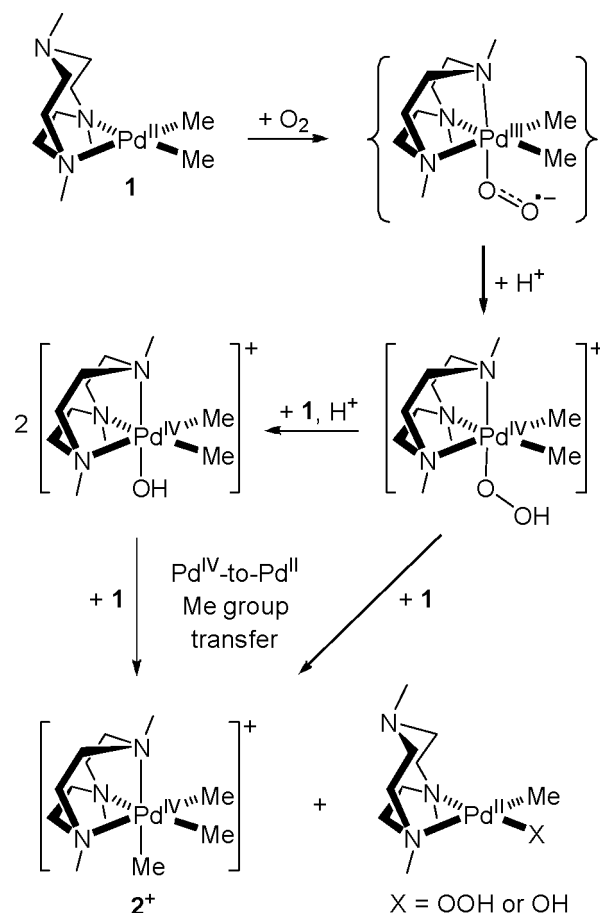
spectrum, while Me₃tacn shows a fluxional behavior even at low temperatures with only one average singlet at 2.18 ppm for the three *N*-Me groups, likely due to the facile exchange between the free and coordinated donor atoms.⁹ The cyclic voltammogram (CV) of **1** in 0.1 M Bu₄NPF₆/MeCN exhibits an irreversible oxidation wave at $E_{pa} \approx -0.71$ V vs Fc⁺/Fc, which is significantly lower than those for analogous Pd^{II}Me₂ complexes with bidentate *N*-donor ligands.⁴ Such a low oxidation peak potential is likely due to the ability of the tridentate tacn-type ligands to effectively stabilize the octahedral or distorted-octahedral geometry of high-valent Pd and Pt centers.^{7,10} Notably, the oxidation peak potential of **1** is even lower than that for the previously reported (^tBuN₄)Pd^{II}Me₂ ($E_{pa} = -0.36$ vs Fc⁺/Fc),^{4,11} presumably due to the presence of amine donors in the equatorial plane and the less rigid structure of Me₃tacn.

Prompted by the previously observed aerobic oxidation of (^tBuN₄)Pd^{II}Me₂,⁴ we set out to investigate the reactivity of **1** toward O₂. When a solution of **1** in MeCN was exposed to O₂, the NMR revealed the rapid formation of a new diamagnetic Pd complex identified as [(Me₃tacn)Pd^{IV}Me₃]⁺ (**2⁺**) (Scheme 2).¹² The yield of **2⁺** was 44% and 34% after 10 min in acetone and MeCN, respectively (the theoretical yield of **2⁺** is 50%),¹³ and did not change in the presence of O₂ for up to 12 h.⁶ Interestingly, the aerobic oxidation of **1** in the presence of water generates **2⁺** in a similar yield but leads to a lower amount of side products, suggesting that the presence of protons is needed to facilitate Pd^{II} oxidation and O₂ reduction (vide infra). The electrospray mass spectrometry analysis (ESI-MS) of **1** in MeCN in the presence of O₂ reveals a strong signal at m/z 322.1482 (calcd for **2⁺** 322.1474). The identity of **2** was further confirmed by the independent synthesis of [(Me₃tacn)Pd^{IV}Me₃]I (**[2]I**) through the reaction of **1** with 1 equiv of MeI in acetone or MeCN.⁶ The NMR spectrum of **[2]I** is identical with that of **2⁺** obtained by the aerobic oxidation of **1**. The X-ray analysis of **[2]I** reveals an octahedral Pd center surrounded by three Me groups and a κ^3 -Me₃tacn ligand coordinated to the Pd^{IV} center by three N atoms (Figure 1b). The Pd–Me bond distances are 2.037–2.038 Å, similar to those of other reported Pd^{IV}Me₃ complexes,¹⁴ while the three Me–Pd–Me angles are all close to 90°, confirming a symmetric, pseudo-C_{3v} geometry.

By analogy with (^tBuN₄)PdMe₂,⁴ the aerobic reactivity of **1** likely involves an inner-sphere oxidation of **1** by O₂, as the formal reduction potential of the O₂/O₂^{•-} couple in MeCN is

~ -1.3 V,¹⁵ significantly more negative than the oxidation potential of **1**. Moreover, the addition of **1** to O₂-saturated EtCN at -70 °C leads to the immediate formation of an orange-yellow species ($\lambda_{max} = 407$ nm, $\epsilon \geq 11\,000$ M⁻¹ cm⁻¹), which then slowly decays over the course of several hours. Although this intermediate was not isolated, we tentatively assign the observed intense absorption band to a charge transfer transition reminiscent of a Pd–superoxo or –(hydro)peroxo species.^{16,17} For example, intense LMCT bands can be observed in superoxo or peroxo complexes of various transition metals.¹⁸ Moreover, the aerobic oxidation of **1** in presence of the spin trap DMPO (DMPO = 5,5-dimethyl-1-pyrroline *N*-oxide) yields an EPR-active DMPO radical adduct (or adducts) that was not formed in the absence of **1** or O₂,⁶ supporting an inner-sphere oxidation of **1** by O₂.⁴ On the basis of previous mechanistic studies of the aerobic oxidation of Pt^{II} and Pd^{II} dimethyl complexes,^{4,16,19} such an inner-sphere oxidation may involve the initial formation of a Pd^{III}–superoxo intermediate, which upon protonation yields a Pd^{IV}–hydroperoxo species (Scheme 3). The Pd^{IV}–OOH intermediate can then oxidize

Scheme 3. Proposed Mechanism for Formation of [(Me₃tacn)Pd^{IV}Me₃]⁺ (**2⁺**) by Aerobic Oxidation of (Me₃tacn)Pd^{II}Me₂ (**1**)



another molecule of **1**, also assisted by protons,¹⁶ to give two molecules of the Pd^{IV}–OH species. Interestingly, ESI-MS analysis of **1** in O₂-saturated MeCN reveals the formation in addition to **2⁺** of two new peaks at m/z 340.1208 and 324.1262, which can be assigned to [(Me₃tacn)Pd^{IV}Me₂(OOH)]⁺ (calcd m/z 340.1216) and [(Me₃tacn)Pd^{IV}Me₂(OH)]⁺ (calcd m/z

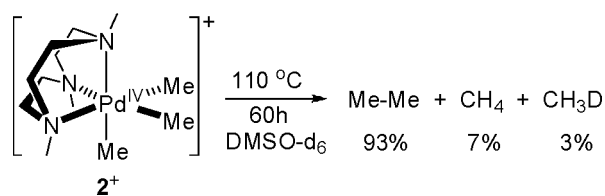
324.1266), respectively. The two peaks decay rapidly and disappear within 1 h, supporting their role as intermediates in the formation of 2^+ .⁶ However, when the oxidation of **1** was performed in 5% H₂O/95% MeCN, the two intermediates exhibited increased stability and were present in the reaction mixture even after 1 day, supporting the need for protons in the proposed Pd^{II} oxidation and O₂ reduction mechanism.²⁰ Analogous Pt^{IV}Me₂(OOH)^{16b} and Pt^{IV}Me₂(OH)^{16,19,21} complexes resulting from aerobic oxidation of Pt^{II}Me₂ precursors have been isolated and structurally characterized previously, while the aerobic oxidation of the [(tacn)Pt^{II}(dmsO)Cl]⁺ complex has been reported to form a peroxo-bridged Pt^{IV} complex.²² In contrast, in our case the electrophilic [(Me₃tacn)-Pd^{IV}Me₂X]⁺ intermediates (X = OOH, OH) likely undergo methyl group transfer to a nucleophilic (Me₃tacn)Pd^{II}Me₂ (**1**) species to afford the trimethyl Pd^{IV} complex 2^+ (Scheme 3). A similar methyl group transfer from electrophilic Pd^{IV}Me₃ complexes to nucleophilic Pt^{II}Me₂ and Pd^{II}Me₂ complexes has been previously reported.²³

The aerobic oxidation of **1** resembles the recently reported oxidatively induced reactivity of (tBu₂bpy)Pd^{II}Me₂ leading to ethane elimination. In that case, chemical oxidation of (tBu₂bpy)Pd^{II}Me₂ with Fc⁺, Ag⁺, or thianthrenyl followed by methyl group transfer generates an unstable (tBu₂bpy)Pd^{IV}Me₃⁺ intermediate that reductively eliminates ethane at room temperature and forms cleanly the Pd^{II} product [(tBu₂bpy)-PdMe(soln)]⁺.¹³ In contrast, the aerobic oxidation of **1** did not yield a stable Pd^{II} monomethyl product, likely due to the instability of the [(Me₃tacn)Pd^{II}MeX]⁺ species (X = OOH, OH) under the employed oxidizing conditions.²⁴

To probe whether the methyl group transfer is required for an efficient aerobic oxidation, preliminary aerobic oxidation studies have employed the palladacyclic Pd^{II} precursor (Me₃tacn)Pd^{II}(CH₂CMe₂C₆H₄-κ²C,C') (**3**), which lacks methyl ligands.^{6,25} While **3** is stable under O₂ in MeCN for up to 1 day, addition of 5% H₂O to the reaction mixture leads to formation of two peaks in the ESI-MS at *m/z* 426.1732 and 442.1685, which are tentatively assigned to (Me₃tacn)-Pd^{IV}(CH₂CMe₂C₆H₄-κ²C,C')(OH)]⁺ (calcd *m/z* 426.1739) and [(Me₃tacn)Pd^{IV}(CH₂CMe₂C₆H₄-κ²C,C')(OOH)]⁺ (calcd *m/z* 442.1688), respectively.⁶ Moreover, NMR studies show the formation in up to 48% yield of a species tentatively assigned as [(Me₃tacn)Pd^{IV}(CH₂CMe₂C₆H₄-κ²C,C')X]⁺ (X = OH, OOH, or other ligand).^{25b,6,26} While this reaction is not quantitative, suggesting that the aerobic oxidation may be hampered by steric factors,^{16b} these preliminary results imply that the oxidation of (Me₃tacn)Pd^{II} precursors to yield Pd^{IV} species does not require an alkyl group transfer.

We next examined the reactivity of 2^+ toward the reductive elimination of ethane. While [**2**]**I** is stable in solution at room temperature, its thermolysis at 110 °C in DMSO-*d*₆ for 60 h leads to the formation of ethane, CH₄, and CH₃D in 93%, 7%, and 3% yields, respectively (Scheme 4). Such reactivity is

Scheme 4. Ethane Elimination from [(Me₃tacn)Pd^{IV}Me₃]**I**



similar to that for the analogous complex [(tacn)Pd^{IV}Me₃]⁺ (tacn = 1,4,7-triazacyclononane), leading to ethane elimination at 140 °C.²⁷ Notably, the reductive elimination of ethane from the Pd^{IV}Me₃ complexes supported by tridentate Me₃tacn and tacn ligands is significantly slower compared to that for analogous Pd^{IV}Me₃ complexes with bidentate N-donor ligands, as the latter systems are expected to more easily access a five-coordinate intermediate.^{13,14c,28} In addition, we have recently reported ethane elimination in high yield at room temperature from the Pd^{IV}Me₃ complex [(κ³-Me₃N₄)Pd^{IV}Me₃]⁺ (Me₃N₄ = N,N'-dimethyl-2,11-diaza[3.3](2,6)pyridinophane), and the faster C–C bond formation reactivity for the latter complex vs that for 2^+ is likely due to the distorted-octahedral geometry of [(κ³-Me₃N₄)Pd^{IV}Me₃]⁺.⁵

In summary, we have shown that (Me₃tacn)Pd^{II}Me₂ undergoes facile aerobic oxidation to yield a stable [(Me₃tacn)-Pd^{IV}Me₃]⁺ complex. Moreover, the latter species can selectively eliminate ethane at elevated temperatures. UV–vis and EPR spectroscopic studies indicate that the aerobic oxidation likely involves an inner-sphere oxidation of (Me₃tacn)Pd^{II}Me₂ with O₂, while ESI-MS studies suggest the formation of Pd^{IV}–OOH and Pd^{IV}–OH intermediates, similarly to analogous Pt complexes. The observed facile aerobic reactivity is likely due to the ability of the Me₃tacn ligand to support the octahedral geometry of a Pd^{IV} center. Moreover, subsequent methyl group transfer leads to further stabilization by formation of a symmetric trimethyl Pd^{IV} complex. Overall, reported herein is one of the first examples of aerobic oxidation of a Pd^{II} organometallic precursor that generates a well-defined Pd^{IV} product.⁵ These results suggest that Pd^{IV} complexes can act as viable intermediates in the Pd-catalyzed aerobic oxidation of organic substrates in general and in oxidative C–C bond coupling in particular. Our current research efforts are aimed at probing the mechanism of this aerobic oxidation and characterization of the observed transient intermediates.

■ ASSOCIATED CONTENT

Supporting Information

Text, tables, figures, and CIF files giving experimental details, spectroscopic characterization, and X-ray crystallographic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: mirica@wustl.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the Department of Chemistry at Washington University for startup funds and the American Chemical Society Petroleum Research Fund (49914-DNI3) and DOE Catalysis Science Program (DE-FG02-11ER16254) for support. L.M.M. is a Sloan Fellow.

■ REFERENCES

- (1) (a) Stoltz, B. M. *Chem. Lett.* **2004**, 33, 362. (b) Stahl, S. S. *Angew. Chem., Int. Ed.* **2004**, 43, 3400. (c) Stahl, S. S. *Science* **2005**, 309, 1824. (d) Beck, E. M.; Grimster, N. P.; Hatley, R.; Gaunt, M. J. *J. Am. Chem. Soc.* **2006**, 128, 2528. (e) Sigman, M. S.; Jensen, D. R. *Acc. Chem. Res.* **2006**, 39, 221. (f) Gligorich, K. M.; Sigman, M. S. *Chem. Commun.* **2009**, 3854. (g) Campbell, A. N.; Stahl, S. S. *Acc. Chem. Res.* **2012**,

DOI: 10.1021/ar2002045. (h) Vedernikov, A. N. *Acc. Chem. Res.* **2012**, DOI: 10.1021/ar200191k. (i) Shi, Z.; Zhang, C.; Tang, C.; Jiao, N. *Chem. Soc. Rev.* **2012**, *41*, 3381.

(2) (a) Zhang, J.; Khaskin, E.; Anderson, N. P.; Zavalij, P. Y.; Vedernikov, A. N. *Chem. Commun.* **2008**, 3625. (b) Zhang, Y.-H.; Yu, J.-Q. *J. Am. Chem. Soc.* **2009**, *131*, 14654. (c) Wang, A.; Jiang, H.; Chen, H. *J. Am. Chem. Soc.* **2009**, *131*, 3846. (d) Zhu, M.-K.; Zhao, J.-F.; Loh, T.-P. *J. Am. Chem. Soc.* **2010**, *132*, 6284.

(3) (a) Boisvert, L.; Denney, M. C.; Kloek, H. S.; Goldberg, K. I. *J. Am. Chem. Soc.* **2009**, *131*, 15802. (b) Chuang, G. J.; Wang, W.; Lee, E.; Ritter, T. *J. Am. Chem. Soc.* **2011**, *133*, 1760.

(4) Khusnutdinova, J. R.; Rath, N. P.; Mirica, L. M. *J. Am. Chem. Soc.* **2012**, *134*, 2414.

(5) We have also recently observed the aerobic oxidation of a Pd^{II}Me₂ complex stabilized by the tetradentate N-donor ligand ^{Me}N4: Tang, F.; Qu, F.; Khusnutdinova, J. R.; Zhang, Y.; Rath, N. P.; Mirica, L. M. Submitted for publication in *Angew. Chem., Int. Ed.*

(6) See the Supporting Information.

(7) Khusnutdinova, J. R.; Rath, N. P.; Mirica, L. M. *Angew. Chem., Int. Ed.* **2011**, *50*, 5532.

(8) (a) de Graaf, W.; Boersma, J.; Grove, D.; Spek, A. L.; van Koten, G. *Recl. Trav. Chim. Pays-Bas* **1988**, *107*, 299. (b) de Graaf, W.; Boersma, J.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1989**, *8*, 2907. (c) Bercaw, J. E.; Chen, G. S.; Labinger, J. A.; Lin, B.-L. *J. Am. Chem. Soc.* **2008**, *130*, 17654.

(9) (a) Hunter, G.; McAuley, A.; Whitcombe, T. W. *Inorg. Chem.* **1988**, *27*, 2634. (b) Bennett, M. A.; Canty, A. J.; Felixberger, J. K.; Rendina, L. M.; Sunderland, C.; Willis, A. C. *Inorg. Chem.* **1993**, *32*, 1951.

(10) (a) Wiegardt, K.; Koeppen, M.; Swiridoff, W.; Weiss, J. *J. Chem. Soc., Dalton Trans.* **1983**, 1869. (b) Blake, A. J.; Holder, A. J.; Hyde, T. I.; Schröder, M. *J. Chem. Soc., Chem. Commun.* **1987**, 987. (c) Blake, A. J.; Gordon, L. M.; Holder, A. J.; Hyde, T. I.; Reid, G.; Schröder, M. *J. Chem. Soc., Chem. Commun.* **1988**, 1452. (d) McAuley, A.; Whitcombe, T. W. *Inorg. Chem.* **1988**, *27*, 3090.

(11) (a) Khusnutdinova, J. R.; Rath, N. P.; Mirica, L. M. *J. Am. Chem. Soc.* **2010**, *132*, 7303. (b) Mirica, L. M.; Khusnutdinova, J. R. *Coord. Chem. Rev.* **2012**, *256*, DOI: 10.1016/j.ccr.2012.04.030.

(12) The counteranion of 2⁺ is most likely OH⁻ resulting from O₂ reduction in the presence of protons. The pH of a solution of **1** in MeCN/H₂O (1/1 v/v) increased by ~4 pH units upon aerobic oxidation, supporting the formation of hydroxide anions (see the Supporting Information).

(13) Lanci, M. P.; Remy, M. S.; Kaminsky, W.; Mayer, J. M.; Sanford, M. S. *J. Am. Chem. Soc.* **2009**, *131*, 15618.

(14) (a) Byers, P. K.; Canty, A. J.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1986**, 1722. (b) Byers, P. K.; Canty, A. J.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1987**, 1093. (c) Byers, P. K.; Canty, A. J.; Skelton, B. W.; White, A. H. *Organometallics* **1990**, *9*, 826. (d) Canty, A. J.; Honeyman, R. T.; Roberts, A. S.; Traill, P. R.; Colton, R.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1994**, *471*, C8. (e) Canty, A. J.; Jin, H.; Roberts, A. S.; Skelton, B. W.; Traill, P. R.; White, A. H. *Organometallics* **1995**, *14*, 199. (f) Canty, A. J.; Dedieu, A.; Jin, H.; Milet, A.; Skelton, B. W.; Trofimenko, S.; White, A. H. *Inorg. Chim. Acta* **1999**, *287*, 27. (g) Bayler, A.; Canty, A. J.; Edwards, P. G.; Skelton, B. W.; White, A. H. *Dalton Trans.* **2000**, 3325.

(15) (a) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877. (b) Sawyer, D. T.; Chiericato, G.; Angelis, C. T.; Nanni, E. J.; Tsuchiya, T. *Anal. Chem.* **1982**, *54*, 1720.

(16) (a) Rostovtsev, V. V.; Labinger, J. A.; Bercaw, J. E.; Lasseter, T. L.; Goldberg, K. I. *Organometallics* **1998**, *17*, 4530. (b) Rostovtsev, V. V.; Henling, L. M.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chem.* **2002**, *41*, 3608.

(17) The complex [2]I does not exhibit absorption bands in the visible region.

(18) Lever, A. B. P. *J. Mol. Struct.* **1980**, *59*, 123.

(19) (a) Prokopchuk, E. M.; Jenkins, H. A.; Puddephatt, R. J. *Organometallics* **1999**, *18*, 2861. (b) Prokopchuk, E. M.; Puddephatt, R. J. *Can. J. Chem.* **2003**, *81*, 476.

(20) A trace amount of water may promote the observed formation of 2⁺ in MeCN or acetone.

(21) (a) Vedernikov, A. N.; Binfield, S. A.; Zavalij, P. Y.; Khusnutdinova, J. R. *J. Am. Chem. Soc.* **2006**, *128*, 82. (b) Vedernikov, A. N. *Chem. Commun.* **2009**, 4781.

(22) Davies, M. S.; Hambley, T. W. *Inorg. Chem.* **1998**, *37*, 5408.

(23) (a) Aye, T.-K.; Canty, A. J.; Crespo, M.; Puddephatt, R. J.; Scott, J. D.; Watson, A. A. *Organometallics* **1989**, *8*, 1518. (b) Markies, B. A.; Canty, A. J.; Boersma, J.; van Koten, G. *Organometallics* **1994**, *13*, 2053.

(24) The CV of the independently synthesized monomethyl chloro complex (Me₃tacn)PdMeCl exhibits an irreversible oxidation wave at a low potential, ~-0.44 V vs Fc⁺/Fc in 0.1 M Bu₄NPF₆/MeCN (see the Supporting Information). Preliminary studies reveal that (Me₃tacn)PdMeCl reacts with O₂ in MeCN at room temperature to produce a mixture of unidentified diamagnetic products. More detailed studies of this aerobic reactivity are currently underway.

(25) (a) Campora, J.; Lopez, J. A.; Palma, P.; del Rio, D.; Carmona, E.; Valerga, P.; Graiff, C.; Tiripicchio, A. *Inorg. Chem.* **2001**, *40*, 4116. (b) Campora, J.; Palma, P.; del Rio, D.; Carmona, E.; Graiff, C.; Tiripicchio, A. *Organometallics* **2003**, *22*, 3345. (c) Campora, J.; Palma, P.; del Rio, D.; Lopez, J. A.; Alvarez, E.; Connelly, N. G. *Organometallics* **2005**, *24*, 3624.

(26) Detailed characterization of the products formed upon the oxidation of (Me₃tacn)Pd^{II}(CH₂CMe₂C₆H₄) (**3**) is currently underway and will be reported separately.

(27) Sobanov, A. A.; Vedernikov, A. N.; Dyker, G.; Solomonov, B. N. *Mendeleev Commun.* **2002**, 14.

(28) Racowski, J. M.; Sanford, M. S. *Top. Organomet. Chem.* **2011**, *35*, 61.