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Binuclear Intermediates in Oxidation Reactions: $\mathrm{[(Me_3SiC{\equiv}C)Me_2(bipy)Pt{-}PtMe_2(bipy)]^+}$ in the Oxidation of $\mathrm{Pt^{II}Me_2(bipy)}$ (bipy = 2,2′-Bipyridine) by $\mathrm{IPh(C{\equiv}CSiMe_3)(OTf)}$ (OTf = Triflate)

Allan J. Canty,*,† Michael G. Gardiner,† Roderick C. Jones,† Thomas Rodemann,‡ and Manab Sharma†

School of Chemistry, University of Tasmania, Private Bag 75, Hobart, Tasmania 7001, Australia, and Central Science Laboratory (CSL), University of Tasmania, Private Bag 74, Hobart, Tasmania 7001, Australia

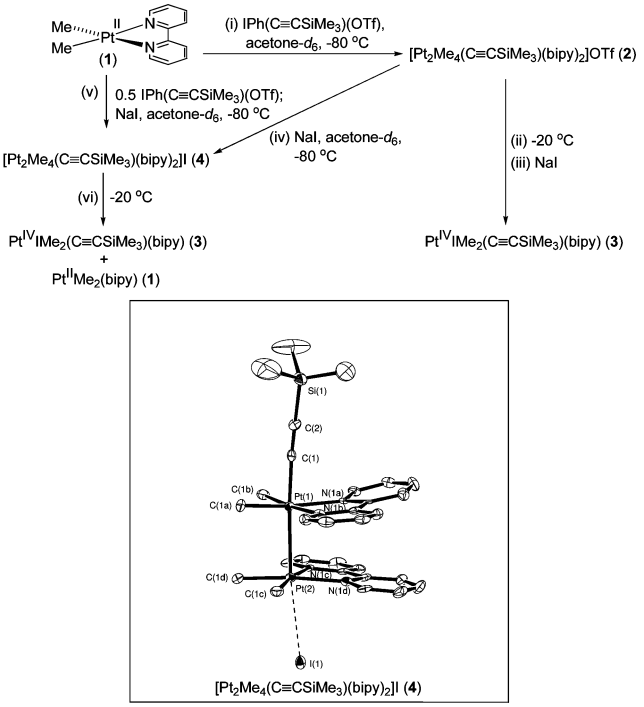
Received April 8, 2009; E-mail: allan.canty@utas.edu.au

Catalytic reactions involving the cyclopalladation of arenes containing a nitrogen donor (N∼CH, e.g., 2-phenyl-3-picoline)[1a,b] or direct palladation at the 2-position of indoles (Ind−H),[1c] lead to the formation of N∼C−Ar and Ind−Ar in the presence of diaryliodine(III) oxidants $\mathrm{[IAr_2]^+}$, presumably via "$\mathrm{Ar^+}$" transfer to $\mathrm{Pd^{II}}$ and reductive elimination from $\mathrm{Pd^{IV}}$(C∼N)Ar and $\mathrm{Pd^{IV}}$(Ind)Ar species.[1] Similarly, the stoichiometric synthesis of benzofurans using $\mathrm{[IAr(alkenyl)]^+}$ and $\mathrm{[IAr(alkynyl)]^+}$ as oxidants for palladacyclic species $\mathrm{Pd^{II}}$(C∼C)(bipy) (bipy = 2,2′-bipyridine), wherein an intermediate containing the motif "$\mathrm{Pd^{IV}}$(C∼C)(CH=CH−$\mathrm{Hex^n}$)(bipy)" was detected by NMR, has been reported.[2] These proposals enjoy support from model reactions,[3] in particular the NMR detection at −50 °C of $\mathrm{Pd^{IV}IMe_2Ph(bipy)}$ upon reaction of $\mathrm{Pd^{II}Me_2(bipy)}$ with $\mathrm{IPh_2(OTf)}$ (OTf = triflate) followed by NaI[3a,c] and of $\mathrm{Pd^{IV}(O_2CPh)(OTf)(C{\equiv}CSiMe_3)(NCN)}$ (NCN = [2,6-(dimethylaminomethyl)phenyl-*N*,*C*,*N*]$^-$) upon reaction of $\mathrm{Pd(O_2CPh)(NCN)}$ with $\mathrm{IPh(C{\equiv}CSiMe_3)(OTf)}$.[3e] The rapidly developing applications of $\mathrm{[IArR]^+}$ oxidants in organic synthesis,[1,2,3f,4] together with an array of potential mechanisms for iodonium species as oxidants (a one-electron process or a two-electron process via nucleophilic attack at $\mathrm{I^{III}}$ or the β-carbon of an alkynyl group),[3f,4a,5] has prompted us to undertake further mechanistic studies.

The substrates $\mathrm{PtMe_2(bipy)}$ and $\mathrm{PdMe_2(bipy)}$ have a remarkable history in the development of current understandings of oxidative addition chemistry.[6] Palladium(IV) species obtained using diorganoiodine(III) reagents are very unstable, but related $\mathrm{Pt^{IV}}$ species synthesized in the same manner have been characterized by X-ray diffraction, in particular $\mathrm{PtIMe_2Ph(bipy)}$[3a,c] and $\mathrm{PtI(O_2CC_6H_4\text{-}4\text{-}CF_3)(C{\equiv}CSiMe_3)(NCN)}$.[3d,e] We report here a study of the reaction of $\mathrm{PtMe_2(bipy)}$ with $\mathrm{IPh(C{\equiv}CSiMe_3)(OTf)}$ at low temperature in acetone, leading to detection of the Pt−Pt-bonded cation $\mathrm{[Pt_2Me_4(C{\equiv}CSiMe_3)(bipy)_2]^+}$, an intermediate in the oxidation of $\mathrm{Pt^{II}}$ to $\mathrm{Pt^{IV}}$. The cation is assessed as $\mathrm{Pt^{III}{-}Pt^{III} \leftrightarrow Pt^{IV}{-}Pt^{II}}$, and at the other extreme may be regarded as a cationic alkynylplatinum(IV) center, "$\mathrm{[Pt^{IV}Me_2(C{\equiv}CSiMe_3)(bipy)]^{+}}$", stabilized by "$\mathrm{Pt^{II}Me_2(bipy)}$" as a donor ligand.

Thus, in Scheme 1(i), an orange solution of $\mathrm{PtMe_2(bipy)}$ (**1**) reacted with 1 equiv of $\mathrm{IPh(C{\equiv}CSiMe_3)(OTf)}$ at −80 °C in acetone-d_6 to instantly give a dark-brown solution that cleared to give a yellow solution after ∼1 min. ^{1}H NMR spectra showed a species subsequently identified (see below) as $\mathrm{[Pt_2Me_4(C{\equiv}CSiMe_3)(bipy)_2]OTf}$ (**2**) and iodobenzene as products, together with some unreacted iodine(III) oxidant. Further reaction with the iodine(III) reagent was extremely slow at −80 °C but proceeded readily at −20 °C to give complex spectra attributed to $\mathrm{Pt^{IV}}$ species[7] and the absence of the iodine(III) reagent [Scheme 1(ii)]; addition of NaI at −20 °C then gave the known complex $\mathrm{Pt^{IV}IMe_2(C{\equiv}CSiMe_3)(bipy)}$ (**3**)[3d,e] and PhI as the only species in solution [Scheme 1(iii)]. Addition of NaI at −80 °C to the mixture obtained from reaction (i) resulted in quenching of unreacted $\mathrm{IPh(C{\equiv}CSiMe_3)(OTf)}$ by iodide and precipitation of orange $\mathrm{[Pt_2Me_4(C{\equiv}CSiMe_3)(bipy)_2]I}$ (**4**) in 85% yield [Scheme 1(iv)]. Complex **4** could also be obtained by reaction of $\mathrm{Pt^{II}Me_2(bipy)}$ with 0.5 equiv of $\mathrm{IPh(C{\equiv}CSiMe_3)(OTf)}$ followed by addition of NaI [Scheme 1(v)]. Warming complex **4** to −50 °C afforded **3** and **1** in a 1:1 ratio [Scheme 1(vi)]. The cations of **2** and **4** exhibited identical ^{1}H NMR spectra, showing one alkynyl, two methyl, and two bipy environments in 1:2:2 ratio, and liquid secondary-ion mass spectrometry (LSIMS) of **4** revealed a peak at *m*/*z* 859.1 corresponding to $\mathrm{[M - I]^+}$.

Scheme 1. Reactivity of $\mathrm{PtMe_2(bipy)}$ (**1**) toward $\mathrm{IPh(C{\equiv}CSiMe_3)(OTf)}$ and the Structure of $\mathrm{[Pt_2Me_4(C{\equiv}CSiMe_3)(bipy)_2]I}$ (**4**)



Crystallographic examination of orange plates of **4** (Scheme 1) revealed Pt−Pt-bonded centers "$\mathrm{PtMe_2(C{\equiv}CSiMe_3)(bipy)}$" and "$\mathrm{PtMe_2(bipy)}$", the latter of which has a weak Pt(2)···I(1) interaction [3.4108(6) Å] that is only ∼0.3 Å less than the sum of the van der Waals radii[8] and significantly longer than expected for a Pt−I

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† School of Chemistry.
‡ Central Science Laboratory.

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bond [e.g., 2.7631(4) Å in $Pt^{IV}IMe_2Ph(bipy)$[3a,c]]. The Pt−Pt interaction in **4** is not supported by bridging groups, unlike all previously reported organoplatinum dimers in the (average) Pt^{III} formal oxidation state.[9−12] Comparison with reported structures containing bridged Pt_2 species indicated that the Pt(1)−Pt(2) distance in **4** [2.7639(4) Å] is within the range observed for symmetrical diorganoplatinum(III)[9a−e] and monoorganoplatinum(III) dimers[9f,g] with octahedral geometry at each Pt^{III} center [2.529(1)−2.7910(2) Å] and similar to that in an unsymmetrical dimer with octahedral geometry at each Pt center, $[MePt(\mu\text{-pop-}P,P)_4PtI]^+$ ($pop^{2-} = P_2O_5H_2^{2-}$) [2.782(1) Å],[10] and related unsymmetrical dimers with one octahedral center and one five-coordinate center (which may have an additional weakly interacting axial group), $[R(H_3N)_2Pt(\mu\text{-L-}N,O)_2Pt(NH_3)_2]^{3+}$ ($\text{L-}N,O^- =$ amidate or pyridonate) [2.676(1)−2.7542(11) Å].[11,12] The $PtMe_2(bipy)$ motifs are parallel [dihedral angle of 2.7(4)° between PtC_2N_2 mean planes] and twisted with respect to each other by ∼40° about the Pt(1)−Pt(2) bond. The alkynyl group has a C(1)−C(2) distance of 1.212(10) Å, and the alkynyl−Pt(1)−Pt(2)···I(1) axis is approximately linear [Si(1)−C(2)−C(1), 175.4(6)°; C(2)−C(1)−Pt(1), 175.9(6)°; C(1)−Pt(1)−Pt(2), 176.54(17)°; Pt(1)−Pt(2)···I(1), 171.544(12)°].

The ^1H NMR data for **4** were consistent with $Pt^{III}-Pt^{III} \leftrightarrow Pt^{IV}-Pt^{II}$, with significant Pt^{IV} and Pt^{II} influences for octahedral Pt(1) and "square pyramidal" Pt(2), respectively. Thus, the ^{1}NMR spectra in $(CD_3)_2CO$ exhibited $^2J(^{195}Pt-H) = 69.5$ Hz, similar to that for methyl groups opposite bipy in the cation $[Pt^{IV}Me_3(bipy)(NCCD_3)]^+$ (68 Hz),[13] and 72.8 Hz, decreased relative to the value reported for $Pt^{II}Me_2(bipy)$ in CD_3CN (86 Hz).[13]

The detection and isolation of the cation $[Pt_2Me_4(C{\equiv}CSiMe_3)(bipy)_2]^+$ provides a number of insights into the mechanisms of oxidation reactions. The intermediate cation may be regarded as "$Pt^{IV}Me_2(C{\equiv}CSiMe_3)(bipy)^{+}$" stabilized via coordination of electron-rich $PtMe_2(bipy)$ acting as a ligand to give the (formally) Pt^{III} dimer; thus even in the presence of oxidant and the relatively weak donor triflate, the second platinum center is protected from reaction leading to completion of oxidation until the temperature is raised. It is also feasible, as proposed by Puddephatt and co-workers,[14] that for complexes of planar diimines, two π-stacked $PtMe_2(N{\sim}N)$ units may be involved in the initial oxidation step to enhance the nucleophilic character of Pt^{II}. Dimeric species similar to cation **4** may be formed as undetected-to-date intermediates in other reactions, including those of other ligands, d^8 metal systems, and oxidants. In this regard, it has been recently reported that $PtMe_2(bipy)$ reacts with diphenyldisulfide to form NMR-characterized $Pt^{III}{}_2(SPh)_2Me_4(bipy)_2$ containing an $S-Pt^{III}-Pt^{III}-S$ axis, leading to the eventual isolation of $Pt^{IV}(SPh)_2Me_2(bipy)$.[14] Theoretical calculations are consistent with the involvement of an undetected cationic intermediate $[Pt_2(SPh)Me_4(bipy)_2]^+$ immediately prior to coordination of PhS^- to form the symmetrical Pt^{III} dimer.[14] This cation is directly analogous to $[Pt_2Me_4(C{\equiv}CSiMe_3)(bipy)_2]^+$. Thus, the results reported here provide evidence of subtleties in the mechanisms of oxidation reactions, not only for organic electrophiles as oxidants relevant to the role of metals in synthesis, such as benzofurans from $Pd^{II}(C{\sim}C)(bipy)$ and $[IPh(alkynyl)]^+$ reagents,[2] but also for inorganic oxidants.

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Supporting Information Available: Synthesis, microanalysis and ^1H NMR characterization, and X-ray crystallographic data (CIF) for **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Kalyani, D.; Deprez, N. R.; Desai, L. V.; Sanford, M. S. *J. Am. Chem. Soc.* **2005**, *127*, 7330. (b) Kalberer, E. W.; Whitfield, S. R.; Sanford, M. S. *J. Mol. Catal. A* **2006**, *251*, 108. (c) Deprez, N. R.; Kalyani, D.; Krause, A.; Sanford, M. S. *J. Am. Chem. Soc.* **2006**, *128*, 4972. (d) Deprez, N. R.; Sanford, M. S. *Inorg. Chem.* **2007**, *46*, 1924.

(2) Chaudhuri, P. D.; Guo, R.; Malinakova, H. C. *J. Organomet. Chem.* **2008**, *693*, 567.

(3) (a) Bayler, A.; Canty, A. J.; Ryan, J. H.; Skelton, B. W.; White, A. H. *Inorg. Chem. Commun.* **2000**, *3*, 575. (b) Canty, A. J.; Rodemann, T. *Inorg. Chem. Commun.* **2003**, *6*, 1382. (c) Canty, A. J.; Patel, J.; Rodemann, T.; Ryan, J. R.; Skelton, B. W.; White, A. H. *Organometallics* **2004**, *23*, 3466. (d) Canty, A. J.; Rodemann, T.; Skelton, B. W.; White, A. H. *Inorg. Chem. Commun.* **2005**, *8*, 55. (e) Canty, A. J.; Rodemann, T.; Skelton, B. W.; White, A. H. *Organometallics* **2006**, *25*, 3996. (f) Canty, A. J.; Rodemann, T.; Ryan, J. H. *Adv. Organomet. Chem.* **2007**, *55*, 279.

(4) (a) Stang, P. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 274. (b) Varvoglis, A. *Tetrahedron* **1997**, *53*, 1179. (c) Zhdankin, V. V.; Stang, P. J. *Tetrahedron* **1998**, *54*, 10927.

(5) Grushin, V. V. *Acc. Chem. Res.* **1992**, *25*, 529.

(6) For example, see: (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 5. (b) Rendina, L. M.; Puddephatt, R. J. *Chem. Rev.* **1997**, *97*, 1735. (c) Canty, A. J. *Acc. Chem. Res.* **1992**, *25*, 83.

(7) Complex spectra were obtained after all of the oxidant was exhausted. The related $Pt^{IV}Me_2Ph$ triflates are unstable,[3c] and isomers may be present; under these conditions, triflate and solvent may compete as ligands [e.g., as in $Pt(OTf)Me_3(tmeda)$ (tmeda = *N,N,N′,N′*-tetramethylethylenediamine); see: Schlecht, S.; Magull, J.; Fenske, D.; Dehnicke, K. *Angew. Chem., Int. Ed.* **1997**, *36*, 1994.] However, water may act as a ligand in some $Pt^{IV}Me_3$ triflate complexes (see: Zhang, F.; Jennings, M. C.; Puddephatt, R. J. *Organometallics* **2004**, *23*, 1396.). Conversion to $PtIMe_2(C{\equiv}CSiMe_3)(bipy)$ upon addition of NaI is consistent with the presence of "$PtMe_2(C{\equiv}CSiMe_3)(bipy)$" in solution.

(8) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(9) (a) Schagen, J. D.; Overbeek, A. R.; Schenk, H. *Inorg. Chem.* **1978**, *17*, 1938. (b) Bancroft, D. P.; Cotton, F. A.; Falvello, L. R.; Schwotzer, W. *Inorg. Chem.* **1986**, *25*, 763. (c) Bancroft, D. P.; Cotton, F. A. *Inorg. Chem.* **1988**, *27*, 1633. (d) Bancroft, D. P.; Cotton, F. A. *Inorg. Chem.* **1988**, *27*, 4022. (e) Bennett, M. A.; Bhargava, S. K.; Bond, A. M.; Edwards, A. J.; Guo, S.-X.; Privr, S. H.; Rae, A. D.; Willis, A. C. *Inorg. Chem.* **2004**, *43*, 7752. (f) Yamaguchi, T.; Sasaki, Y.; Ito, T. *J. Am. Chem. Soc.* **1990**, *112*, 4038. (g) Dick, A. R.; Kampf, J. W.; Sanford, M. S. *Organometallics* **2005**, *24*, 482.

(10) Che, C.-M.; Mak, T. C. W.; Gray, H. B. *Inorg. Chem.* **1984**, *23*, 4386.

(11) (a) Matsumoto, K.; Matsunami, J.; Mizuno, K.; Uemura, H. *J. Am. Chem. Soc.* **1996**, *118*, 8959. (b) Matsumoto, K.; Nagai, Y.; Matsunami, J.; Mizuno, K.; Abe, T.; Somazawa, R.; Kinoshita, J.; Shimura, H. *J. Am. Chem. Soc.* **1998**, *120*, 2900. (c) Lin, Y.-S.; Takeda, S.; Matsumoto, K. *Organometallics* **1999**, *18*, 4897. (d) Lin, Y.-S.; Misawa, H.; Yamada, J.; Matsumoto, K. *J. Am. Chem. Soc.* **2001**, *123*, 569. (e) Matsumoto, K.; Ochiai, M. *Coord. Chem. Rev.* **2002**, *231*, 229. (f) Ochiai, M.; Lin, Y.-S.; Yamada, J.; Misawa, H.; Arai, S.; Matsumoto, K. *J. Am. Chem. Soc.* **2004**, *126*, 2536. (g) Ochiai, M.; Fukui, K.; Iwatsuki, S.; Ishihara, K.; Matsumoto, K. *Organometallics* **2005**, *24*, 5528.

(12) Matsumoto, K.; Arai, S.; Ochiai, M.; Chen, W.; Nakata, A.; Nakai, H.; Kinoshita, S. *Inorg. Chem.* **2005**, *44*, 8552.

(13) Crespo, M.; Puddephatt, R. J. *Organometallics* **1987**, *6*, 2548.

(14) Bonnington, K. J.; Jennings, M. C.; Puddephatt, R. J. *Organometallics* **2008**, *27*, 6521.

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