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DIRECT ALKOXYLATION OF ORGANOPALLADIUM COMPOUNDS BASED ON A NEW TYPE OF C-O COUPLING MEDIATED BY MOLYBDENUM PEROXIDES.

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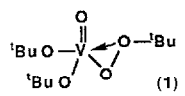
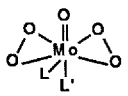
Molybdenum peroxide (2) reacts with organopalladium compounds in alcoholic solvents to form alkoxylated products instead of products derived from oxygen insertion in the C-Pd bond

The search for new methods for the selective oxygenation of organic compounds is an important topic in today's chemistry[1]. In principle, the oxidation of cyclopalladated complexes offers a route for the very selective oxy-functionalisation of a C-H bond. Surprisingly, although cyclopalladated compounds have found widespread application in organic synthesis[2], their behaviour towards oxygenating agents has been investigated only to a very small extent. Chakravorty *et al.* have shown that cyclopalladated azobenzene derivatives can be converted smoothly into their corresponding phenolates by reaction with *meta*-chloroperoxybenzoic acid[3]. Recently, we reported that cyclopalladated *N,N*-dimethyl benzylamines can be oxygenated in the *ortho*-position by *tert.*-butylhydroperoxide (TBHP) and a vanadium catalyst (*e g.* $VO(acac)_2$ or $VO(OBu^t)_3$)[4]. As in epoxidation reactions by this system, the catalytically active oxygenating species is very likely a V(V)-oxo-*tert.*-butylperoxide (**1**)

During further research on reactions of inorganic peroxo species with organopalladium complexes, we found that molybdenumperoxide (**2**) displays a strikingly different reactivity.

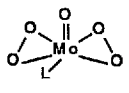


(1)



L = HMPT

(2) L' = H_2O,
(3). L' = py;



L = HMPT

(4)

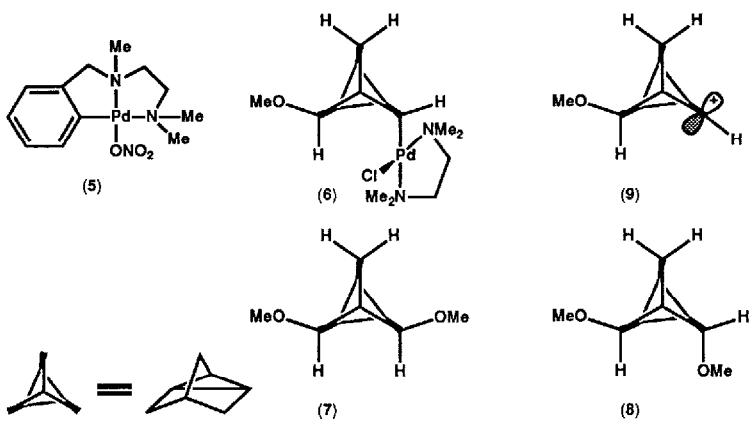
Whereas the closely related peroxides (**3**) and (**4**) are good reagents for effecting oxygen insertion in the C-M bond of organometallic compounds of some main group metals[5], the expected oxygen insertion was only of minor importance in reactions of (**2**) with organopalladium complexes. Instead, when organopalladium compounds were allowed to react with (**2**) in alcoholic solvents, good yields of alkoxylated products were obtained. This reaction is very general (table). The presence of quaternary ammonium alkoxides did not improve the yield of the reaction, except for complex (**5**), which produced a substantial amount of the hydrolyzed ligand in the absence of benzyltrimethyl ammonium methoxide. Other oxidants, like $Na_2Cr_2O_7$ or CAN (Ce(IV) ammonium nitrate) produced only naphthalene in their reaction with [Pd(ONO_2)(1-naphthyl)(tmeda)] in methanol; no 1-methoxynaphthalene could be detected by gas chromatography. Therefore, it seems likely that a peroxidic function is necessary to effect the alkoxylation.

Table. Products of the alkoxylation of organopalladium compunds by reaction with (**2**).

	Substrate[a]	Solvent	Products	Yield
1.	[Pd(ONO_2)(phenyl)(tmeda)]	MeOH[b]	anisole	55 %[c]
2.	[Pd(ONO_2)(1-naphthyl)(tmeda)]	MeOH	1-methoxynaphthalene	66 %[c]
3.	[PdCl(1-naphthyl)(tmeda)]	MeOH	1-methoxynaphthalene	56 %[c]
4.	[Pd(ONO_2)(1-naphthyl)(tmeda)]	EtOH	1-ethoxynaphthalene	82 %[c]
5.	[PdCl(C-N)(py)][d]	MeOH	(C-N)OMe	57 %[c]
			(C-N)Cl	4 %[c]
6.	[Pd(ONO_2)(C-N-N)][e] (**5**)	MeOH[b]	(C-N-N)OMe[f]	74 %
			(C-N-N)OH[g]	7 %

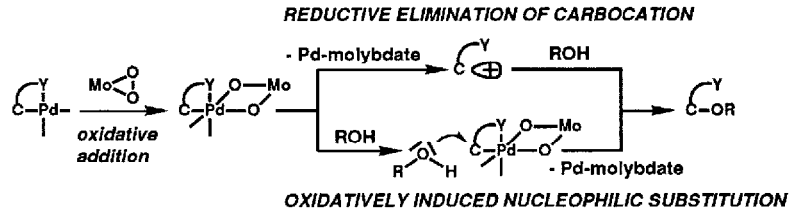
[a] All compounds were identified by their spectroscopic and analytical data. [b] Reaction performed in the presence of [$PhCH_2NMe_3$]OMe. [c] Yield determined by gaschromatography. [d] (C-N) = (2-$C_6H_4CH_2NMe_2$). [e] (C-N-N) = {2-$C_6H_4CH_2N(Me)CH_2CH_2NMe_2$}. [f] Compound isolated in the form of its $PdCl_2$ coordination adduct. [g] Compound isolated in the form of its PdCl phenolate complex.

From the stereochemistry of the reaction of (**2**) with the alkylpalladium compound (**6**) some insight in the mechanism can be obtained. After work-up, the *exo, exo-* (**7**) and *exo, endo-* (**8**) dimethoxy ethers were obtained in a 1.15 : 1 ratio.



Thus, both a mechanism based on reductive elimination of an intermediate palladium alkoxide[6], which should proceed with retention of configuration at the palladated carbon atom[7], and a mechanism based on oxidatively induced nucleophilic substitution, for which inversion of configuration is expected[7,8], seem to be not involved. We propose that the O-O bond of (**2**) 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 (scheme). Support for this mechanism comes from the observation that

carbocation (**9**), when generated electrochemically from norbornadiene, reacts in methanolic solution to a mixture of (**7**) and (**8**) in the same ratio as found in our reaction[9†].



Scheme.

The presence of a carbocationic intermediate in the oxidative cleavage of a β-phenethyl palladium compound with copper(II)chloride has been deduced from deuterium labeling studies[10]. Scrambling of stereochemistry to a 1:1 mixture of *exo, endo-* and *exo, exo*-compounds is also observed when a tricycloheptyl palladium complex that is closely related to (**6**) is treated with copper(II)bromide as the oxidant[11]. Thus formation of carbocations in the oxidative cleavage of organopalladium compounds may be more general than previously thought. Since carbocations derived from tricycloheptane are rather special in that they are strongly stabilized by the cyclopropane unit, the proposed mechanism based on carbocation intermediates not necessarily holds for arylpalladium species too as aryl cations are much less stable than tricycloheptyl cations. We believe that arylpalladium compounds more likely react *via* an oxidatively induced nucleophilic substitution in which the palladium centre is turned into a very good leaving group (*i.e.* a very strong two electron oxidant) by the oxidative addition of the molybdenum peroxide (scheme). Although a radical mechanism can be ruled out as aryl radicals are known to be unreactive towards alkoxide nucleophiles[12], a carbocation mechanism nevertheless cannot be excluded based on the information now available.

The proposed mechanism not only explains the necessity of a peroxidic functionality in the oxidant and the observed stereochemistry in the reaction with (**6**), but also explains the different chemistry of vanadium alkylperoxide (**1**). A side-on approach of the O-O bond, leading to oxidative addition, is in this case very unlikely in view of the bulky nature of the *tert*-butyl group. As suggested earlier[4], oxygen insertion in the C-Pd bond requires an end-on attack of the peroxide.

Finally, it should be noted that not only alkoxide nucleophiles, but also halide anions can be coupled to the palladated carbon atom in a very selective way by reaction of organopalladium compounds with (**2**) in the presence of quaternary ammonium halides. Full details about this novel type of reaction will be published shortly.

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

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