Oxygenation of Cyclopalladated *N,N*-Dimethylbenzylamine Complexes by Inorganic and Organic Peroxides: Oxygen Insertion into the Palladium–Carbon Bond

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Summary: Oxygenation of cyclopalladated benzylamine complexes of the type [Pd($C_6H_4CH_2NMe_2$-2)X] (1, X = $(MeCN)_2BF_4$; 2, X = $C_6H_4CH_2NMe_2$-2; 3, X = OC_6H_4-CH_2NMe_2-2; 5, X = Cl) with tert-butyl hydroperoxide (TBHP) and a vanadium catalyst (e.g. $VO(acac)_2$) affords the corresponding phenolate complexes. The rate of oxygenation increases strongly with the nucleophilicity of the organopalladium substrate. Complex 3 crystallizes in the monoclinic space group $P2_1/c$ with a = 11.171(1) Å, b = 8.524(1) Å, c = 18.101(1) Å, β = 94.31(1)°, V = 1718.7(3) Å^3, and Z = 4; the structure was refined to R = 0.026 and R_w = 0.030 for 2938 observed reflections.

Little is known about the reactivity of d^8 organometallic complexes with either organic or inorganic peroxo species as electrophiles. It is remarkable that, despite the current interest in the chemistry of late-transition-metal alkoxides and phenoxides,[2] a preparative method based on oxygen insertion into the metal–carbon bond of organometallic compounds has so far remained unexplored. The search for selective methods for the oxy-functionalization of hydrocarbons[3] provides a stimulus for the study of this subject. The C–H activating property of many late transition metals,[4] combined with the kinetic lability of the late-transition-metal–oxygen bond[2,5] formed by subsequent oxygenation of the metal–carbon bond, may form the basis for a catalytic process to reach the desired selectivity.

A highly selective stoichiometric method for the *ortho* hydroxylation of azobenzene derivatives is based on a reaction sequence of cyclopalladation and subsequent oxygen insertion into the Pd–C bond with *m*-CPBA.[1c,6] Recently, several catalytic processes for the direct hydroxylation of simple aromatic compounds, such as benzene or anisole, with either hydrogen peroxide and a platinum catalyst[7] or oxygen and a palladium catalyst[8] have been reported. Moreover, palladium catalyzes the trifluoroacetoxylation of methane with peroxytrifluoroacetic acid.[9] However, information concerning the mechanism of these oxygenations is very scarce. For example, it is not known whether organometallic intermediates are involved in the catalytic reactions. Also, there is very limited information about both the mode of interaction between late-transition-metal complexes and peroxides[10] and the factors that influence the ease of oxygen insertion into the metal–carbon bond. That the reaction between organopalladium compounds and peroxides does not always lead to oxygen insertion as the preferred reaction pathway is shown by our work on the reactivity of organopalladium compounds toward the molybdenum peroxide complex [$MoO(O_2)_2$·HMPT·H_2O]. Surprisingly, this inorganic peroxide mediates C–halide or C–OR coupling of halide or alkoxide nucleophiles, respectively, to the palladated carbon atom.[11] In contrast, we have recently demonstrated that cyclopalladated *N,N*-dimethylbenzylamine can be oxygenated with *tert*-butyl hydroperoxide and a vanadium catalyst,[12] whereas, interestingly, the same oxidizing system reacts further to a 1,4-quinone system in the case of a related [2-((dimethylamino)methyl)-3-naphthyl]palladium complex (eq 1).[13]

This note deals with some aspects of the oxygenation of organopalladium complexes with either *tert*-butyl hydroperoxide (TBHP) or a system comprising TBHP

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(1) (a) Debye Institute. (b) Bijvoet Center for Biomolecular Research. (c) Abbreviations: acac = acetylacetonate; HMPT = hexamethylphosphoric triamide; *m*-CPBA = *m*-chloroperoxybenzoic acid; TBHP = *tert*-butyl hydroperoxide.

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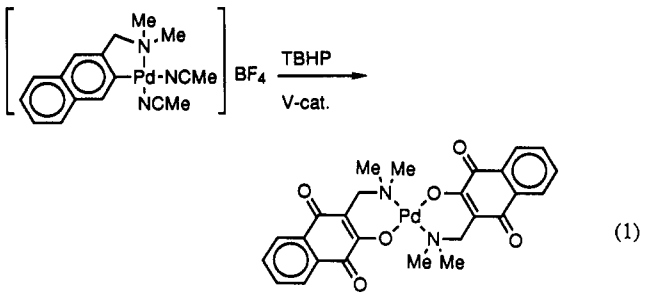
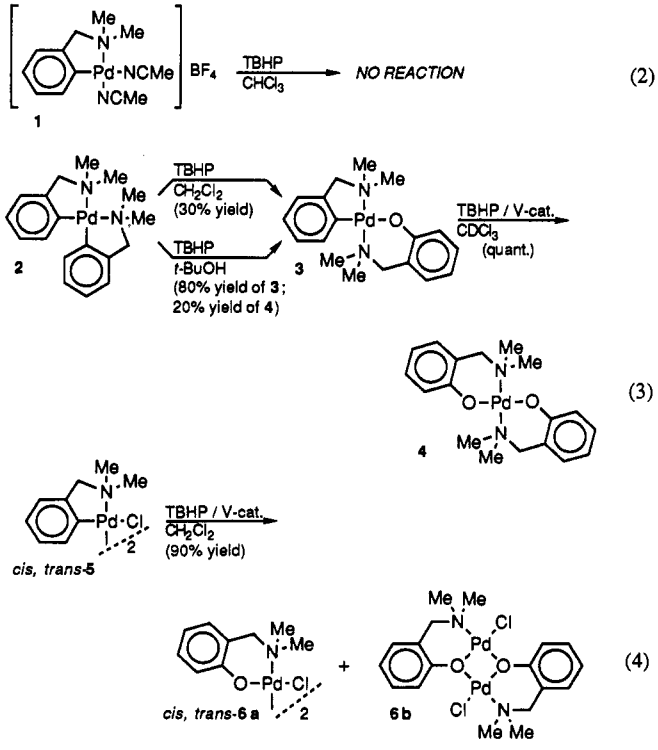


(1)

and a vanadium catalyst with cyclopalladated *N,N*-dimethylbenzylamine complexes as the model species (substrates). The influences exerted by the ligands surrounding the palladium center, the vanadium catalyst, and the solvent on the course of the reaction are discussed.

Results

The oxygenation reactions studied in this work are summarized in eqs 2–4. First we investigated the reaction



(2)

(3)

(4)

of the cationic cyclopalladated (*N,N*-dimethylbenzylamine)palladium compound $[Pd(C_6H_4CH_2NMe_2\text{-}2)(MeCN)_2]BF_4$ (1) with TBHP. This cationic derivative was chosen since Chakravorty *et al.* recently suggested that oxidation with *m*-CPBA can be promoted by increasing the electrophilicity of the palladium center to strengthen coordination of the peroxidic oxygen atom to the metal center.[6c] It was therefore surprising to find that the cationic complex **1**, despite its electrophilicity being higher than that of the neutral biscyclopalladated compound **2** (*cf.* eqs 2 and 3), is almost inert toward TBHP. Consequently, we assume that initial coordination of the peroxide *via* the oxygen lone pairs is only of minor importance in the transition state. It is noteworthy that reaction of the diaryl compound *cis*-$[Pd(C_6H_4CH_2NMe_2\text{-}2)_2]$ (**2**) with TBHP in dichloromethane as solvent goes to completion within a few minutes. However, in this reaction only a 30% yield of the *monooxygenated* compound *trans*-$[Pd(OC_6H_4CH_2NMe_2\text{-}2)(C_6H_4CH_2NMe_2\text{-}2)]$ (**3**) is obtained (eq 3); the other products have not been identified. Further oxidation of **3** to the double phenolate *trans*-$[Pd(OC_6H_4CH_2NMe_2\text{-}2)_2]$ (**4**) occurs only very slowly over the course of several days.

In the presence of $VO(acac)_2$ as catalyst (1–5 mol %), **4** can be obtained in almost quantitative yield by oxygenation of **3** with TBHP (eq 3). Similarly, at room temperature the chlorine-bridged compound $[PdCl(C_6H_4CH_2NMe_2\text{-}2)]_2$ (**5**) does not react with excess TBHP but is readily converted within several hours into the phenolate $[Pd(OC_6H_4CH_2NMe_2\text{-}2)_2Cl]_2$ (**6**)[13] by addition of a catalytic amount (1–5 mol %) of either $VO(acac)_2$ or $VO(O^tBu)_3$ (see eq 4). Workup by reduction with hydrazine afforded the *ortho*-substituted 2-[(dimethylamino)methyl]phenol in 80% yield. As for epoxidation reactions with TBHP catalyzed by vanadium,[15] the active catalyst in the present reaction is very likely to be the vanadium(V) *tert*-butylperoxo species $VO(OO^tBu)(O^tBu)_2$.

There is a significant solvent effect on the oxygenation of **2** with TBHP. Although as noted above, in homogeneous solution (chloroform; dichloromethane) total conversion of **2** is readily achieved, the yield of **3** is only 30%. However, in a heterogeneous system with *tert*-butyl alcohol as medium a slow, but clean, reaction occurs to give a mixture of **3** (80% yield) and **4** (20% yield) (see eq 3). That a substantial amount of **4** is still formed in this reaction is probably due to the fact that the initially formed monooxygenated complex **3** is soluble in *tert*-butyl alcohol, whereas the starting material **2** is insoluble in this solvent and is therefore converted much more slowly than **3**.

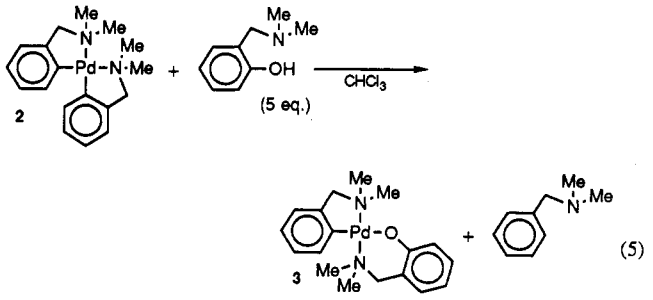
The palladium phenolates **3**, **4**, and **6** have also been prepared by an independent synthesis *via* a nonoxidative route. Phenolates **4** and **6** can be prepared from Li_2PdCl_4 and the appropriate amount of $[NaOC_6H_4CH_2NMe_2\text{-}2]$, whereas **3** is most conveniently synthesized by reaction of **2** with an excess of $HOC_6H_4CH_2NMe_2\text{-}2$. Remarkably, only one 2-((dimethylamino)methyl)phenyl ligand is exchanged for a phenolate anion in this reaction, despite the excess of phenol used (eq 5).[16]

In order to establish whether the organopalladium phenolate **3** has a *cis* or *trans* structure, a single-crystal X-ray study was undertaken; some selected bond lengths and bond angles are collected in Table I. The oxygen atom of the phenolate ligand is bonded *trans* to the aryl ring of the $C_6H_4CH_2NMe_2\text{-}2$ moiety (Figure 1). This feature is also observed in the crystal structure of a related palladium complex with an *N*-phenylsalicylaldiminato

(14) Phenolate **6** exists in three isomeric forms in noncoordinating solvents such as chloroform. The ^1H NMR spectrum of **6** in $CDCl_3$ shows three different signals for both the CH_2N as well as the CH_3N protons in a 1:1:10 ratio. Moreover, an *ortho* proton is present as a doublet at 7.95 ppm, whereas other palladium phenolates containing the $OC_6H_4CH_2NMe_2\text{-}2$ moiety (see Experimental Section) show characteristic high-field shifts of the aromatic protons (δ 6.5–7.2 ppm). After addition of pyridine-d_5 to the solution, a well-defined first-order pattern arises in the aromatic region and only one signal is observed for the CH_2N- and CH_3N-protons. These results can be rationalized by ascribing the low-intensity signals to the chlorine-bridged dimer **6a** (equimolar amounts of the *cis* and *trans* forms are present), whereas the high-intensity signals belong to the oxygen-bridged dimer **6b**. In the latter compound the *ortho* protons are low-field-shifted because of their proximity to the nonbridging chlorine atoms. After the addition of pyridine, bridge cleavage occurs and a well-defined monomeric phenolate chloride species is formed.

(15) Chong, A. O.; Sharpless, K. B. *J. Org. Chem.* **1977**, *42*, 1587.

(16) The higher susceptibility of diorganopalladium compounds (compared to monoorganopalladium compounds) to protonation by weak acids has also been noted by Yamamoto *et al.* (Kim, Y.-J.; Osakada, K.; Takenaka, A.; Yamamoto, A. *J. Am. Chem. Soc.* **1990**, *112*, 1096).



group bonded *trans* to a cyclopalladated *N,N*-dimethylbenzylamine ligand.[17] The main structural difference between the two compounds is found in the geometry of the six-membered chelate ring of the phenolate moiety. Whereas this ring adopts a boat conformation in **3**, it is essentially planar for the *N*-phenylsalicylaldiminato group. The C–O bond length in **3** (1.321(3) Å) is longer than that in the *N*-phenylsalicylaldiminato complex (1.284(11) Å). Both bond lengths are considerably shorter than the C–O bond length found in phenols (*ca.* 1.37 Å).[18] Such short C–O bonds are a common feature of late-transition-metal alkoxides and phenolates.[2,19] The shortness of the C–O bond length in the salicylaldiminato complex compared to that in **3** may be ascribed to more favorable conjugation of a lone-pair p orbital on the phenolate oxygen atom with the π system of the aryl ring in the salicylaldiminato group due to the presence of the *ortho* imine function.[20]

Discussion

The relative reactivities of the investigated [Pd(C_6H_4-CH_2NMe_2-2)X] species toward oxygenation, *i.e.* **2** ≫ **3** > **5** ≥ **1**, indicate that the oxygenation, at least in this series of compounds, is strongly enhanced by increasing the nucleophilicity of the metal center. Complexes **3** and **5** require the presence of a vanadium catalyst for efficient oxygenation (although **3** can be oxygenated very slowly with TBHP alone), but the highly nucleophilic diorganopalladium compound **2** is sufficiently reactive to react readily without a vanadium catalyst. The solvent effect observed in the oxygenation of **2** merits further comment. The beneficial effect of protic solvents (such as *t*-BuOH) in oxygenation reactions with alkyl hydroperoxides has long been recognized.[21] Moreover, a recent detailed theoretical study by Bach *et al.* on oxygen transfer from hydroperoxide species to ammonia has shown that protic solvents lower the barrier for a 1,2-hydrogen shift in the hydroperoxide (ROOH) to form an alcohol oxide species (RHO–O), which is not only much more easily formed in protic than in aprotic solvents but which is also strongly stabilized by hydrogen bonding to the protic solvent.[22] These alcohol oxide intermediates (*i.e. tert*-butyl alcohol oxide in the case of TBHP) can provide an oxenoid oxygen atom and a neutral leaving group in oxygenation reactions and are very likely to be the actual oxygen donating agent in oxygen transfer reactions by hydroperoxide reagents. It is tempting to assume that the reaction between an organopalladium compound and *tert*-butyl alcohol oxide as oxenoid donor leads to the formation of a transient Pd(IV) oxo species. Since this intermediate is (formally) a d^6 oxo species, it is expected to be unstable[23] and subsequently reacts to give products derived from oxygen insertion into the Pd–C bond. The mechanism of the actual oxygen insertion may be complex (see below), but a concerted one-step process leading to direct O insertion into the Pd–C bond (as has been proposed for the oxygenation of cyclopalladated azobenzenes with *m*-CPBA)[6] cannot be excluded for these reactions with TBHP as the (terminal) oxygen donor.

We propose that the formation of this oxo species can be best envisioned as an S_N2 type attack of the d_{z^2} HOMO

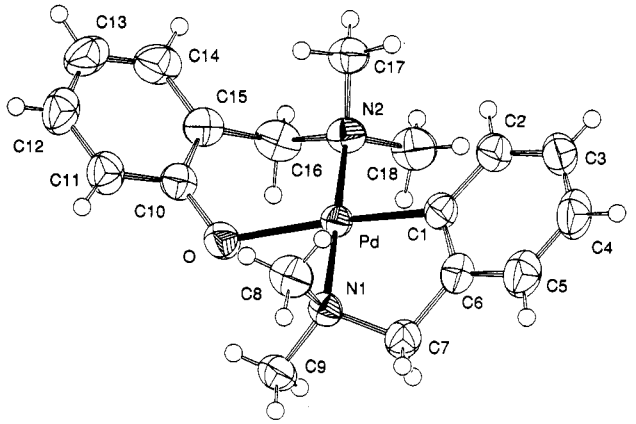


Figure 1. ORTEP drawing (50% probability level) of the molecular structure of [Pd($OC_6H_4CH_2NMe_2$-2)($C_6H_4CH_2$-NMe_2-2)] (**3**) together with the adopted numbering scheme.

Table I. Selected Interatomic Distances (Å) and Angles (deg) for [Pd($OC_6H_4CH_2NMe_2$-2)($C_6H_4CH_2NMe_2$-2)] (3)

	Distances		
Pd–O	2.098(2)	Pd–N(2)	2.115(2)
Pd–C(1)	2.021(3)	C(10)–O	1.321(3)
Pd–N(1)	2.075(2)		
	Angles		
O–Pd–N(1)	86.00(9)	N(1)–Pd–N(2)	176.76(9)
O–Pd–N(2)	92.26(9)	Pd–O–C(10)	118.48(16)
C(1)–Pd–O	167.36(10)		

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(18) *Tables of Interatomic Distances and Configuration in Molecules and Ions*; Mitchell, A. D., Cross, L. C., Eds.; The Chemical Society: London, 1958; p S17.

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(20) Alternatively, the shorter C–O bond in the *N*-phenylsalicylaldiminato complex could be due to the planarity of the phenolate chelate ring that may also lead to more efficient resonance stabilization than in **3**, which has a strongly folded N,O ring. (Day, V. W.; Glick, M. D.; Hoard, J. L. *J. Am. Chem. Soc.* **1968**, *90*, 4803). With respect to bis(salicylaldiminato)palladium complexes, for which the degree of planarity depends strongly on the nature of the substituent attached to the Schiff base nitrogen (Manotti Lanfredi, A. M.; Ugozolli, F.; Ghedini, M.; Licoccia, S. *Acta Crystallogr.* **1985**, *C41*, 192 and references therein), there seems to be no correlation between the degree of nonplanarity and the C–O bond length. The C–O length is fairly constant (*ca.* 1.31 Å), *i.e.* almost equal to the C–O bond length in **3**. Resonance delocalization due to the *ortho* imine function is more likely to be responsible for the relatively short C–O bonds in these complexes, even though they lack a strong *trans*-labilizing ligand opposed to the phenolate oxygen atom as in **3**.

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(22) (a) Bach, R. D.; Owensby, A. L.; Gonzalez, C.; Schlegel, H. B.; McDouall, J. J. W. *J. Am. Chem. Soc.* **1991**, *113*, 6001. (b) See also: Bosch, E.; Lluch, J. M.; Bertrán, J. *Can. J. Chem.* **1990**, *68*, 666 for related calculations on 1,2-hydrogen migration of hydrogen peroxide.

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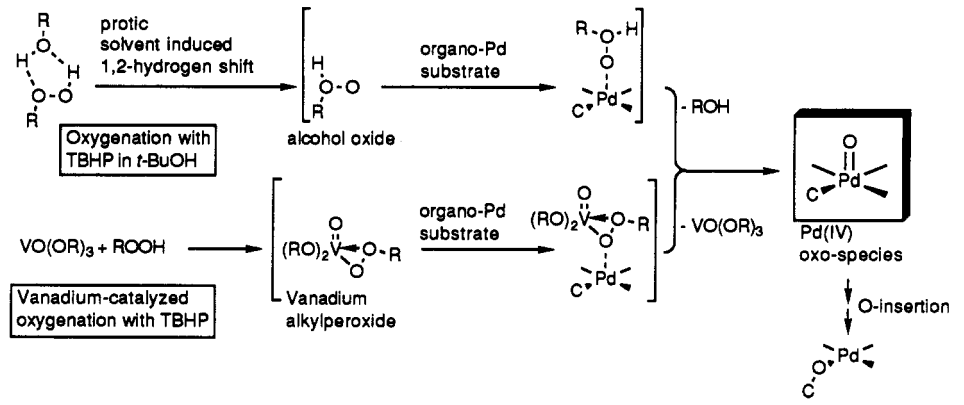
Scheme I



of the palladium center on the (weak) O–O σ bond of *tert*-butyl alcohol oxide. This O-O bond is thereby lengthened and yields a low energy empty σ^* orbital that serves as an electrophile. As such, the reaction strongly resembles the oxygen transfer of water oxide (or alcohol oxide) to ammonia, where ammonia oxide is formed by nucleophilic attack of the nitrogen lone pair at the O–O σ bond.[22a] In the presence of a vanadium catalyst, the O–O bond of a vanadium alkylperoxide probably attacks the palladium center in an analogous end-on way (Scheme I).

This proposed mechanism is very similar to experimental[24] and computational[25] results of the oxidative addition of dihalogens to square-planar d^8 metal complexes, which also proceeds *via* an end-on, nucleophilic, attack of the metal on the σ^* LUMO within the dihalogen (X_2) and concomitant splitting off of an X^- anion (*cf.* alcohol as leaving group in the case of alcohol oxide as oxidant). The S_N2 type of attack is in accordance with the experimental finding that the rate of oxygenation increases strongly with the nucleophilicity of the metal center. We suggest that the formation of the Pd(IV) oxo species is rate-determining.[26]

Conclusions

Cyclopalladated *N,N*-dimethylbenzylamine complexes can be oxygenated either with TBHP alone (diorganopalladium complex **2**) or with TBHP and a vanadium catalyst (complexes **3** and **5**). The reactivity increases strongly with the nucleophilicity of the metal center. The initial stage of the reaction probably involves a nucleophilic end-on attack of the metal center on the O–O bond of either a *tert*-butyl alcohol oxide intermediate (oxygenations with TBHP in *t*-BuOH) or a vanadium alkylperoxide (vanadium-catalyzed oxygenations with TBHP). Viewed as such, a σ back-donation from metal d_{z^2} to the σ^* LUMO of the peroxide occurs in the transition state and, ultimately, a Pd(IV) oxo species[26] is formed. This mechanism is very similar to that of the initial stage of the oxidative addition of dihalogens to square-planar d^8 metal complexes. The oxygenation described has an interesting scope and is now being explored for the oxygenation of 2-substituted naphthalenes to the corresponding 2-substituted 1,4-naphthaquinones.[28]

Experimental Section

General Considerations. Et_2O and pentane were freshly distilled from sodium benzophenone ketyl. CH_2Cl_2 was distilled from calcium hydride, and chloroform was distilled from calcium chloride. ^1H and ^{13}C NMR spectra were recorded on Bruker AC 200 or Bruker AC 300 spectrometers. Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer. Elemental analyses were carried out by the Institute of Applied Chemistry (TNO), Zeist, The Netherlands. The organopalladium compounds **1**,[29] **2**,[30] and **5**,[31] (2-(dimethylamino)methyl)phenol,[31] and $VO(O^tBu)_3$[32] were prepared according to literature procedures. Abbreviation: td = triplet of doublets.

Nonoxidative Syntheses of Palladium Phenolates. [Pd($OC_6H_4CH_2NMe_2$-2)($C_6H_4CH_2NMe_2$-2)] (3). A solution of **2** (0.24 g, 0.64 mmol) and 2-(dimethylamino)methyl)phenol (0.48 g, 3.17 mmol) in chloroform (25 mL) was stirred for 36 h at room

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(25) Bickelhaupt, F. M.; Baerends, E. J.; Ravenek, W. *Inorg. Chem.* **1990**, *29*, 350.

(26) The oxygenation of some cyclopalladated 2-(alkylsulfinyl)azobenzene derivatives with *m*-CPBA follows a straightforward second-order rate law (first order in both organopalladium substrate and in the oxidant).[6c,d] This is in agreement with a rate-limiting S_N2 type attack of the palladium center at the O–O bond as discussed above. On the other hand, oxygen insertion by *m*-CPBA with a related cyclopalladated 2-(alkylthio)azobenzene species as substrate followed an unexpected third-order rate law (*second* order in the organopalladium substrate; first order in the oxidant).[6b] Perhaps related to this second-order dependence of the reaction rate on the organometallic substrate concentration is the fact that the hydroxylation of arenes with H_2O_2 catalyzed by platinum(II) complexes (which are assumed to activate the arene by metalation, affording arylplatinum species) also shows a second-order dependence on the catalyst concentration.[7] These kinetic results, which are not well understood, indicate that the oxygenation may proceed by a multistep process. We propose that the Pd(IV) oxo species itself may serve as an oxygen transfer agent to the organopalladium substrate; *i.e.* an *intra*molecular oxygen insertion in the oxo species itself may be much more difficult than an *inter*molecular oxygen transfer leading to oxygen insertion. Support for the view that the postulated Pd(IV) oxo intermediate has oxygen transfer ability is provided by the fact that nickel(II)[27a] or palladium(II)[27b] catalyzes alkene epoxidation reactions in the presence of single oxygen donors as terminal oxidants. These reactions are also postulated to proceed *via* Ni(IV) or Pd(IV) oxo species as the actual oxygenating agent. In our computational studies we are currently exploring the electronic structures of both the above proposed palladium(IV) oxo species and its alternative structure, *i.e.* the palladium oxide: Dedieu, A., to be submitted for publication.

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temperature. After evaporation of the solvent, excess phenol and liberated *N,N*-dimethylbenzylamine were removed *in vacuo* (1 mmHg) from the oily residue at 50 °C. The greenish yellow solid was washed with pentane (5 × 8 mL) and taken up in CH_2Cl_2, after which metallic palladium was filtered off over Celite. The yellow filtrate was evaporated to dryness: yield 0.23 g (92%) of **3** as an air-stable yellow powder, which was about 95% pure according to its ^1H NMR spectrum. The compound can be further purified by slow evaporation of a CH_2Cl_2/Et_2O solution. A large yellow crystal suitable for an X-ray structure determination was obtained fortuitously by evaporation of a $CDCl_3$ solution of the complex. Dec pt: >147 °C. IR (KBr; ν/cm^{-1}): 1310 (C–O). Anal. Calcd for $C_{18}H_{24}N_2OPd$: C, 55.31; H, 6.20; N, 7.16. Found: C, 54.18; H, 6.23; N, 7.07. ^1H NMR (300 MHz, $CDCl_3$): δ 7.18 (m, 2H, Ar *H*), 6.98 (m, 4H, Ar *H*), 6.77 (dd, 1H, ^3J = 8.1 Hz, ^4J = 0.7 Hz, OAr *H*), 6.49 (td, 1H, ^3J = 7.2 Hz, ^4J = 1.0 Hz, OAr *H*), 3.90 (s, 2H, NCH_2), 3.37 (s, 2H, NCH_2), 2.81 (s, 6H, NCH_3), 2.76 (s, 6H, NCH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 167.90 (O*C*(*ipso*)), 148.55, 146.66, 124.29 (CH_2C(*ipso*) and Pd*C*(*ipso*)), 132.94, 130.61, 130.37, 124.70, 123.86, 121.68, 118.82, 113.07 (Ar), 73.70, 67.11 (NCH_2), 50.91 (two coincident signals. NCH_3).

[Pd(OC$_6$H$_4$CH$_2$NMe$_2$-2)$_2$] (4). A mixture of $PdCl_2$ (0.64 g, 3.62 mmol) and LiCl (0.31 g, 7.31 mmol) was dissolved in hot (~60 °C) water (15 mL). The solution was diluted with MeOH (50 mL), and Na_2CO_3 (1.00 g, excess) was added, followed by addition of $HOC_6H_4CH_2NMe_2$-2 (1.09 g, 7.23 mmol) in MeOH (20 mL). After the mixture had been stirred for 3 h at 50 °C, the volatiles were removed under reduced pressure, the grayish solid residue was extracted with CH_2Cl_2, and the extract was filtered over Celite. The yellow filtrate was evaporated to a small volume, after which the yellow-orange product was precipitated by addition of pentane. After the temperature was lowered to −30 °C, the product was filtered off, washed with pentane (3 × 10 mL), and dried: yield 0.90 g (61%); mp 175 °C dec. IR (KBr; ν/cm^{-1}): 1280 (C–O). ^1H NMR (200 MHz, $CDCl_3$): δ 7.10 (td, 1H, ^3J = 7.9 Hz, ^4J = 1.7 Hz, Ar *H*), 6.94 (dd, 1H, ^3J = 7.3 Hz, ^4J = 1.7 Hz, Ar *H*), 6.76 (dd, 1H, ^3J = 7.9 Hz, ^4J = 1.0 Hz, Ar *H*), 66.2 (td, 1H, ^3J = 7.3 Hz, ^4J = 1.0 Hz, Ar *H*), 3.19 (s, 2H, NCH_2), 2.63 (s, 6H, NCH_3). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 166.56 (O*C*(*ipso*)), 126.73 (CH_2C(*ipso*)) 130.48, 130.28, 118.88, 116.03 (Ar), 63.78 (NCH_2), 48.33 (NCH_3). ^1H NMR and IR data are in accordance with the literature data.[34]

[PdCl(OC$_6$H$_4$CH$_2$NMe$_2$-2)]$_2$ (6). A mixture of $PdCl_2$ (0.87 g, 4.91 mmol) and LiCl (0.44 g, 10.38 mmol) was dissolved in hot (~60 °C) water (10 mL). The aqueous solution was diluted with MeOH (30 mL). To this solution was added dropwise over 15 min a solution of [$NaOC_6H_4CH_2NMe_2$-2] (0.85 g, 4.91 mmol) in MeOH (15 mL), and this resulted in the precipitation of a red solid. After the mixture was stirred for 20 h, the powder was isolated by filtration and washed succesively with methanol (5 × 5 mL), CH_2Cl_2 (5 × 2 mL), and Et_2O (5 × 5 mL). The brick red powder was dried under vacuum: yield 1.07 g (75%); dec pt >160 °C. IR (KBr; ν/cm^{-1}): 1240 (C–O). Anal. Calcd for $C_9H_{12}ClNOPd$: C, 37.01; H, 4.15; N, 4.80. Found: C, 36.24; H, 4.37; N, 4.78. ^1H NMR (200 MHz, $CDCl_3$): δ 7.92 (d, ^3J = 8.1 Hz, Ar *H*(*ortho*) of O-bridged dimer), 7.23–7.35 (m, Ar *H*), 6.82 (m, Ar *H*), 2.99 (s, NCH_2 of *cis*/*trans* isomers of Cl-bridged dimer), 2.96 (s, NCH_2 of *cis*/*trans* isomers of Cl-bridged dimer), 2.85 (s, NCH_2 of O-bridged dimer), 2.59 (s, NCH_3 of *cis*/*trans* isomers of Cl-bridged dimer), 2.49 (s, NCH_3 of *cis*/*trans* isomers of Cl-bridged dimer), 2.55 (s, NCH_3 of O-bridged dimer). According to the integrals, the ratio of O-bridged dimer to Cl-bridged dimer is 4.7:1 (the *cis* and *trans* isomers of the Cl-bridged dimer are present in equimolar quantities). After addition of pyridine-d_5: ^1H NMR (200 MHz, $CDCl_3$) δ 7.15 (td, 1H, ^3J = 7.9 Hz, ^4J = 1.7 Hz, Ar *H*), 6.97 (dd, 1H, ^3J = 7.3 Hz, ^4J = 1.7 Hz, Ar *H*), 6.87 (dd, 1H, ^3J = 7.3 Hz, ^4J = 1.0 Hz, Ar *H*), 6.67 (td, 1H, ^3J = 7.3 Hz, ^4J = 1.0 Hz, Ar *H*), 3.13 (s, 2H, NCH_2), 2.69 (s, 6H, NCH_3).

Oxygenation Reactions. Oxygenation of 2. To a suspension of **2** (0.1507 g, 0.402 mmol) in *tert*-butyl alcohol (25 mL) at 35 °C was added TBHP (75 μL, 0.6 mmol). After the mixture was stirred for 22 h at 35 °C, a clear yellow solution formed. The mixture was evaporated to dryness *in vacuo*, and the solid residue was washed with Et_2O (3 × 2 mL): yield 0.15 g of a yellow powder, which according to its ^1H NMR spectrum consisted of a mixture of **3** (80%) and **4** (20%). Addition of TBHP (2 equiv) to a CD_2Cl_2 solution of **2** resulted in the formation of a complex reaction mixture (conversion complete within 10 min), which contained about 30% of the monooxygenated product **3**, as confirmed by addition of an independently prepared sample.

Oxygenation of 3. To a mixture of **3** (0.0473 g, 0.121 mmol) and $VO(acac)_2$ (0.000 54 g, 0.002 mmol) in $CDCl_3$ (0.7 mL) was added CH_2Cl_2 (7.76 μL, 0.121 mmol) as internal standard with a microsyringe and TBHP (30 μL, 0.240 mmol). The reaction was followed by ^1H NMR spectroscopy. Clean conversion of **3** into **4** was observed without detection of intermediates. The reaction was complete after *ca.* 1.5 h, at which time the solution was red. The yield was nearly quantitative, as measured by integration of the two CH_2N integrals against the CH_2Cl_2 integral. Addition of an independently prepared sample of **4** definitely confirmed its formation by oxygenation of **3**. The oxygenation proceeds much more slowly in the absence of the vanadium catalyst; the conversion after 5 days was only 60%.

Oxygenation of 5. To a mixture of **5** (0.1012 g, 0.367 mmol) and $VO(acac)_2$ (0.0024 g, 0.009 mmol), dissolved in CH_2Cl_2 (6 mL), was added TBHP (0.12 mL, 0.96 mmol). The deep red solution was stirred for 12 h. The mixture was evaporated to dryness *in vacuo*, and the red solid residue was washed with Et_2O (5 × 2.5 mL): yield 0.10 g (93%) of **6**, identical with the product obtained by the nonoxidative route described above. Reduction with excess hydrazine hydrate in CH_2Cl_2 gave a yellow oil, which was identified as almost pure 2-((dimethylamino)-methyl)phenol by comparison with an authentic sample prepared *via* the nonoxidative route described in the literature.[32] $VO(O^tBu)_3$ can also be used as catalyst instead of $VO(acac)_2$.

Reactivity of 1 toward TBHP. ^1H NMR spectra of a mixture of **1** (0.013 38 g, 0.033 mmol) and TBHP (10 μL, 0.08 mmol) in $CDCl_3$ (0.6 mL) were measured immediately after addition and after 20 h. No reaction was observed.

Table II. Crystal Data and Details of the Structure Determination for 3

Crystal Data	
empirical formula	$C_{18}H_{24}N_2OPd$
fw	390.82
cryst syst	monoclinic
space group	$P2_1/c$ (No. 14)
a (Å)	11.171(1)
b (Å)	8.524(1)
c (Å)	18.101(1)
β (deg)	94.31(1)
V (Å^3)	1718.7(3)
Z	4
D_{calc} (g cm^{-3})	1.510
F(000) (e)	800
μ(Mo Kα) (cm^{-1})	10.7
cryst size (mm)	0.32 × 0.30 × 0.25
Data Collection	
temp (K)	295
radiation (Mo Kα; Zr-filtered) (Å)	0.710 73
θ_{min}, θ_{max} (deg)	1.1, 27.5
scan type	$\omega/2\theta$
$\Delta\omega$ (deg)	0.55 + 0.35 tan θ
Horiz and vert aperture (mm)	3.00, 6.00
ref rfln(s)	049, 0,–4,9 (no decay)
data set	h, −14 to +14; k, 0–10; l, 0–23
total and unique no. of data	3881; 3615
no. of obsd data ($I > 2.5\sigma(I)$)	2941
Refinement	
no. of refined params	274
R, R_w, S	0.026, 0.030, 0.82
weighting scheme	$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{av}$	0.007
max residual density (e/Å^3)	0.30

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X-ray Data Collection, Structure Determination, and Refinement of [Pd($OC_6H_4CH_2NMe_2$-2)($C_6H_4CH_2NMe_2$-2)] (3). Crystal data and numerical details of the structure determinations are given in Table II. X-ray data were collected for a yellowish block-shaped crystal glued on top of a glass fiber on an Enraf-Nonius CAD4 diffractometer. Unit cell parameters were determined from a least-squares treatment of SET4 setting angles of 25 reflections in the range $14° < \theta < 20°$ and checked for the presence of higher lattice symmetry.[35] Intensity data were corrected for Lp and absorption (DIFABS[36] correction range 0.80–1.17) and merged into a unique data set. The structure was solved with the PATT option of SHELXS86.[37] Subsequent refinement was done on F by full-matrix least squares with SHELX76.[38] Hydrogen atoms were located from a difference map and their positions refined with three common isotropic thermal parameters. All non-hydrogen atoms were refined with anisotropic thermal parameters. Weights based on counting statistics were introduced in the final refinement cycles. Neutral-atom scattering factors were taken from Cromer and Mann[39] and corrected for anomalous dispersion.[40] Geometrical calculations, including the thermal motion ellipsoid plots, were done with PLATON[41] on a DEC5000/ULTRIX system. All other calculations were done on a MicroVax-II cluster.

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Supplementary Material Available: Tables of fractional coordinates for the hydrogen atoms, anisotropic thermal parameters, and bond distances and angles for the non-hydrogen and hydrogen atoms of **3** (4 pages). Ordering information is given on any current masthead page.

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