Reactivity of Organopalladium Compounds toward Molybdenum Peroxides: Oxygen Insertion versus C–Cl and C–O Coupling. Evidence for Palladium(IV) Molybdate Intermediates

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Received August 27, 1992

The molybdenum peroxide [$MoO(O_2)_2$·HMPT·H_2O] (1) reacts with organopalladium compounds preferentially to give products derived from coupling of nucleophiles (halide or alkoxide) to the palladated carbon atom. Oxygen insertion into the Pd–C bond is only of minor importance for this peroxide. No other oxidants were able to effect this type of transformation as efficiently as 1. The C–O coupling mediated by 1 comprises the first method for the direct alkoxylation of organopalladium compounds and constitutes the basis for a very selective one-pot conversion of a C–H bond into an ether function by a sequence of cyclopalladation and alkoxylation. Evidence was found that the reaction can be described as an oxidatively induced S_N2 reaction, which proceeds via a palladium(IV) intermediate formed by oxidative addition of the O–O bond to the organopalladium(II) substrate. Steric hindrance either in the alkyl group attached to palladium or in the alkoxide nucleophile suppresses the alkoxylation and leads to oxygenation of the organopalladium compound. This oxygen insertion probably proceeds via the same Pd(IV) intermediate as the nucleophilic substitution. The mechanism of the oxidative addition, in which a Pd–Mo interaction may be a critical step, is discussed.

Introduction

The study of reactions of alkyl or aryl metal compounds leading to C–X bond formation (X = O, N) is a research field that is just beginning to develop. By contrast, homogeneously catalyzed C–C bond formations are among the chemical transformations of organometallic compounds that have already gained importance as a synthetic tool in organic chemistry.[1] Much information about the intimate steps involved in these reactions, like oxidative addition, reductive elimination, and migratory insertion, is available.[1a] One of the reasons for the scarcity of information concerning C–X bond formation is the presumed instability of late transition metal alkoxides and amides, which may serve as model compounds for the study of C–O or C–N coupling by reductive elimination or (migratory) insertion reactions into the M–O or M–N bond.[2] It is only recently that both approaches to effect C–X (and H–X) coupling reactions have been demonstrated on well-characterized late transition metal alkoxides and amides.[2–4]

With respect to C–O coupling reactions, oxygen insertion into the late transition metal–carbon bond (oxygenation) presents an alternative approach that has received much less attention.[5–7] We have recently demonstrated that cyclopalladated *N,N*-dimethylbenzylamine complexes can be oxygenated with *tert*-butyl hydroperoxide and a vanadium catalyst,[7] whereas, interestingly, the same oxidizing system reacts further to a quinone system in the case of a related [2-[(dimethylamino)methyl]-3-naphthyl]-palladium complex (eqs 1 and 2).[8] The actual oxygenating agent in these reactions is most likely a vanadium alkyl peroxide.

Although oxygen insertion into a metal–carbon bond seems a conceptually simple reaction, the scope of the vanadium-catalyzed oxygenation with TBHP (TBHP =

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(1) (a) Brown, J. M.; Cooley, N. A. *Chem. Rev.* **1988**, *88*, 1031. (b) Maryanoff, C. A.; Mills, J. E.; Stanzione, R. C.; Hortenstine, J. T. In *Catalysis of Organic Reactions*; Rylander, P. N., Greenfield, H., Augustine, R. L., Eds.; Marcel Dekker: New York, 1988; p 359. (c) Negishi, E.-i.; Takahashi, T.; Akiyoshi, K. in ref 1b, p 381.

(2) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163.

(3) Insertion reactions in M–O bonds: (a) Bryndza, H. E.; Calabrese, J. C.; Wreford, S. S. *Organometallics* **1984**, *3*, 1603. (b) Rees, W. M.; Atwood, J. D. *Organometallics* **1985**, *4*, 402. (c) Bryndza, H. E. *Organometallics* **1985**, *4*, 1686. (d) Kim, Y. J.; Osakada, K.; Sugita, K.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1988**, *7*, 2182. (e) Green, L. M.; Meek, D. W. *Organometallics* **1989**, *8*, 659. (f) Cowan, R. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1989**, *111*, 4750. (g) Osakada, K.; Kim, Y. J.; Yamamoto, A. *J. Organomet. Chem.* **1990**, *382*, 303. (h) Kim, Y. J.; Osakada, K.; Takenaka, A.; Yamamoto, A. *J. Am. Chem. Soc.* **1990**, *112*, 1096.

(4) C–O and H–O coupling via reductive elimination: (a) Bryndza, H. E.; Calabrese, J. C.; Wreford, S. S. *Organometallics* **1984**, *3*, 1603. (b) Bernard, K. A.; Atwood, J. D. *Organometallics* **1987**, *6*, 1133. (c) Bernard, K. A.; Atwood, J. D. *Organometallics* **1988**, *7*, 235. (d) Bernard, K. A.; Atwood, J. D. *Organometallics* **1989**, *8*, 795. (e) Bernard, K. A.; Churchill, M. R.; Janik, T. S.; Atwood, J. D. *Organometallics* **1990**, *9*, 12. (f) Thompson, J. S.; Bernard, K. A.; Rappoli, B. J.; Atwood, J. D. *Organometallics* **1990**, *9*, 2727. (g) Glueck, D. S.; Newman Winslow, L. J.; Bergman, R. G. *Organometallics* **1991**, *10*, 1462. (h) Thompson, J. S.; Randall, S. L.; Atwood, J. D. *Organometallics* **1991**, *10*, 3906.

(5) O-insertion into Pd–C bond of cyclopalladated azobenzenes: (a) Mahapatra, A. K.; Bandyopadhyay, D.; Bandyopadhyay, P.; Chakravorty, A. *J. Chem. Soc., Chem. Commun.* **1984**, 999. (b) Mahapatra, A. K.; Bandyopadhyay, D.; Bandyopadhyay, P.; Chakravorty, A. *Inorg. Chem.* **1986**, *25*, 2214. (c) Sinha, C.; Bandyopadhyay, D.; Chakravorty, A. *J. Chem. Soc., Chem. Commun.* **1988**, 468. (d) Sinha, C.; Bandyopadhyay, D.; Chakravorty, A. *Inorg. Chem.* **1988**, *27*, 1173. (e) Chattopadhyay, S.; Sinha, C.; Basu, P.; Chakravorty, A. *Organometallics* **1991**, *10*, 1135.

(6) Oxyfunctionalizations of hydrocarbons with Pd and Pt catalysts that possibly proceed via oxygenation of organometallic intermediates: (a) Strukul, G.; Marsella, A.; Pinna, F. Proceedings of the Seventh International Symposium on Homogeneous Catalysis, Lyon-Villeurbanne, France, 1990, p 77. (b) Jintoku, T.; Nishimura, K.; Takaki, K.; Fujiwara, Y. *Chem. Lett.* **1990**, 1687. (Erratum: *Chem. Lett.* **1991**, 193.) (c) Kao, L.-Ch.; Hutson, A. C.; Sen, A. *J. Am. Chem. Soc.* **1991**, *113*, 700.

(7) Alsters, P. L.; Teunissen, H. T.; Boersma, J.; van Koten, G. *Recl. Trav. Chim. Pays-Bas* **1990**, *109*, 487.

(8) Valk, J. M.; Maassarani, F.; Boersma, J.; van Koten, G. Proceedings of the Fourth International Symposium on Activation of Dioxygen and Homogeneous Catalytic Oxidation, Balatonfüred, Hungary, 1990, p 75.

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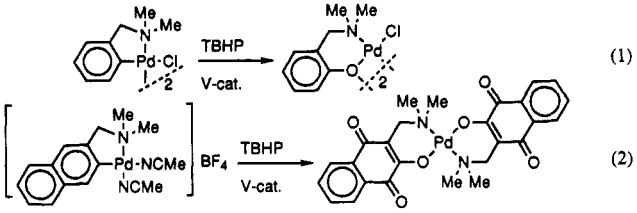


tert-butyl hydroperoxide) was found to be limited to cyclopalladated *N,N*-dimethylbenzylamine complexes. With other substrates complex reaction mixtures were obtained. As this may be caused by the tendency of vanadium peroxo species to react via a nonselective radical mechanism (in addition to the occurrence of concerted oxygenation in eqs 1 and 2),[9] we turned our attention to the molybdenum peroxide $[MoO(O_2)_2 \cdot HMPT \cdot H_2O]$ (1) (HMPT = hexamethylphosphoric triamide).

Surprisingly, we found that the expected oxygenation of the Pd–C bond was only observed in special cases. More generally, this molybdenum peroxide mediates coupling of nucleophiles (chloride or alkoxide) to the palladated (aryl or alkyl) carbon atom.[10] The mechanism of these reactions will be discussed, and a rationale for the observed differences in reactivity will be given. It is pointed out that the molybdenum peroxide is a unique reagent to effect the C–X coupling reactions.

Results

Synthesis of Organopalladium Substrates. The reactivity of molybdenum peroxide 1 toward organopalladium complexes was investigated for a variety of substrates, including cyclopalladated and noncyclopalladated aryl- and alkylpalladium compounds (see Scheme I). Noncyclopalladated arylpalladium complexes of the type [PdX(Ar)(tmeda)] (X = Cl, NO_3) (2–5) (tmeda = *N,N,N′,N′*-tetramethylethane-1,2-diamine) were synthesized by oxidative addition of the aryl iodide ArI to Pd(dba)$_2$ (dba = dibenzylideneacetone) in the presence of tmeda,[11] followed by standard metathesis reactions. The alkylpalladium derivative **15** (vide infra, Figure 1) was prepared from the coordination adduct of $PdCl_2$ with norbornadiene via a classical sequence of $\pi \rightarrow \sigma$ rearrangement induced by nucleophilic attack of methoxide ion on a coordinated double bond[12] followed by conversion of the norbornenyl metal system into a nortricyclenyl metal system by addition of 1 equiv of tmeda to the chloride-bridged dimer.[13] All other cyclopalladated complexes were prepared by direct palladation in methanol, either with Li_2PdCl_4 (**6**, **7**) or with Pd(OAc)$_2$ (**8**, **9**, **13**, and **18** (vide infra, Figure 2)).[14]

Chlorination of Organopalladium Complexes. Reaction of organopalladium chlorides with molybdenum peroxide **1** in dichloromethane gives rise to the formation of chlorinated products instead of phenols. Addition of (triethyl)(benzyl)ammonium chloride ([TEBA]Cl) increases the yield of these chlorinated products, although

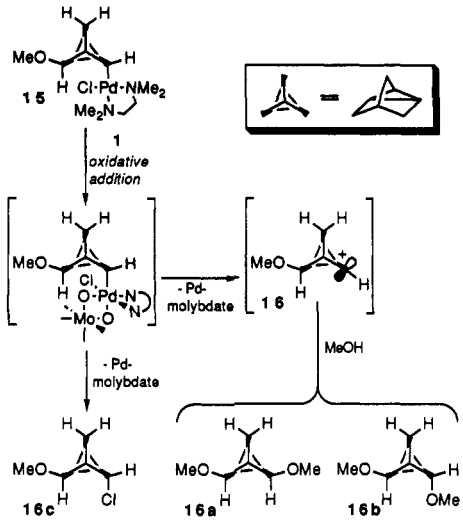


Figure 1. Reaction of $[MoO(O_2)_2 \cdot HMPT \cdot H_2O]$ (1) with tricycloheptylpalladium complex **15**. Product ratio: **16c**:**16a**:**16b** = 1:11:10.

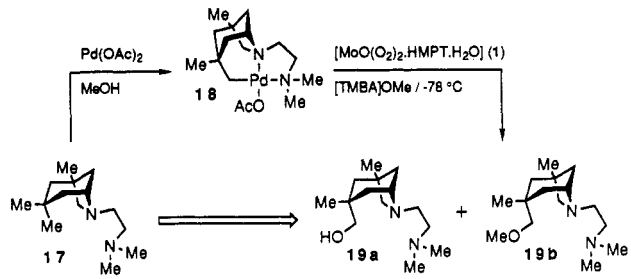
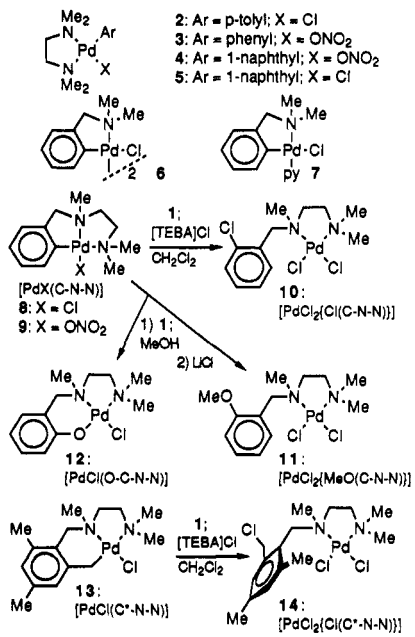


Figure 2. Selective one-pot oxyfunctionalization of a nonactivated aliphatic C–H bond by a sequence of cyclopalladation and oxidation with 1. Product ratio **19a**:**19b** = 6:1.

Scheme I



(9) (a) Mimoun, H.; Saussine, L.; Daire, E.; Postel, M.; Fisher, J.; Weiss, R. *J. Am. Chem. Soc.* **1983**, *105*, 3101. (b) Bonchio, M.; Conte, V.; Di Furia, F.; Modena, G. *J. Org. Chem.* **1989**, *54*, 4368.

(10) Parts of this work have been published: (a) Alsters, P. L.; Boersma, J.; van Koten, G. *Tetrahedron Lett.* **1991**, *32*, 675. (b) Alsters, P. L.; Teunissen, H. T.; Boersma, J.; van Koten, G. Proceedings of the Fourth International Symposium on Activation of Dioxygen and Homogeneous Catalytic Oxidation, Balatonfüred, Hungary, 1990, p 47. (c) Alsters, P. L.; Teunissen, H. T.; Boersma, J.; van Koten, G. Proceedings of the Seventh International Symposium on Homogeneous Catalysis, Lyon-Villeurbanne, France, 1990, p 97.

(11) de Graaf, W.; van Wegen, J.; Boersma, J.; Spek, A. L.; van Koten, G. *Recl. Trav. Chim. Pays-Bas* **1989**, *108*, 275.

(12) Stille, J. K.; Morgan, R. A. *J. Am. Chem. Soc.* **1966**, *88*, 5135.

(13) For related conversions with 2,2′-bipyridine or 1,10-phenanthroline: Pietropaolo, R.; Cusmano, F.; Rotondo, E.; Spadaro, A. *J. Organomet. Chem.* **1978**, *155*, 117.

(14) A paper with details about the preparation and properties of the terdentate organopalladium complexes used in this work is in preparation. Alsters, P. L.; Spek, A. L.; van Koten, G. *Organometallics*, in press.

Table I. Oxidation of Organopalladium Compounds by Reaction with $[MoO(O_2)_2 \cdot HMPT \cdot H_2O]$ (1) in Dichloromethane

entry	substrate	equiv of 1[a] ([TEBA]Cl)[a]	products	yield (%)
1	**2** [PdCl(*p*-tolyl)(tmeda)]	2.4 (3.2)	*p*-chlorotoluene	79[b]
2	**6** $[PdCl\{C_6H_4(CH_2NMe_2)\text{-}2\}]_2$	2.5 (0)	$2\text{-}HOC_6H_4CH_2NMe_2$	48[c]
3	**7** $[PdCl\{C_6H_4(CH_2NMe_2)\text{-}2\}(py)]$	2.4 (0)	$2\text{-}HOC_6H_4CH_2NMe_2$	31[c]
			$2\text{-}ClC_6H_4CH_2NMe_2$	22[c]
4	**7**	2.4 (3.2)	$2\text{-}ClC_6H_4CH_2NMe_2$	61[c]
			$2\text{-}HOC_6H_4CH_2NMe_2$	26[c]
5	**8** [PdCl(C–N–N)]	2.5 (3.1)	$[PdCl_2\{Cl(C\text{–}N\text{–}N)\}]$	95[d]
6	**13** [PdCl(C*–N–N)]	2.5 (3.1)	$[PdCl_2\{Cl(C^*\text{–}N\text{–}N)\}]$	69[d]

[a] Equivalents (mol/mol) of **1** or [TEBA]Cl relative to substrate. [b] Yield determined by gas chromatography. [c] Yield determined by gas chromatography after reduction with hydrazine. [d] Isolated yield.

Table II. Oxidation of Organopalladium Compounds by Reaction with $[MoO(O_2)_2 \cdot HMPT \cdot H_2O]$ (1) in Alcohols

entry	solv	substrate	equiv of 1[a] ([TMBA]OMe)[a]	products	yield (%)
1	MeOH	**3** $[Pd(NO_3)(phenyl)(tmeda)]$	2.4 (0)	anisole	58[b]
2	MeOH	**3**	2.5 (1.1)	anisole	59[b]
3	*t*-BuOH	**3**	1.1 (0)	phenol	58[b]
				biphenyl	25[b]
4	MeOH	**4** $[Pd(NO_3)(1\text{-naphthyl})(tmeda)]$	1.2 (0)	1-methoxynaphthalene	66[b]
5	MeOH	**4**	2.7 (1.2)	1-methoxynaphthalene	68[b]
6	EtOH	**4**	1.2 (0)	1-ethoxynaphthalene	82[b]
7	BnOH	**4**	2.5 (0)	1-(benzyloxy)naphthalene	73[b]
8	MeOH	**5** [PdCl(1-naphthyl)(tmeda)]	1.2 (0)	1-methoxynaphthalene	56[b]
				1-chloronaphthalene	trace
9	MeOH	**7** $[PdCl\{C_6H_4(CH_2NMe_2)\text{-}2\}(py)]$	1.2 (0)	$2\text{-}MeOC_6H_4CH_2NMe_2$	57[c]
				$2\text{-}ClC_6H_4CH_2NMe_2$	4[c]
10	MeOH	**9** $[Pd(NO_3)(C\text{–}N\text{–}N)]$	2.5 (3.0)	$[PdCl_2\{MeO(C\text{–}N\text{–}N)\}]$	74[d]
				[PdCl(O–C–N–N)]	7[d]

[a] Equivalents (mol/mol) of **1** or [TMBA]OMe relative to substrate. [b] Yield determined by gas chromatography. [c] Yield determined by gas chromatography after reduction with hydrazine. [d] Isolated yield.

its presence is not a prerequisite for their formation. This reaction is applicable to a variety of substrates (Table I). The halogenation is not restricted to cyclopalladated complexes; simple aryl compounds react as well (entry 1). The benzylpalladium species [PdCl(C*–N–N)] (**13**) also reacts cleanly (entry 6). Only in the case of cyclopalladated *N,N*-dimethylbenzylamine complexes are substantial amounts of phenols formed (entries 2–4).

An important aspect of this new halogenation reaction is that overchlorination is not observed, even though an excess of both the molybdenum peroxide and [TEBA]Cl is used. This gives the reaction an advantage from a practical point of view over the more commonly used halogenation with gaseous dichlorine, which is often much less selective and produces substantial amounts of polychlorinated[15] or other products[16] (unless exactly 1 equiv of dichlorine is added).[17]

Alkoxylation of Organopalladium Complexes. Based on the reactants used in the chlorination, i.e. an oxidant (the molybdenum peroxide) and a halide nucleophile ([TEBA]Cl), we directed our attention to C–O coupling of alkoxide nucleophiles and organopalladium compounds mediated by the molybdenum peroxide. The resulting alkoxylation would be of great interest as it offers a very easy and highly selective route for the transformation of a C–H bond into an ether function. The conversion of a C–H bond into an alkoxy group is a virtually nonexistent chemical operation in organic chemistry, although recently some examples (with very restricted applicability) have been described.[18] There is also in organotransition metal chemistry no satisfactory method for the direct alkoxylation of a carbon–metal bond.

Indeed, when organopalladium compounds were allowed to react with **1** in alcoholic solvents, good yields of alkoxylated products were obtained. As with the chlorination, this reaction is very general (Table II). The presence of quaternary ammonium alkoxides did not improve the yield of the reaction, except for complex **9**, which produced a substantial amount of the hydrolyzed ligand in the absence of (trimethyl)(benzyl)ammonium methoxide ([TMBA]OMe). Surprisingly, chloride ligands attached to palladium interfere only slightly (entries 8 and 9). The reaction is not restricted to methanol; ethanol (entry 6) and benzyl alcohol (entry 7) can also be coupled to the palladated carbon atom in good yield. As benzyl ethers are easily cleaved to the corresponding alcohols,[19] this is an indirect route for introducing hydroxy groups at positions that can be palladated. However, direct hydroxylation was observed in the reaction of the phenylpalladium compound **3** with **1** in *tert*-butyl alcohol (containing some dichloromethane to improve the solubility of **1**); only a trace amount of *tert*-butoxybenzene was detected by gas chromatography. In this reaction, a substantial amount of biphenyl was also formed (entry 3).

Upon addition of other oxidants to the naphthylpalladium complex **4** in methanol (e.g. $Na_2Cr_2O_7$, CAN (Ce(IV) ammonium nitrate), $Cu(OAc)_2$, or tetrachlorobenzoquinone), either no or only a trace amount of 1-methoxynaphthalene could be detected by gas chromatography.

(15) Fahey, D. R. *J. Chem. Soc. D* **1970**, *7*, 417.
(16) Wong, P. K.; Stille, J. K. *J. Organomet. Chem.* **1974**, *70*, 121.
(17) *Houben-Weyl Methoden der Organischen Chemie, Band XIII/9b*; Segnitz, A., Ed.; Georg-Thieme Verlag: Stuttgart, 1984; p 917.
(18) (a) Alkoxylation of anthracene: Sugiyama, T. *Chem. Lett.* **1987**, 1013. (b) Alkoxylation of pyridine: Hebel, D.; Rozen, S. *J. Org. Chem.* **1988**, *53*, 1123. See also: Stavber, S.; Zupan, M. *Tetrahedron Lett.* **1990**, *31*, 775. (c) Alkoxylation of benzylketones: Schmittel, M.; Abufarag, A.; Luche, O.; Levis, M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1144.
(19) Greene, Th. W. *Protective Groups in Organic Synthesis*; Wiley: New York, 1981; p 97.

Therefore, it seems likely that a peroxide function is necessary to effect the alkoxylation. However, other molybdenum peroxides like $[MoO(O_2)_2 \cdot bpy]$ (bpy = 2,2′-bipyridine) or $[MoO(O_2)(pydic) \cdot HMPT]$ (pydic = 2,6-pyridinedicarboxylic acid) were also not able to effect C–X coupling reactions. The much lower reactivity of $[MoO(O_2)(pydic) \cdot HMPT]$ was also confirmed by ^1H NMR, which showed that **8** was stable for hours against a 10-fold excess of this peroxide, whereas an immediate reaction was observed upon addition of $[MoO(O_2)_2 \cdot HMPT \cdot H_2O]$ (**1**). To date, **1** is the only oxidant we have found that is able to effect alkoxylations and halogenations of organopalladium compounds via this type of reaction. The significance of the lower reactivity of the other molybdenum peroxides will be discussed below.

As with the chlorination, the alkoxylation is not restricted to arylpalladium compounds. After reaction with **1**, the tricycloheptylpalladium derivative **15** yielded the *exo,exo*- (**16a**) and *exo,endo*-dimethoxy (**16b**) ethers in a 1.15:1 ratio, together with a small amount (ca. 5%) of the *exo*-methoxy-*endo*-chlorotricycloheptyl derivative **16c** (Figure 1).

However, preferential oxygenation instead of alkoxylation was observed when the primary alkylpalladium complex **18** was used as the substrate.[20] After addition of the molybdenum peroxide **1** at low temperature (−78 °C),[21] two products were isolated in a 6:1 ratio. These were characterized as the alcohol **19a** (major product) and the methoxy ether **19b** (minor product), respectively, see Figure 2.

An attractive feature of this new reaction is that the two-step sequence of palladation and oxyfunctionalization can, in principle, be carried out in one pot since cyclopalladation is often performed in alcoholic solvents like methanol or ethanol. This possibility has been demonstrated for *N*-benzyl-*N*,*N*′,*N*′-trimethyldiaminoethane [(C–N–N)H], which can be converted to its *o*-methoxy derivative (68% yield)[22] without isolation of the arylpalladium acetate intermediate. This is done by adding [TMBA]OMe and then **1** after the cyclopalladation with palladium acetate in methanol is complete. A small amount of the phenolate is also formed. Note that the palladium center plays two roles in this reaction: firstly it activates specific C–H bonds and secondly it prevents oxidation of amine functionalities by coordination to the metal center in the subsequent oxidation. A similar one-pot procedure was used for the aliphatic oxygenation of the 1,3,3-trimethyl-6-azabicyclo[3.2.1]octane derivative **17** (Figure 2). The success of this procedure illustrates the ease and utility of the method for affecting the regiospecific and stereoselective oxyfunctionalization of unactivated C–H bonds at positions which are difficult to functionalize via classical organic routes. To our knowledge, no efficient reagent is known for the direct oxygenation of σ-alkylpalladium compounds.[23] The relevance of this transformation is illustrated by the work of Carr and Sutherland, who tried to oxyfunctionalize a steroid derivative at an unactivated methyl group via a sequence of cyclopalladation and oxidation with *m*-CPBA (*m*-CPBA = *m*-chloroperoxybenzoic acid).[24] Treatment of a model alkylpalladium chloride with *m*-CPBA unexpectedly resulted in the formation of the chlorinated derivative: an observation that was not understood by the authors but that seems to be related to the halogenation induced by the molybdenum peroxide **1**.

Discussion

Reaction of **1** with organopalladium compounds either leads to coupling of nucleophiles (chloride or alkoxide) to the palladated carbon atom or results in products formally derived from oxygen insertion into the Pd–C bond. The former pathway is most commonly observed. Spectroscopic study of the mechanism of these reactions is hampered by the fact that addition of the molybdenum peroxide to the organopalladium complexes results in the rapid precipitation of insoluble yellow-orange amorphous powders. These have been characterized as $PdCl_2$ coordination adducts in the case of halogenation in dichloromethane in the presence of [TEBA]Cl but are likely to be inorganic palladium molybdates in the case of alkoxylation reactions in methanol.[25]

However, from the stereochemistry of the reaction of **1** with the alkylpalladium compound **15** some insight into the mechanism can be obtained, see Figure 1. The observed epimerization that gives a nearly 1:1 mixture of the *exo,exo*- (**16a**) and *exo,endo*-dimethoxy (**16b**) ethers indicates that both a mechanism based on reductive elimination of an intermediate palladium alkoxide,[4] which should proceed with retention of configuration at the palladated carbon atom,[26] and a mechanism based on oxidatively induced nucleophilic substitution, for which inversion of configuration is expected,[26,27] seem to be not involved. We propose that the O–O bond of **1** first oxidatively adds to the organopalladium compound and that subsequently the organopalladium(IV) intermediate eliminates a carbocation which reacts with alcoholic solvents to alkoxylated products (Figure 1).[28] This mechanism is supported by the observation that carbocation **16**, when generated electrochemically from norbornadiene, reacts in methanolic solution to a mixture of **16a** and **16b** in the same ratio as found in our reaction.[29,30] The presence of a carbocationic intermediate in the oxidative cleavage

(20) This compound has not been isolated, but has been identified by following the cyclometalation in CD_3OD solution with ^1H NMR spectroscopy. This showed that the reaction was almost quantitative. The corresponding chloride and nitrate derivatives, which will not be discussed in this paper, have been fully characterized by spectroscopy and elemental analysis.

(21) Addition of **1** at room temperature results in a much less selective reaction. The organic product mixture isolated after work-up shows many resonances in the olefinic region in the ^1H NMR spectrum. These may indicate that the reaction follows at least partly a carbocation mechanism at room temperature. The organic products have, however, not been further identified.

(22) Isolated in the form of its $PdCl_2$ coordination adduct (see Experimental Section).

(23) *m*-CPBA reacts with σ-alkylpalladium and -platinum compounds to give mainly *m*-chlorobenzoate esters with retention of configuration at carbon. (a) Harvie, I. J.; McQuillin, F. J. *J. Chem. Soc., Chem. Commun.* **1976**, 369. (b) Harvie, I. J.; McQuillin, F. J. *J. Chem. Soc., Chem. Commun.* **1977**, 241.

(24) Carr, K.; Sutherland, J. K. *J. Chem. Soc., Chem. Commun.* **1984**, 1227.

(25) The precipitate formed in the reaction of **5** with **1** in methanol has beenisolated and characterized by means of IR and elemental analysis (see Experimental Section).

(26) Bäckvall, J. F. *Acc. Chem. Res.* **1983**, *16*, 335.

(27) Bäckvall, J. E. *Tetrahedron Lett.* **1977**, 467.

(28) It has been suggested (ref 13) that the 2,2′-bipyridine analogue of **15** dissociates in methanol solution with concomitant rearrangement from a nortricyclenyl structure to a norbornenyl structure. Such a process has, however, no effect on the nature of the carbocation that is eliminated.

(29) (a) Shono, T.; Ikeda, A.; Hayashi, J.; Hakozaki, S. *J. Am. Chem. Soc.* **1975**, *97*, 4261. (b) Baggaley, A. J.; Brettle, R.; Sutton, J. R. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1055.

(30) The anodic oxidation of norbornadiene gives a small amount of *exo*-5,*syn*-7-dimethoxybicyclo[2.2.1]hept-2-ene as a byproduct.

of a β-phenethylpalladium compound with copper(II) chloride has been deduced from deuterium-labeling studies.[31] Loss of stereochemistry to a 1:1 mixture of exo,endo and exo,exo compounds is also observed when a tricycloheptylpalladium complex that is closely related to **15** is treated with copper(II) bromide as the oxidant.[32] Thus, formation of carbocations in the oxidative cleavage of organopalladium compounds may be more general than previously thought.

Because carbocations derived from tricycloheptane are rather special, in that they are strongly stabilized by the cyclopropane unit,[33] the proposed mechanism based on carbocation intermediates does not necessarily hold for arylpalladium species too, since aryl cations are much less stable than tricycloheptyl cations. We believe that organopalladium compounds that cannot eliminate a stable carbocation are more likely to react via an oxidatively induced S_N2 mechanism in which the palladium center is turned into a very good leaving group (i.e. a strong two-electron oxidant) by the oxidative addition of the molybdenum peroxide. As aryl radicals are known to be unreactive toward alkoxide nucleophiles,[34] a radical mechanism can be ruled out.

The outcome of the oxidation of the alkylpalladium compound **18** provides some evidence for nucleophilic substitution as the mechanism of the alkoxylation (and chlorination). Complex **18** has a neopentyl unit attached to palladium, and the observation that the oxygenative (O-insertion) pathway dominates over the oxidatively induced methoxylation is in accordance with the fact that nucleophilic substitutions at neopentyl derivatives are very difficult.[35] The fact that phenyl compound **3** forms (mainly) phenol instead of *tert*-butoxybenzene in *tert*-butyl alcohol upon reaction with **1** can be explained similarly, except that the oxidatively induced nucleophilic substitution is now blocked by steric crowding in the nucleophile instead of in the substrate.

The reason for the formation of biphenyl from **3** as a side product when *tert*-butyl alcohol is used as the solvent (vide supra) is not clear. A tentative explanation is that phenyl group transfer occurs from the palladium(II) starting material to the palladium(IV) intermediate formed, and the latter reductively eliminates biphenyl in a subsequent reaction. The occurrence of this transfer may be due to the relatively long lifetime of the Pd(IV) intermediate; an intramolecular C–O coupling is apparently quite difficult and is only observed when the intermolecular pathway is blocked for steric reasons. A similar transfer of a methyl group has been observed in the case of platinum complexes, and it has been argued that transfer of an organic group from platinum(II) to platinum(IV) is a thermodynamically favorable process since an organic group stabilizes the high-oxidation-state Pt(IV) better than the Pt(II) state.[36] The fact that biphenyl is often formed in oxidizing media containing palladium(II),[37] whereas we have never observed any scrambling of aryl groups between palladium(II) complexes of the type used in the oxidation reactions, gives further support for the proposed explanation.

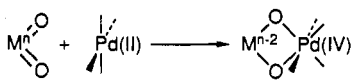


Figure 3. Possible formation of oxo-bridged intermediates by 2-electron transfer from Pd to an early transition metal oxo species.

The hypothesis of the intermediacy of a Pd(IV) compound is not only supported by the generation of carbocations from **15**, but also by the work of Stille et al., who noted that halogenation of alkylpalladium compounds in methanol gives rise to the formation of methoxy ethers as side products. From the stereochemistry of the latter it was concluded that these were formed via a nucleophilic attack of methanol at the palladated carbon atom of the presumed (alkyl)trichloropalladium(IV) complex that had been produced by oxidative addition of dichlorine to the alkylpalladium chloride.[16] Also, the direct conversion of methane into methyl chloride and methanol mediated by a $PtCl_4^{2-}/PtCl_6^{2-}$ mixture in aqueous solution studied by Shilov et al.[36] has been shown to proceed via a Pt(IV)–methyl complex. A nucleophilic substitution at the carbon atom by Cl^- or water was suggested as a possible mechanism to explain the formation of methyl chloride and methanol. Alkylpalladium compounds that cannot eliminate a stable carbocation, e.g. **18**, are likely to be alkoxylated in a similar way through such an S_N2 type attack on an alkyl–Pd(IV) intermediate. Intermediates related to the (early transition metal) di-μ-oxo-bridged palladium(IV) dinuclear species assumed to be formed by oxidative addition of the O–O bond to a Pd(II) compound may well be present in other, little understood, palladium-catalyzed acetoxylations of aromatic compounds with terminal oxidants such as $K_2Cr_2O_7$[38] or heteropolyacids.[39] For these nonperoxidic oxidants such oxo-bridged dimers may be formed by concomitant 2-electron reduction of the metal in the oxidant (Figure 3). Very recently, the structure of a stable Pd(IV) tellurato complex containing a bidentate Te(VI)-O_2 unit coordinated to palladium (analogous to the Pd(IV) molybdate intermediates proposed here) has been determined.[40] The proposed mechanism explains the different chemistry of vanadium *tert*-butyl peroxides. The bulky nature of the *tert*-butyl group inhibits a side-on oxidative addition to the O–O bond and forces the peroxide to approach the palladium complex in an end-on way, which results in oxygen insertion into the Pd–C bond of an arylpalladium compound.

Some comments should be made as to the mechanism of the O–O bond addition. Although this can be easily depicted as a side-on approach toward the Pd substrate, we feel that such a direct attack of the peroxide bond is unlikely. Molecular orbital calculations on $MoO(O_2)_2$ show that the LUMOs in this species (which should accept electrons from the palladium center in order for the O–O

(31) Bäckvall, J. E.; Nordberg, R. E. *J. Am. Chem. Soc.* **1980**, *102*, 393.
(32) Budnik, R. A.; Kochi, J. K. *J. Organomet. Chem.* **1976**, *116*, C3.
(33) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; p 145.
(34) Bunnet, J. F. *Acc. Chem. Res.* **1978**, *11*, 413.
(35) Streitwieser, A. *Solvolytic Displacement Reactions*; McGraw-Hill: New York, 1962; p 13.
(36) Kushch, L. A.; Lavrushko, V. V.; Misharin, Y. S.; Moravsky, A. P.; Shilov, A. E. *Nouv. J. Chim.* **1983**, *7*, 729. The reversed process, i.e. alkyl transfer from Pd(IV) to Pt(II) or from Pd(IV) to Pd(II), has recently been reported: (a) Aye, K.-T.; 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.; Janssen, M. D.; Spek, A. L.; Boersma, J.; van Koten, G. *Recl. Trav. Chim. Pays-Bas* **1991**, *110*, 477.
(37) Davison, S. F.; Maitlis, P. M. in *Organic Syntheses by Oxidation with Metal Compounds*; Mijs, W. J., de Jonge, C. R. H. I., Eds.; Plenum Press: New York, 1986; p 491 and references therein.
(38) (a) Henry, P. M. *J. Org. Chem.* **1971**, *36*, 1886. (b) Eberson, L.; Jonsson, L. *Acta Chem. Scand.* **1974**, *B28*, 771.
(39) Lyons, J. E. *Catal. Today* **1988**, *3*, 245.
(40) Levason, W.; Spicer, M. D.; Webster, M. *Inorg. Chem.* **1991**, *30*, 967.

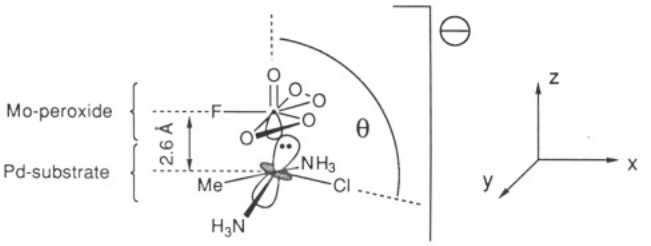


Figure 4. Stabilizing interaction between the d_{z^2} HOMO on the organopalladium substrate and a d_{z^2}/p_z hybrid LUMO on the molybdenum peroxide during attack trans to the oxo group on Mo according to extended Hückel calculations. The d_{xz} orbital on Pd mixes in second order into the d_{z^2} orbital.

bond to be broken during the oxidative addition) are strongly metal-centered.[41] In particular, these calculations show that nucleophiles can easily donate electron density either into an equatorial position or into an axial position. This is fully confirmed by the crystal structures of **1** and [$MoO(O_2)_2$.HMPT.py] (py = pyridine).[42] In **1**, the labile aqua ligand adopts the axial position. Therefore, it seems reasonable that an essential step in the oxidative addition is an electron donation from the palladium center into the LUMOs in the axial position on molybdenum. Qualitatively, a good overlap can be expected since the LUMOs on Mo are empty d_{z^2}, d_{xz}, and d_{yz} orbitals,[41] which find their filled counterpart in the HOMOs on Pd. In order to obtain more quantitative information about such an interaction, an extended Hückel calculation[43] was performed on an axial approach of *trans*-[Pd(Me)Cl(NH_3)$_2$] toward [$MoO(O_2)_2F$]$^-$ (where F^- has been substituted for HMPT). The interaction is slightly stabilizing, with a structure in which the ligands around Pd are bent away from the molybdenum center being some 0.4 eV more stable (at θ = 97°, optimized value) than the separate fragments (Mo peroxide and Pd substrate) (Figure 4).

The π-type interactions between the d_{xz} and d_{yz} orbitals on Pd and Mo are calculated to be very small. The major interaction is a σ-type charge transfer from the filled d_{z^2} HOMO on Pd to the empty d_{z^2} orbital on Mo (Mulliken population analysis shows a 0.32 increase of positive charge on Pd and a 0.30 decrease of charge on Mo). Several well-characterized examples of organoplatinum(II) compounds containing a heteronuclear metal–metal interaction between Pt and a metal electrophile are known.[44] In these square-pyramidal compounds the metal electrophile adopts the apical position, i.e. it probably attacks the d_{z^2} HOMO of the platinum complex.

Via a translation of the Pd center toward one of the peroxo ligands (tetrahedral transition state), the final oxidative addition can be easily envisioned. As described in this way, the palladium center behaves as a nucleophile toward molybdenum, and we feel this is reasonable for an oxidation reaction. However, the very first step may well

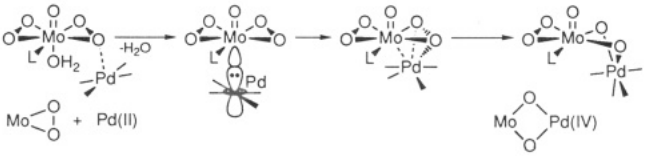


Figure 5. Mechanism for oxidative addition of **1** to an organopalladium complex based on attack of Pd trans to the oxo ligand in **1** and subsequent translation toward the O–O bond.

be a coordination of the peroxidic group to palladium, at that stage acting as an electrophile. Such a coordination is very likely to proceed perpendicular to the MoO_2 plane, leading to an η^1:η^2 coordination of the peroxo group as found in the crystal structure of [$RhCl(O_2)(PPh_3)_2$]$_2$[45] (only one peroxygen atom coordinates as the $\pi_g^*(\perp)$ HOMO on the peroxygens has a nodal plane between the two oxygen atoms).[46] This mode of approach brings the palladium atom in an ideal position for further movement toward molybdenum, and it is this movement (together with a subsequent oxidative addition) that is blocked by strongly coordinating ligands trans to the oxo ligand. The whole process of oxidative addition is depicted in Figure 5.

This mechanism explains why coordinatively saturated peroxides like [$MoO(O_2)_2$.bpy] or [$MoO(O_2)$(pydic).HMPT] are so much less reactive than **1**. For these compounds a direct side-on approach of the O–O bond would still be sterically possible. Since the structural and spectral features of the peroxidic O–O bonds in these compounds are very similar,[47-49a] it seems likely that the inhibition can be ascribed to a blocking of a Pd–Mo interaction rather than to an electronic difference between the peroxo groups in these peroxides. Moreover, quaternary ammonium chlorides retard the halogenation somewhat, although, as mentioned above, they strongly increase the yield. We believe that this retardation results from coordination of the chloride anion of the quaternary ammonium salt to the axial position, so that approach of the Pd nucleophile toward the Mo center is hindered. Such anionic molybdenum peroxo complexes are well-known.[49] Experimental evidence for the formation of an anionic molybdenum peroxide in the presence of a quaternary ammonium chloride is provided by the observation that the HMPT signal in the ^{1}H NMR spectrum of **1** (CD_2Cl_2) shifts to higher field by 0.18 ppm upon addition of 1 equiv of [Et_4N]Cl. As further support for an oxidative addition proceeding via a substrate–molybdenum interaction, it should be noted that such an interaction is now generally accepted for epoxidation reactions with **1**[41,50] and that in

(41) Jørgensen, K. A.; Hoffmann, R. *Acta Chem. Scand.* **1986**, *B40*, 411.

(42) Le Carpentier, J.-M; Schlupp, R.; Weiss, R. *Acta Crystallogr.* **1972**, *B28*, 1278.

(43) (a) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. (b) Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686.

(44) (a) van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K. *J. Organomet. Chem.* **1982**, *226*, 93. (b) van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K.; Spek, A. L.; Duisenberg, A. J. *Organometallics* **1982**, *1*, 1066. (c) Usón, R.; Forniés, J.; Tomás, M.; Casas, J.; Cotton, F. A.; Falvello, L. R. *J. Am. Chem. Soc.* **1985**, *107*, 2556. (d) Usón, R.; Forniés, J.; Tomás, M.; Ara, I.; Casas, J. M.; Martín, A. *J. Chem. Soc., Dalton Trans.* **1991**, 2253.

(45) Bennett, M. J.; Donaldson, P. B. *J. Am. Chem. Soc.* **1971**, *93*, 3307.

(46) Gubelmann, M. H.; Williams, A. F. *Struct. Bonding* **1983**, *55*, 1.

(47) The O–O bond length in peroxides does not depend on the nature of the metal and its ligands (Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; p 469).

(48) The crystal structures of **1** (ref 42) and [$MoO(O_2)_2$·bpy] (Schlemper, E. O.; Schrauzer, G. N.; Hughes, L. A. *Polyhedron* **1984**, *3*, 377) show that the bonding features of the oxo and peroxo oxygen atoms are similar in both compounds. In particular, both compounds have an O–O distance that does not differ significantly from the O–O bond distance found in the O_2^{2-} ion or hydrogen peroxide (ref 46, p 449, 457). Since the O–O bond lengths for both compounds (1.496(8) for **1**; 1.459(6) for [$MoO(O_2)_2$·bpy]) and ν(O–O) in the IR spectra (ref 55) (865 and 875 for **1**; 860 and 865 for [$MoO(O_2)_2$·bpy]) differ only slightly, it seems unlikely that a change of neutral ligands around Mo has a strong effect on the oxidation of organopalladium compounds.

(49) (a) Jacobson, S. E.; Tang, R.; Mares, F. *Inorg. Chem.* **1978**, *17*, 3055. (b) Djordjevic, C.; Covert, K. J.; Sinn, E. *Inorg. Chim. Acta* **1985**, *101*, L37.

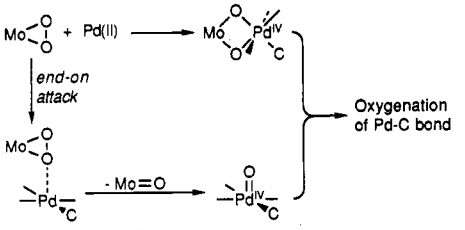


Figure 6. Two mechanisms for oxygenation of an organopalladium compound with molybdenum peroxide 1: (1) via a Pd(IV) oxo species formed by end-on attack of 1 on Pd; (2) via oxidative addition of the O–O bond.

these cases too peroxides with strongly complexing bidentate or tridentate ligands are unreactive.[50b]

Finally, it is worthwhile to compare oxygenations by vanadium *alkyl* peroxides with those by molybdenum peroxide 1 (i.e. that with 18 or the oxygenation observed in *tert*-butyl alcohol with 3). For the latter, these oxygen insertions may either result from a direct end-on electrophilic attack of the O–O bond on the palladium complex (as assumed for the V-catalyzed oxygenation)[7] or result from involvement of the same palladium(IV) intermediate as in the oxidatively induced nucleophilic substitutions (Figure 6).

We prefer the latter for several reasons. Firstly, the low reactivity of coordinatively saturated molybdenum peroxides, for which only an interaction with the molybdenum center (followed by oxidative addition) is blocked, but not a direct end-on attack on the peroxygens, suggests that the latter is an unimportant pathway. Secondly, there is an electronic difference between vanadium alkyl peroxides and molybdenum peroxides. The former have a peroxygen σ^* orbital among the LUMOs, which has the largest amplitude on the terminal oxygen atom of the ROO$^-$ fragment, making this oxygen electrophilic[50b,51] and susceptible to a nucleophilic attack by the d_{z^2} HOMO of palladium. Such an empty, low-lying σ^* acceptor orbital on the peroxygens is not available for the molybdenum peroxide, which, as mentioned before, has its LUMOs strongly concentrated on the metal.[41] Moreover, the O_2 unit in such peroxo species behaves with respect to its structural, spectroscopic, and chemical properties like a typical peroxide, i.e. a formally anionic O_2^{2-} ligand which exhibits *kinetically* a low electrophilicity (although it is thermodynamically a strong oxidant) and which typically reacts as a nucleophile;[46,52] very probably in a way as described above for the initial coordination to palladium. Therefore, a *direct* end-on electrophilic attack of the O–O bond on the palladium compound analogous to the vanadium-catalyzed oxygenation seems not very likely.[53] Thirdly, if one assumes that an oxidative addition proceeds in dichloromethane (halogenation) and primary alcohols (alkoxylation), then it seems unlikely that an oxidative addition would not occur in a *tert*-butyl alcohol/dichloromethane mixture—the solvent system in which oxygenation is found for 3. Finally, the reaction of organopalladium compounds with *m*-CPBA follows a mechanism that almost certainly proceeds via an end-on attack of the

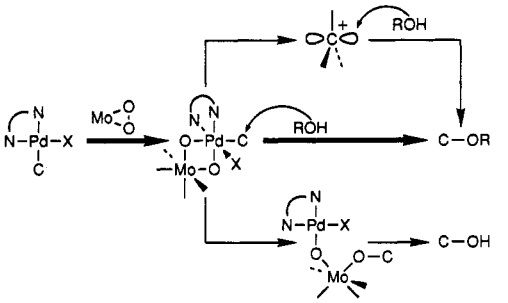


Figure 7. Proposed mechanisms for alkoxylation and oxygenation of organopalladium compounds with 1. Main pathway (bold arrows): oxidatively induced nucleophilic substitution. Upper pathway: elimination of carbocation (if relatively stable). Lower pathway: C–O coupling (oxygenation) by reductive elimination (if main route is inhibited for steric reasons).

O–O bond on the metal in a manner analogous to the vanadium-catalyzed oxygenation.[5,7] However, this results only for arylpalladium complexes in oxygen insertion; in the case of alkylpalladium compounds, products derived from reductive coupling are formed (vide supra).[23,24] Thus, the fact that oxygenation of the alkylpalladium compound 18 can be performed by 1 suggests that the oxygen insertion does not proceed via an end-on attack, but that it follows a different pathway. We feel that the preferential formation of an alcohol from 18 and phenol from 3 in *tert*-butyl alcohol is best explained by assuming that the Pd(IV) molybdate is a common intermediate in both the oxygenation and alkoxylation, and that oxygenation results from intramolecular C–O coupling[4] via reductive elimination to give a palladium(II) alkoxymolybdate complex. Intramolecular C–O coupling predominates when pathways leading to alkoxylation (or chlorination) are blocked for steric or electronic reasons (Figure 7).

Conclusion

The reaction of organopalladium compounds with the molybdenum peroxide 1 is a novel method to effect C–O and C–Cl coupling reactions in a selective way. Figure 7 summarizes our mechanistic rationale for the observed reactivity of 1. Evidence has been given that the molybdenum peroxide oxidatively adds to the organopalladium substrate to afford a Pd(IV) molybdate. This intermediate can react further via three distinct pathways: (i) via an oxidatively induced nucleophilic substitution of alkoxide or chloride on the palladated carbon atom (main pathway), (ii) via elimination of a carbocation and subsequent reaction with an alcoholic solvent (occurring when the carbocation is relatively stable as for 15), and (iii) via a reductive elimination to afford a molybdenum alkoxide

(50) (a) Mimoun, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 734. (b) Jørgensen, K. A. *Chem. Rev.* **1989**, *89*, 431.

(51) Bach, R. D.; Wolber, G. J.; Coddens, B. A.; *J. Am. Chem. Soc.* **1984**, *106*, 6098.

(52) The most simple example of this nucleophilic behavior is the protonation of the peroxo group by acids to give hydroperoxide, as used in this paper for an alternative preparation of [MoO(O$_2$)(pydic)·HMPT] (see Experimental Section).

(53) We believe that the electrophilic character of metal peroxo species is (for most substrates) only manifested when the electronic structure of the peroxo unit is strongly perturbed. This may be achieved (inter alia) by μ-η^2:η^2 coordination to two metal centers. Recent work of Karlin et al. supports this idea. These authors showed that a binuclear copper(II) peroxide with a bent "butterfly" μ-η^2:η^2-peroxo coordination (analogous to the tetrahedral transition state shown in Figure 5) has unusual electrophilic properties, whereas copper peroxides with terminal η^1-peroxo groups coordination have the usual basic or nucleophilic character. (a) Paul, P. P.; Tyeklár, Z.; Jacobson, R. R.; Karlin, K. D. *J. Am. Chem. Soc.* **1991**, *113*, 5322. (b) Sanyal, I.; Strange, R. W.; Blackburn, N. J.; Karlin, K. D. *J. Am. Chem. Soc.* **1991**, *113*, 4692. Due to such an μ-η^2:η^2 coordination the σ^*(O–O) orbital may be lowered in energy, thus allowing an oxidative addition process by 2-electron transfer from d_{xz} on Pd to σ^*(O–O) with concomitant cleavage of the O–O bond during a side-on approach of Pd toward the peroxo group (with the O–O bond along the *x*-axis).

(occurring when the oxidatively induced nucleophilic substitution is blocked by steric hindrance either in the nucleophile (*tert*-butyl alcohol as solvent) or in the organo unit attached to Pd (neopentyl derivative 18)). This pathway yields products derived from oxygenation.

Whereas this scheme will certainly oversimplify several mechanistic aspects of the reaction, it does provide some working hypotheses that explain the observed differences in reactivity.

Experimental Section

General. Oxidation reactions performed in alcoholic solvents were carried out in an atmosphere of nitrogen using standard Schlenk techniques. C_6H_6, Et_2O, and pentane were freshly distilled from sodium benzophenone ketyl. CH_2Cl_2 was distilled from calcium hydride. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 200 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer. Gas chromatography was done on either a Pye-Unicam apparatus (equipped with an UC WG 82 column and with a Carbowax 20M column), or on a Philips PU 4600 gas chromatograph (equipped with a CP-sil 5-CB capillary column). Elemental analyses were carried out by the Institute of Applied Chemistry (TNO), Zeist, The Netherlands. The GC–MS analyses were carried out at the Analytical Chemical Laboratory of the University of Utrecht. The following compounds were prepared according to literature procedures: 1,[54] $[MoO(O_2)_2.bpy]$,[55] bis(μ-chloro)bis(*exo*-6-methoxy-2-norbornene-*endo*-5σ,2π)dipalladium,[12] **6**,[56] **7**,[57] 2-hydroxy-1-[(*N*,*N*-dimethylamino)methyl]benzene,[58] 2-chloro-1-[(*N*,*N*-dimethylamino)-methyl]benzene,[59] 2-methoxy-1-[(*N*,*N*-dimethylamino)methyl]benzene,[60] *tert*-butoxybenzene,[61] 1-(benzyloxy)naphthalene,[62] 2-acetoxybenzyl bromide,[63] $Pd(dba)_2$.[64] Abbreviations: dt = doublet of triplets, td = triplet of doublets.

Synthesis of Pd Complexes via Oxidative Addition. Synthesis of [PdI(1-naphthyl)(tmeda)]. To a solution of $Pd(dba)_2$ (1.25 g, 2.17 mmol) in C_6H_6 (120 mL) was added a mixture of 1-iodonaphthalene (0.60 g, 2.36 mmol) and tmeda (0.27 g, 2.32 mmol) in C_6H_6 (5 mL) under a nitrogen atmosphere. The deep purple mixture turned yellow-brown upon slow heating to 80 °C. After a further 5 min of stirring at this temperature the turbid mixture was allowed to cool to room temperature. The green-yellow precipitate was filtered off and washed with 6 × 20 mL of Et_2O. The solid was taken up in CH_2Cl_2, and the solution was filtered over Celite to remove traces of metallic palladium. The filtrate was evaporated to dryness in vacuo, and the yellow residue was washed again with Et_2O (6 × 10 mL). Yield 0.99 g (96%); yellow, air-stable powder. Mp: 188 °C (dec >160 °C). Anal. Calcd: C, 40.31; H, 4.87; N, 5.89. Found: C, 39.91; H, 4.65; N, 5.53. ^1H NMR (200 MHz, $CDCl_3$): δ 8.90 (dd, 1 H, ^3J = 7.9 Hz, ^4J = 1.0 Hz, ArH(8)), 7.62 (dd, 1 H, ^3J = 7.9 Hz, ^4J = 1.0 Hz, ArH), 7.25–7.47 (m, 4 H, ArH), 7.11 (dd, 1 H, ^3J = 8.0, 7.1 Hz, ArH), 2.78, 2.76, 2.37, 1.87 (s, 3 H, NCH_3), 2.43–2.87 (m, 4 H, NCH_2-CH_2N). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 146.40, 139.59, 133.85 (quaternary Ar), 134.06, 132.70, 127.66, 124.48, 124.43, 123.63, 122.69 (Ar), 62.06, 58.32 (NCH_2), 51.33, 50.45, 48.96, 48.63 (NCH_3).

Synthesis of [PdI(Ph)(tmeda)]: from $Pd(dba)_2$ and iodobenzene in the presence of tmeda as described for [PdI(1-naphthyl)(tmeda)] with the following variations. Metallic Pd was removed by filtration over Celite after cooling the reaction mixture to room temperature, and the filtrate was evaporated to dryness to afford the product as an orange powder, which was washed extensively with Et_2O (in contrast to the naphthyl analogue, this complex is soluble in C_6H_6). Yield 78% of an orange powder. Analytical and spectroscopic data have been published before.[11]

Synthesis of [PdI(*p*-tolyl)(tmeda)]: via oxidative addition of 4-iodotoluene to $Pd(dba_2)$ as described for [PdI(Ph)(tmeda)]. Yield 88% as an orange powder. Mp: 195 °C (dec >174 °C). Anal. Calcd: C, 35.43; H, 5.27; N, 6.36. Found: C, 35.31; H, 5.33; N, 6.18. ^1H NMR (200 MHz, $CDCl_3$): δ 7.08, 6.75 (d, 2 H, ^3J = 7.8 Hz, ArH), 2.71, 2.55 (m, 2 H, NCH_2), 2.65, 2.32 (s, 6 H, $N(CH_3)_2$), 2.20 (s, 3 H, $ArCH_3$).

Synthesis of Organopalladium Nitrates. Synthesis of [Pd(ONO_2)(1-naphthyl)(tmeda)] (4). A mixture of [PdI(1-naphthyl)(tmeda)] (2.06 g, 4.32 mmol) and $AgNO_3$ (0.76 g, 4.47 mmol) in MeOH (250 mL) was stirred for 18 h in the dark. Silver iodide was filtered off, and the yellow filtrate was evaporated to dryness in vacuo. After having redissolved the solid residue in CH_2Cl_2, the solution was filtered over Celite. The filtrate was evaporated, and the pale yellow solid residue was washed with Et_2O (4 × 20 mL). Yield 1.76 g (99%). Mp: >136 °C dec. Anal. Calcd: C, 46.66; H, 5.64; N, 10.21. Found: C, 46.28; H, 5.53; N, 10.08. ^1H NMR (200 MHz, $CDCl_3$): δ 9.09 (dd, 1 H, ^3J = 7.9 Hz, ^4J = 1.0 Hz, ArH(8)), 7.63 (dd, 1 H, ^3J = 7.9 Hz, ^4J = 1.0 Hz, ArH), 7.29–7.49 (m, 4 H, ArH), 7.07 (dd, 1 H, ^3J = 8.0, 7.1 Hz, ArH), 2.70, 2.57, 2.52, 2.04 (s, 3 H, NCH_3), 2.30–2.82 (m, 4 H, NCH_2-CH_2N).

Synthesis of [Pd(ONO_2)(Ph)(tmeda)] (3): prepared almost quantitatively according to the same procedure used for **4**. Pale yellow powder (from [PdI(Ph)(tmeda)] and $AgNO_3$). Mp: 135 °C (dec >100 °C). IR (KBr): ν/cm^{-1} 1450, 1380, 1280 (NO_3). Anal. Calcd: C, 39.84; H, 5.86; N, 11.62. Found: C, 39.55; H, 5.70; N, 11.25. ^1H NMR (200 MHz, $CDCl_3$): δ 7.32 (m, 2 H, ^3J = 7.3 Hz, ArH(ortho)), 6.85–6.97 (m, 3 H, ArH), 2.70, 2.55 (m, 2 H, NCH_2), 2.58, 2.48 (s, 6 H, $N(CH_3)_2$).

Synthesis of Arylpalladium Chlorides from the Nitrates. Synthesis of [PdCl(1-naphthyl)(tmeda)] (5). A mixture of **4** (0.59 g, 1.43 mmol) and LiCl (0.62 g, 14.6 mmol) was stirred for 15 min in MeOH (125 mL). Removal of the solvent and extraction of the solid residue with CH_2Cl_2 afforded 0.53 g (96%) of **5** as a pale yellow powder after several washes with Et_2O. Mp: 210 °C dec. Anal. Calcd: C, 49.88; H, 6.03; N, 7.27. Found: C, 49.42; H, 5.94; N, 7.07. ^1H NMR (200 MHz, $CDCl_3$): δ 9.08 (dd, 1 H, ^3J = 7.9 Hz, ^4J = 1.0 Hz, ArH(8)), 7.64 (dd, 1 H, ^3J = 7.9 Hz, ^4J = 1.0 Hz, ArH), 7.30–7.49 (m, 4 H, ArH), 7.13 (dd, 1 H, ^3J = 8.0, 7.1 Hz, ArH), 2.75, 2.67, 2.52, 2.05 (s, 3 H, NCH_3), 2.49–2.92 (m, 4 H, NCH_2CH_2N).

Synthesis of [PdCl(p-tolyl)(tmeda)] (2): as for the naphthyl compound **5**, from [PdI(*p*-tolyl)(tmeda)] by conversion to the nitrate (not isolated) and subsequent addition of excess LiCl to the methanolic filtrate obtained after filtering off the precipitated AgI. Pale yellow powder, yield 95%. Mp: >180 °C dec. Anal. Calcd: C, 44.71; H, 6.65; N, 8.02. Found: C, 44.01; H, 6.60; N, 8.13. ^1H NMR (200 MHz, $CDCl_3$): δ 7.12, 6.77 (d, 2 H, ^3J = 7.8 Hz, ArH), 2.71, 2.55 (m, 2 H, NCH_2), 2.58, 2.42 (s, 6 H, $N(CH_3)_2$), 2.19 (s, 3 H, $ArCH_3$).

Synthesis of [PdCl(*exo*-3-methoxy-*endo*-5-tricyclo[2.2.1.0^{2,6}]-heptyl)(tmeda)] (15). To a solution of bis(μ-chloro)bis(*exo*-6-methoxy-2-norbornene-*endo*-5σ,2π)dipalladium (0.90 g, 3.40 mmol) in CH_2Cl_2 (100 mL) was added tmeda (0.47 g, 4.04 mmol). The solvent was removed in vacuo, and the solid residue was washed with Et_2O (5 × 20 mL). After drying, 1.24 g (96%) of a yellow powder was obtained. Mp: 145 °C (dec >110 °C). Anal. Calcd: C, 44.10; H, 7.15; N, 7.35. Found: C, 43.80; H, 7.05; N, 7.27. ^1H NMR (200 MHz, $CDCl_3$): δ 4.29 (t, 1 H, ^3J = 1.6 Hz, CHOMe), 3.31 (s, 3 H, OCH_3), 2.77 (m, 1 H, NCHH), 2.58, 2.54, 2.50, 2.47 (s, 3 H, NCH_3), 2.30–2.63 (m, 3 H, NCH*H*), 1.96 (bs,

(54) Vedejs, E.; Larsen, S. *Organic Syntheses*; Wiley: New York, 1990; Collect. Vol. VII, p 277.
(55) Mimoun, H. Seree de Roch, I.; Sajus, L. *Bull. Soc. Chim. Fr.* **1969**, 1481.
(56) Cope, A. C.; Friedrich, E. C. *J. Am. Chem. Soc.* **1968**, *90*, 909.
(57) Deeming, A. J.; Rothwell, I. P.; Hursthouse, M. B.; New, L. *J. Chem. Soc., Dalton Trans.* **1978**, 1490.
(58) Brugidou, J.; Christol, H. *Compt. Rend.* **1963**, *256*, 3149.
(59) Eliel, E. L.; Ferdinand, T. N.; Herrmann, M. C., Sr. *J. Org. Chem.* **1954**, *19*, 1693.
(60) Roveri, P.; Ferdenzi, A.; Salvadorini, S. *Boll. Chim. Farm.* **1975**, *114*, 710.
(61) Lawesson, S. O.; Yang, N. C. *J. Am. Chem. Soc.* **1959**, *81*, 4230.
(62) Maslak, P.; Guthrie, R. D. *J. Am. Chem. Soc.* **1986**, *108*, 2637.
(63) Ramage, R. *Tetrahedron* **1971**, *27*, 1499.
(64) Rettig, M. F.; Maitlis, P. M.; Cotton, F. A.; Webbs, T. R. *Inorg. Synth.* **1971**, 134.

1 H, CH), 1.65 (dt, 1 H, ^2J = 8.5 Hz, ^3J = 1.4 Hz, CH*H*), 1.25–1.37 (m, 3 H, CH), 1.13 (m, 2 H, CH).

Synthesis of [MoO(O$_2$)(pydic)·HMPT]. A solution of 2,6-pyridinedicarboxylic acid (4.48 g, 26.8 mmol) in hot MeOH (80 mL) was added to a solution of **1** (10.00 g, 26.8 mmol) in MeOH (150 mL) at 55 °C. An orange precipitate was formed. After 30 min the mixture was cooled to room temperature. The precipitate was filtered off, washed with MeOH (3 × 20 mL), and Et_2O (3 × 50 mL), and air-dried. Yield 9.87 g (75%). Spectroscopic data have been published before.[49a] Calcd O (active): 6.55. Found (*iodometric titration*) O (active): 6.54.

Synthesis of HOC$_6$H$_4${CH$_2$N(Me)CH$_2$CH$_2$NMe$_2$}-2. To a solution of *N,N,N'*-trimethyldiaminoethane (12.4 g, 0.12 mol) in C_6H_6 (125 mL) was added dropwise (1 h) 2-acetoxybenzyl bromide (22.5 g, 0.10 mol), dissolved in C_6H_6 (25 mL). The mixture was stirred for another hour, and the solvent was removed *in vacuo*. To the viscous residue was added a hot aqueous solution of NaOH (80 g/160 mL). The mixture was allowed to cool to room temperature overnight while being stirred and subsequently extracted with Et_2O (5 × 100 mL). After drying (NaOH pellets) and evaporation of the solvent, distillation (bp: 100–110 °C (0.03 mmHg)) afforded a yellow oil that slowly crystallized (14.1 g, 69%). Mp: 42 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 10.3 (bs, 1 H, OH), 7.15 (td, 1 H, ^3J = 7.9 Hz, ^4J = 1.7 Hz, ArH), 6.97 (dd, 1 H, ^3J = 7.3 Hz, ^4J = 1.7 Hz, ArH(ortho)), 6.83 (dd, 1 H, ^3J = 7.3 Hz, ^4J = 1.0 Hz, ArH(ortho)'), 6.74 (td, 1 H, ^3J = 7.3 Hz, ^4J = 1.0 Hz, ArH), 3.60 (s, 2 H, ArCH$_2$N), 2.53 (m, 4 H, NCH$_2$-CH$_2$N), 2.25 (s, 9 H, NCH$_3$).

Independent Synthesis of [PdCl(OC$_6$H$_4${CH$_2$N(Me)CH$_2$-CH$_2$NMe$_2$}-2)] (12). A mixture of Pd(OAc)$_2$ (0.61 g, 2.72 mmol) and the phenol HOC$_6$H$_4${CH$_2$N(Me)CH$_2$CH$_2$NMe$_2$}-2 (0.58 g, 2.78 mmol) in MeOH (100 mL) was heated on a water bath (50 °C) until a clear yellow solution was obtained (1 h). To this solution was added LiCl (0.32 g; 7.55 mmol), dissolved in a minimum of MeOH. After cooling to room temperature, the orange-brown precipitate was filtered off and washed with MeOH (3 × 20 mL), Et_2O (3 × 20 mL), and pentane (3 × 20 mL). The product (0.87 g, 92%) was air-dried. The compound is almost insoluble in common organic solvents. Therefore, only selected ^{1}H NMR data are given. Anal. Calcd: C, 41.27; H, 5.50; N, 8.02. Found: C, 40.84; H, 5.45; N, 8.07. ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.82, 3.11 (d, 1 H, ^2J = 12.6 Hz, ArCH*H*N), 2.90, 2.75, 2.51 (b) (s, 3 H, NCH$_3$).

Chlorination of 13 with 1 and [TEBA]Cl. To a solution of **13** (0.30 g, 0.80 mmol) and [TEBA]Cl (0.58 g, 2.54 mmol) in CH_2Cl_2 (25 mL) was added a solution of **1** (0.74 g, 1.98 mmol) in CH_2Cl_2 (25 mL). The mixture was stirred for 22 h, during which a yellow-orange solution containing a white precipitate was formed. The solution was filtered, and the precipitate was washed with CH_2Cl_2. The combined filtrates were washed with water (3 × 50 mL) and dried over $MgSO_4$. Evaporation of the solvent in vacuo gave an orange powder, which was washed with MeOH (5 × 7.5 mL) and Et_2O (5 × 7.5 mL). After drying 0.25 g of **14** (70%) was obtained as an orange powder. Mp: 175 °C dec. Anal. Calcd: C, 40.38; H, 5.66; N, 6.28; Cl, 23.84. Found: C, 39.86; H, 5.60; N, 6.23; Cl, 22.93. ^{1}H NMR (200 MHz, $CDCl_3$, 60 °C): δ 7.25, 7.10 (s, 1 H, ArH), 5.42 (vb, 1 H, ArCH*H*Cl), 5.22 (d, 1 H, ^2J = 12.5 Hz, ArCH*H*Cl), 4.77, 4.22 (d, 1 H, ^2J = 14.2 Hz, ArCH*H*N), 3.08, 2.77, 2.74 (b), 2.55, 2.34 (s, 3 H, NCH$_3$ and ArCH$_3$), 2.23–2.95 (m, 4 H, NCH$_2$CH$_2$N).

Using the same method, **10** was prepared as a yellow-orange solid in 95% yield starting from **8**. The ^{1}H NMR spectrum of the material obtained in this way was identical to that of the coordination adduct prepared via the independent route described before.[14] Demetalation for GC–MS analysis was performed by reducing the product with hydrazine hydrate in CH_2Cl_2. GC–MS: *m/z* (relative intensity) 226/228 (M$^{\bullet+}$, 3/1), 168/170 (M$^{\bullet+}$ –CH$_2$NMe$_2$, 100/32), 125/127 (M$^{\bullet+}$ – CH$_2$NMe$_2$ – MeN=CH$_2$, 95/31), 58 (Me$_2$NCH$_2^+$, 69), 42 (C$_2$H$_4$N$^+$, 10).

Alkoxylation of 9 with 1 in MeOH. To a suspension of **9** (0.31 g, 0.86 mmol) in MeOH (7.5 mL) was added 1.30 mL of a 40% (by weight) solution of [PhCH$_2$NMe$_3$]OMe in MeOH. This resulted in the formation of a clear yellow solution, which rapidly turned into a white suspension.[65] To this suspension was added dropwise (3 min) a solution of **1** (0.80 g, 2.14 mmol) in MeOH (7.5 mL). A red-brown, slightly turbid solution was formed, which slowly turned orange with concomitant precipitation of a yellow powder (within 15 min). After stirring for 2 h, an excess of LiCl was added (0.60 g, 14 mmol). The mixture was evaporated on a rotary evaporator, and the remaining syrupy solid was extracted with CH_2Cl_2 (150 mL). After filtering off the insoluble residue, the orange filtrate was washed with water (3 × 50 mL) and dried ($MgSO_4$). The solvent was removed in vacuo, and the remaining orange residue was washed with Et_2O (5 × 20 mL). Yield 0.28 g (81%) of **11**, contaminated with a small amount (<5%) of **12**. Demetalation for GC–MS analysis was performed by reducing the product with hydrazine hydrate in CH_2Cl_2. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.55 (dd, 1 H, ^3J = 7.5 Hz, ^4J = 1.6 Hz, ArH(ortho)), 7.43 (td, 1 H, ^3J = 7.5 Hz, ^4J = 1.6 Hz, ArH), 7.18 (td, 1 H, ^3J = 7.5 Hz, ^4J = 1.0 Hz, ArH), 6.95 (dd, 1 H, ^3J = 7.5 Hz, ^4J = 1.0 Hz, ArH(ortho)'), 4.59, 3.85 (d, 1 H, ^2J = 12.8 Hz, ArCH*H*N), 3.85 (s, 3 H, ArOCH$_3$), 3.00, 2.73, 2.36 (s, 3 H, NCH$_3$), 2.63–2.95, 2.36 (m, 2 H, NCH*H*). GC–MS [relative retention time], *m/z* (relative intensity). Phenol derivative from **12**: [10], 208 (M$^{\bullet+}$, 2), 150 (M$^{\bullet+}$ – CH$_2$NMe$_2$, 33), 107 (M$^{\bullet+}$ – CH$_2$NMe$_2$ – MeN=CH$_2$, 37), 78 (C$_6$H$_6^{\bullet+}$, 13); 58 (Me$_2$NCH$_2^+$, 100), 44 (C$_2$H$_6$N$^+$, 94). Methoxy ether derived from **11**: [10.6], 222 (M$^{\bullet+}$, 1), 164 (M$^{\bullet+}$ – CH$_2$NMe$_2$, 36), 121 (M$^{\bullet+}$ – CH$_2$NMe$_2$ – MeN=CH$_2$, 100), 91 (C$_7$H$_7^+$, 45), 58 (Me$_2$NCH$_2^+$, 39).

Oxidation of 15 with 1 in MeOH. To a solution of **15** (1.06 g, 2.78 mmol) in MeOH (12.5 mL) was added a solution of **1** (1.24 g, 3.32 mmol) in MeOH (7.5 mL). A slightly exothermic reaction occurred instantaneously and an orange-yellow powder precipitated. After 30 min of stirring at room temperature, hydrazine hydrate (0.5 mL) was added, which resulted in the slow formation of metallic Pd. After 1 h, Pd^0 was filtered off over Celite, and the filtrate was evaporated in vacuo (at room temperature). The remaining oil was dissolved in pentane (125 mL). The organic phase was washed with water (5 × 25 mL) and subsequently dried over $MgSO_4$. Removal of the solvent at a rotary evaporator (without heating) gave 0.20 g of a colorless oil. This oil was shown to consist mainly (>90%) of the *exo,exo* (**16a**) and *exo,endo*-dimethoxy ethers (**16b**) in a ratio **16a**:**16b** = 1.15 by comparison of the ^{1}H NMR spectrum with known literature data.[29a] A third product (<10%) was shown to be the exo,endo chlorinated compound **16c**.[66] The assignments based on the ^{1}H NMR spectra were further confirmed by a GC–MS analysis of the oil, GC–MS [retention time], *m/z* (relative intensity). *exo,endo*-Dimethoxy ether **16b**: [10], 154 (M$^{\bullet+}$, 0.8), 153 (M$^{\bullet+}$ – 1, 0.7), 139 (M$^{\bullet+}$ – CH$_3$, 0.9), 122 (M$^{\bullet+}$ – CH$_3$OH, 13), 109 (7), 107 (8), 91 (18), 75 (MeOC(H)OMe$^+$, 100), 45 (13). *exo,exo*-Dimethoxy ether **16a**: [10.4], 154 (M$^{\bullet+}$, 1.3), 153 (M$^{\bullet+}$ – 1, 1.6), 139 (M$^{\bullet+}$ – CH$_3$, 1.9), 122 (M$^{\bullet+}$ – CH$_3$OH, 20), 109 (13), 107 (11), 91 (26), 75 (MeOC(HO)OMe$^+$, 100), 45 (13). Note that the ratio of (M$^{\bullet+}$)/(M$^{\bullet+}$ – 1) is reversed for the exo,exo and exo,endo isomers. Chlorinated compound **16c**: [10.7], 160/158 (M$^{\bullet+}$, 1.3/0.4), 123 (M$^{\bullet+}$ – Cl, 100), 91 (49), 79 (19), 65 (9), 45 (14). The GC–MS analysis also revealed the presence of a trace amount of a not further identified compound with molecular weight *m/z* 126 which probably contains a methoxy group: [5], 126 (M$^{\bullet+}$, 3), 111 (M$^{\bullet+}$ – CH$_3$, 6), 94 (M$^{\bullet+}$ – CH$_3$OH, 100), 79 (56), 66 (61), 58 (19), 41 (20).

One-Pot Oxidation of 17. A mixture of Pd(OAc)$_2$ (2.23 g; 10 mmol) and ligand **17** (2.21 g, 10 mmol) in MeOH (150 mL) was stirred under a nitrogen atmosphere until an almost clear yellow solution was obtained. The solution was heated for 24 h at 60 °C (bath temperature). After cooling to room temperature, a 40% (by weight) solution of [PhCH$_2$NMe$_3$]OMe in MeOH (5.0 mL, 1 equiv) was added to the yellow solution, which contained a very small amount of metallic Pd. The mixture was cooled to −78 °C, and a solution of **1** (7.5 g, 20 mmol) in MeOH (50 mL)

(65) The white precipitate was shown to be **8** by ^{1}H NMR spectroscopy; its formation is probably a result of small amounts of chloride in commercially available [TMBA]OMe.

(66) Coulson, D. R. *J. Am. Chem. Soc.* **1969**, *91*, 200.

was added in one portion. The mixture was allowed to warm to room temperature (circa 1.5 h); at −45 °C a yellow precipitate was formed. After 2 h $H_2NNH_2·H_2O$ (1 mL) was added, which resulted in the formation of a gray suspension, followed by the addition of $H_2NCH_2CH_2NH_2$ (10 mL) to decoordinate the oxidation products from the metals. The mixture was stirred overnight. The precipitate was filtered off, and the solvents were removed from the filtrate in vacuo. The brown oily residue was dissolved in Et_2O (200 mL), and the organic layer was washed with water (1 × 50 mL, 3 × 20 mL). After drying (NaOH pellets), evaporation of the solvent afforded 1.70 g of a viscous colourless oil. This oil consisted according to its ^1H NMR spectrum of a 6:1 mixture of the alcohol **19a** and methoxy ether **19b**, respectively, together with a small amount (<10%) of an aromatic impurity stemming from the quaternary ammonium methoxide. A purified mixture (1.51 g, 63%) of **19a** and **19b** was obtained by collecting the fraction of 150–220 °C (0.5 mmHg) of a microdistillation, by which the volatile impurity was removed. Preparative separation of the two compounds proved very difficult. A small amount of the main product **19a** could be obtained pure by column chromatography over neutral alumina (eluens: C_6H_6/MeOH, 95/5 v/v). The ^1H NMR data for **19b** are selected data obtained from the mixture of both products. Alcohol **19a**: ^1H NMR (200 MHz, $CDCl_3$): δ 7.7 (vb, 1 H, OH), 3.28, 3.23 (d, 1 H, ^2J = 10.1 Hz, C*H*$_2$OH), 3.02, 2.09 (dd, 1 H, ^2J = 8.8 Hz, ^4J = 1.9 Hz, C(quaternary)-CH*H*N), 3.00 (m, 1 H, C_2CHN), 2.76, 2.62 (m, 1 H, NCH*H* of NCH_2CH_2N unit), 2.36 (m, 2 H, NCH*H* or NCH_2-CH_2N unit), 2.20 (s, 6 H, $N(CH_3)_2$), 1.97 (dm, 1 H, ^2J = 13.8 Hz, C_2CHH), 1.77 (dd, 1 H, ^2J = 14.4 Hz, ^4J = 2.0 Hz, C_2CHH), 1.58 (ddt, 1 H, ^2J = 10.9 Hz, ^3J = 6.5 Hz, ^4J = 2.1 Hz, C(NCH)CH*H*), 1.42 (dd, 1 H, ^2J = 14.3 Hz, ^4J = 1.9 Hz, C_2CHH), 1.37 (dd, 1 H, ^2J = 13.9 Hz, ^4J = 2.0 Hz, C_2CHH), 1.13 (dd, 1 H, ^2J = 10.9 Hz, ^4J = 1.5 Hz, C_2CHH), 1.01, 0.87 (s, 3 H, CCH_3). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 76.05 (CH_2OH), 66.91, 61.15, 58.32, 55.25 (NCH_2, NCH), 49.44, 45.12, 41.67 (C_2CH_2), 45.78 (NCH_3), 40.30, 34.64 (quaternary C), 32.35, 25.18 (CCH_3). Methoxy ether **19b**: ^1H NMR (200 MHz, $CDCl_3$): δ 3.53, 3.32 (d, 1 H, ^2J = 8.6 Hz, CH_2OMe), 3.31 (s, 3 H, OCH_3), 2.22 (s, 6 H, $N(CH_3)_2$), 0.98, 0.89 (s, 3 H, CCH_3). GC–MS [relative retention time], *m/z* (relative intensity). Methoxy ether **19b**: [10], 254 ($M^{•+}$, 1), 196 ($M^{•+}$ − CH_2NMe_2, 100), 72 ($C_4H_{10}N^+$, 7), 58 ($Me_2NCH_2^+$, 9), 44 ($C_2H_6N^+$, 6). Alcohol **19a**: [12], 240 ($M^{•+}$, 1), 182 ($M^{•+}$ − CH_2NMe_2, 100), 152 ($M^{•+}$ − CH_2NMe_2 − CH_2O, 22); 72 ($C_4H_{10}N^+$, 6), 58 ($Me_2NCH_2^+$, 12), 44 ($C_2H_6N^+$, 15).

Reaction of 2, 6, and 7 with 1 in CH_2Cl_2. Reactions were carried out as described for **13** in the presence of an internal standard (for **2**, *p*-xylene; for **6** and **7**, mesitylene). Amounts of [TEBA]Cl and **1** relative to the Pd substrate are given in Table I. The crude reaction mixture of the halogenation of **2** was analyzed with GC without further treatment. For **6** and **7**, reduction with $H_2NNH_2·H_2O$ was carried out before GC analysis. Products were identified by GC–MS and by comparison of retention times with those of independently prepared or commercially available substances. Yields were determined by using measured relative response factors of products vs internal standard. Alternatively, the yield was determined from the increase of the integral upon addition of a known amount of an authentic sample. Both independent methods gave similar yields (discrepancy between the two methods ± 5%). The following columns were used for GC analysis: reaction of **2**, UC WG 82; reaction of **6** and **7**, Carbowax 20M. MS data are given below.

Reaction of 3–5 and 7 with 1 in Alcoholic Solvents. Reactions were carried out in as described for **15** and **9** (when [TMBA]OMe was added) in the presence of an internal standard (for **3** in MeOH, naphthalene; for **3** in *t*-BuOH, 1,3,5-trichlorobenzene; for **4** in MeOH or EtOH, biphenyl; for **4** in BnOH, anthracene (added after the reaction in a small amount of CH_2Cl_2); for **5**, 1-chloronaphthalene (added after the reaction; could be used since only a trace amount of 1-chloronaphthalene is formed in the reaction); for **7**, 1,3,5-trichlorobenzene). Amounts of [TMBA]OMe and **1** relative to the Pd substrate are given in Table II. The crude reaction mixtures were analyzed with GC without further treatment. For **7**, reduction with $H_2NNH_2·H_2O$ was carried out before GC analysis. Columns used for GC analysis: reaction of **3**, **4**, and **7** in MeOH or EtOH, UC WG 82; reaction of **5**, Carbowax 20M; reaction of **4** in BnOH, CP-sil 5-CB (capillary column). Further details can be found in the description of the reaction of **2**, **6**, and **7** with **1** in CH_2Cl_2. MS data are summarized below.

GC–MS *m/z* (relative intensity). Anisole: 108 ($M^{•+}$, 85), 93 ($M^{•+}$ − CH_3, 16), 78 ($M^{•+}$ − CH_2O, 74), 65 ($C_5H_5^+$, 100), 51 (26), 39 (42). 1-Methoxynaphthalene: 158 ($M^{•+}$, 75), 143 ($M^{•+}$ − CH_3, 32), 115 ($C_9H_7^+$, 100). 1-Ethoxynaphthalene: 172 ($M^{•+}$, 77), 144 ($M^{•+}$ − C_2H_4, 100), 115 ($C_9H_7^+$, 50). 1-(Benzyloxy)naphthalene: 234 ($M^{•+}$, 34); 91 ($C_7H_7^+$, 100). Phenol: 94 ($M^{•+}$, 100), 66 ($M^{•+}$ − CO, 15). *tert*-Butoxybenzene: 150 ($M^{•+}$, 2), 94 ($M^{•+}$ − $Me_2C{=}CH_2$, 100). 2-Methoxy-1-[(*N*,*N*-dimethylamino)methyl]benzene: 165 ($M^{•+}$, 86), 150 ($M^{•+}$ − CH_3, 22), 134 ($M^{•+}$ − OCH_3, 10), 121 ($M^{•+}$ − NMe_2, 81), 91 ($C_9H_7^+$, 100), 77 ($C_6H_5^+$, 10), 65 ($C_5H_5^+$, 12), 58 ($Me_2NCH_2^+$, 82), 42 ($C_2H_4N^+$, 12). 2-Chloro-1-[(*N*,*N*-dimethylamino)methyl]benzene: 169/171 ($M^{•+}$, 37/11), 125/127 ($M^{•+}$ − NMe_2, 35/13), 58 ($Me_2NCH_2^+$, 100), 42 ($C_2H_4N^+$, 13). 2-Hydroxy-1-[(*N*,*N*-dimethylamino)methyl]benzene: 151 ($M^{•+}$, 100), 107 ($M^{•+}$ − NMe_2, 40), 77 ($C_6H_5^+$, 18), 58 ($Me_2NCH_2^+$, 40), 44 (NMe_2^+, 68).

Isolation of Palladium Molybdate in the Reaction of 5 with 1 in MeOH. The orange powder formed on addition of **1** (0.22 g, 0.59 mmol) to a solution of **5** (0.22 g, 0.57 mmol) in MeOH (5 mL) was isolated by filtration and washed with MeOH (5 × 2 mL) and pentane (5 × 4 mL). The product was dried in vacuo. Yield 0.25 g of an orange-brown powder. The product analyzed as [PdCl{$OMo(O)_2(OH)$}(tmeda)·MeOH] (Yield: 97%). Anal. Calcd for $C_7H_{21}ClMoN_2O_5Pd$: C, 18.64; H, 4.70; N, 6.21; Cl, 7.86. Found: C, 18.36; H, 4.04; N, 5.84; Cl, 7.32. IR (KBr): ν/cm^{-1} 900 (broad, strong (Mo=O)), 320 (Pd–Cl). Bands around 2900 cm^{-1} (weak) and at 1470 cm^{-1} (strong) point to the presence of Pd-coordinated tmeda. Signals of HMPT were absent in the IR spectrum.

Extended Hückel Calculations. Parameters of C,[43a] H,[43a] Cl,[67] Mo,[41] N,[43a] O,[43a] and Pd[69] were taken from earlier work. A weighted H_{ij} approximation was used.[43b] Geometrical assumptions included the following (see also Figure 4): C–H = 1.06 Å; N–H = 1.03 Å; Mo=O = 1.66 Å; Mo–O = 1.94 Å; Mo–F = 2.00 Å; Mo–Pd = 2.60 Å; Pd–C = 2.03 Å; Pd–N = 2.10 Å; Pd–Cl = 2.38 Å; methyl group tetrahedral; Pd–N–H = 115°, O–Mo–O (within a peroxo unit) = 45°. The position of the CH_3 and NH_3 ligands was such that one of the hydrogen atoms had coordinates defined by a dihedral angle Mo–Pd–X–H = 180° (X = C or N).

Acknowledgment. We thank the Innovation Oriented Research Program on Catalysis for financial support (to P.L.A.). Dr. A. Dedieu (Université Louis Pasteur, Strasbourg) is thanked for his interest and computational support. Thanks are due to Dr. J. T. B. H. Jastrzebski for organizing the manuscript.

OM9205298

(67) Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 7240.
(68) Anderson, A. B.; Hoffmann, R. *J. Chem. Phys.* **1974**, *60*, 4271.
(69) Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857.