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The Oxygenation of Cyclopalladated *N,N*-dimethylbenzylamine Derivatives with *Tert*-butyl Hydroperoxide

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Abstract. Cyclopalladated *N,N*-dimethylbenzylamine complexes can be oxygenated with *tert*-butyl hydroperoxide to the corresponding phenolates in good yield (> 80 %); the rate of oxygenation is highly enhanced by increasing the nucleophilicity of the metal center or by addition of a vanadium catalyst.

Recently, Chakravorty *et al.* showed that *m*-chloroperoxybenzoic acid (mCPBA) is a very effective reagent for the insertion of an oxygen atom into the aryl-palladium bond of cyclopalladated azobenzene derivatives[1]. Contrary to the statement of these authors that other, less reactive peroxidic species like hydrogen peroxide or *tert*-butyl hydroperoxide (TBHP)# are not appropriate to effect this transformation[1b], we discovered that the latter reagent can be used for the oxygenation of cyclopalladated *N,N*-dimethylbenzylamine complexes provided that the metal is surrounded by suitable ligands. Moreover, we found that aryl palladium compounds which do not react with TBHP alone can be oxidized smoothly to the corresponding phenolates in the presence of an early transition metal catalyst.

We have investigated the reaction of the cationic palladium compound $[\{Pd(C_6H_4CH_2NMe_2\text{-}2)(MeCN)_2\}BF_4]$ (**1**) with TBHP since it was suggested by Chakravorty *et al.* that oxidation with mCPBA can be promoted by increasing the electrophilicity of the palladium centre to strengthen coordination of the peroxidic oxygen atom with the metal[1c]. Despite the high electrophilicity of the metal centre this species is almost inert towards TBHP. Consequently, we assume that coordination *via* the lone pairs on the peroxide with the metal is only of minor importance in the transition state. Noteworthy is that the diaryl compound *cis*-$[Pd(C_6H_4CH_2NMe_2\text{-}2)_2]$ (**2**) is converted very rapidly (within several minutes) upon reaction with TBHP in dichloromethane as solvent into the *mono*-oxygenated compound *trans*-$[Pd(C_6H_4CH_2NMe_2\text{-}2)(OC_6H_4CH_2NMe_2\text{-}2)]$ (**3**)[3]. Further oxidation to the double phenolate *trans*-$[Pd(OC_6H_4CH_2NMe_2\text{-}2)_2]$ (**4**) does not occur. However, in the presence of $VO(acac)_2$ as catalyst, (**4**) can be obtained in almost quantitative yield by oxygenation of (**3**) with TBHP. 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 $[Pd(OC_6H_4CH_2NMe_2\text{-}2)Cl]_2$ (**6**) by addition of a small amount (1-5 mol %) of $VO(acac)_2$. Work-up by reduction with hydrazine afforded the phenol in 80 % yield.

There is a significant solvent effect on the oxygenation of (**2**) with TBHP. Although in homogeneous solution (CH_2Cl_2) total conversion is readily achieved, the yield of (**3**) is only 30 %. However, in a heterogeneous system with *tert.*-butyl alcohol as solvent a slow but clean reaction occurs to give a mixture of (**3**) (80 %) and (**4**) (20 %).

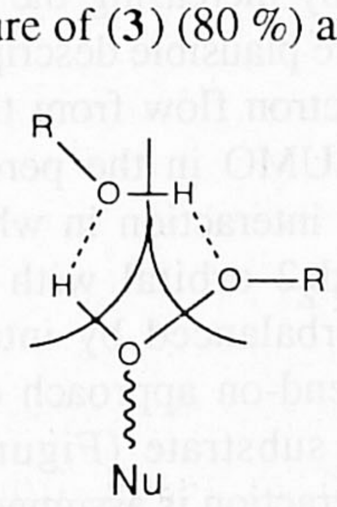
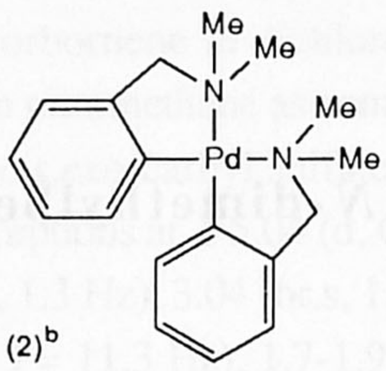
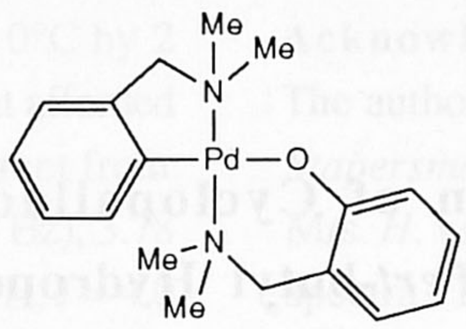
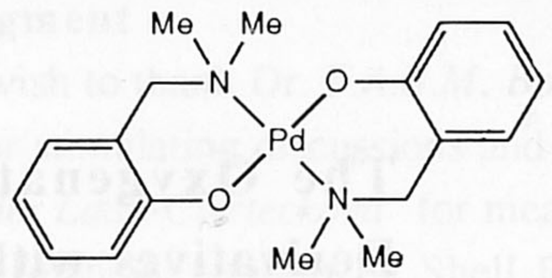
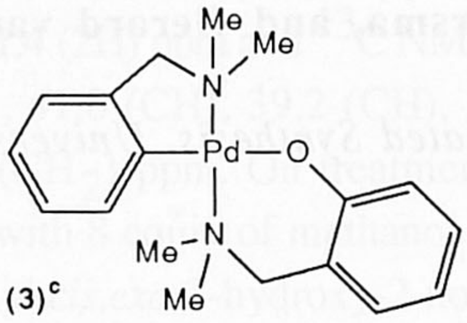
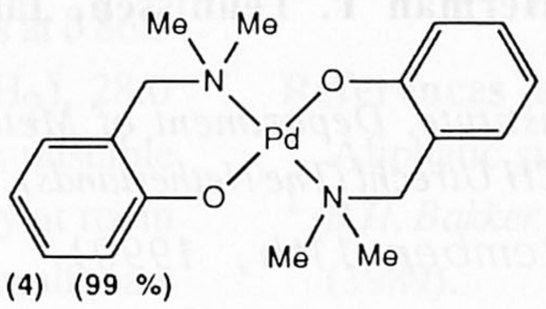
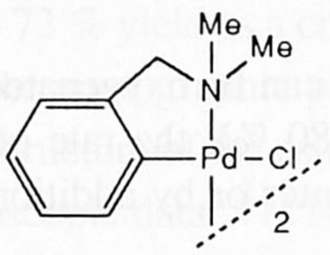
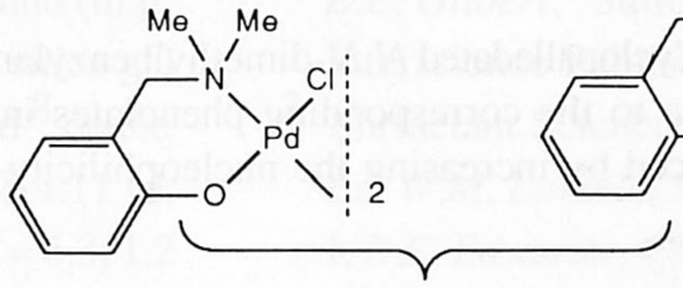
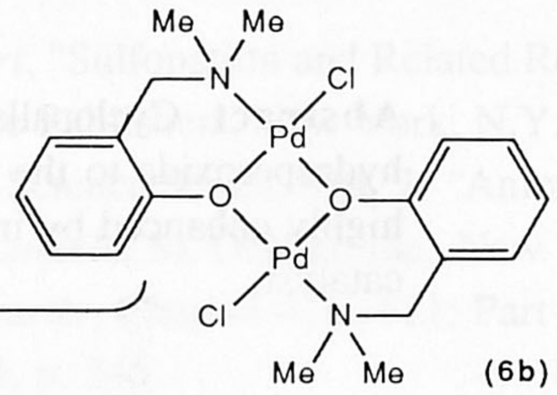
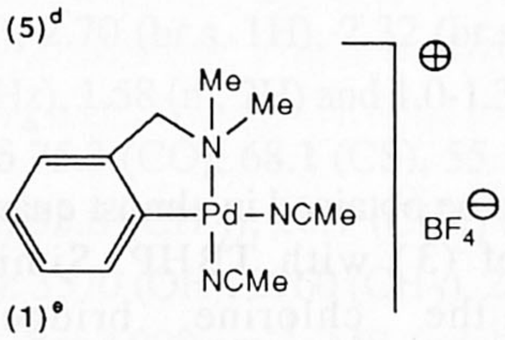


Fig. 1. Participation of protic solvents in the transition state during an end-on attack of a nucleophile (e.g. alkene or d^8-metal centre) on the peroxide.

The beneficial effect of *t*-BuOH in oxygenations with TBHP can be explained by participation of the solvent in the transition state as depicted in figure 1, whereby charge separation due to loss of the acidic proton of the peroxide[2] is avoided.

Table. *Direct or V-catalyzed oxygenation of cyclopalladated N,N-dimethylbenzylamine complexes with tert-butyl hydroperoxide.*

SUBSTRATE[a]	PRODUCTS (yield)
 (2)[b]	 (3) (80 %)  (4) (20 %)
 (3)[c]	 (4) (99 %)
 (5)[d]	 (6a) (6) (90 %)  (6b)
 (1)[e]	NO REACTION

[a] In the order of decreasing reactivity. Superscripts denote specific reaction conditions. [b] 1.5 eq. TBHP; *t*-BuOH - solv.; 35 °C. [c] 2.0 eq. TBHP; $CDCl_3$- solv.; 2 mol % $VO(acac)_2$; 20 °C. [d] 2.6 eq. TBHP; CH_2Cl_2- solv.; 3 mol % $VO(acac)_2$; 20 °C. [e] 2.6 eq. TBHP; $CDCl_3$- solv.; 20 °C.

Considering the relative reactivities of the investigated $Pd(C_6H_4CH_2NMe_2\text{-}2)X$ species towards oxygenation, *i.e.* **(2)** >> **(3)** > **(5)** ≥ **(1)**, we believe that oxygenation is strongly enhanced by increasing the nucleophilicity of the metal centre. A more plausible description for the transition state is that the electron flow from the d_z2 HOMO of the metal to the σ^* LUMO in the peroxide occurs *via* a 4 electron - 3 orbital interaction in which the unfavourable interaction of the d_z2 orbital with the σ orbital of the peroxide is counterbalanced by interaction with the σ^* LUMO during an end-on approach of the peroxidic O-O bond towards the substrate (Figure 2). An analogous HOMO-LUMO interaction is assumed to be involved in the vanadium-catalyzed epoxidation of alkenes with TBHP, in which the alkene π-bond is also presumed to attack the peroxidic O-O bond on the backside[4]. This simple qualitative MO picture explains the similarity in the dependence of the oxygenation rate on the nucleophilicity of both organopalladium compounds and alkenes, which is a result of the identical symmetries of the d_z2 orbital and the alkene π orbital during an end-on attack on the peroxide. Furthermore, this behaviour can be correlated to our findings about the highly nucleophilic platinum(II) compounds $[PtX(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ (X = I or Br), which form stable, isolable square pyramidal complexes with other electrophiles such as I_2 or SO_2[5], respectively.

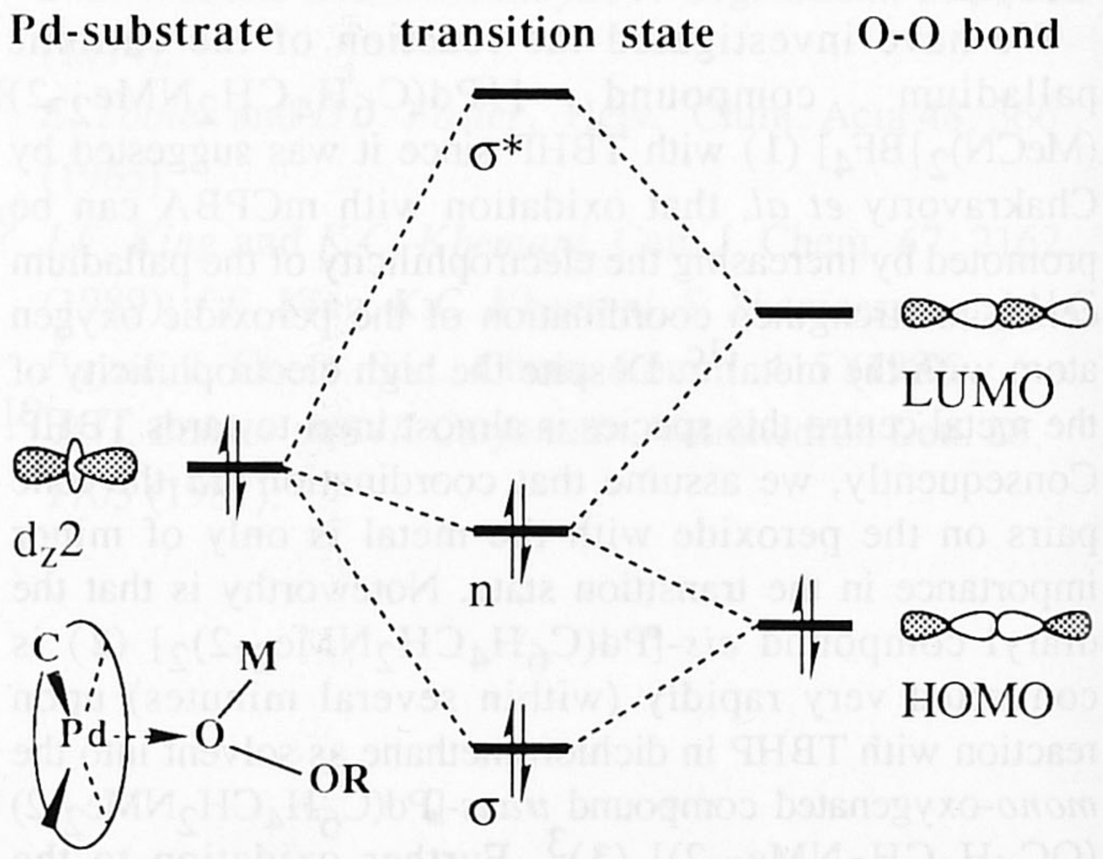


Fig. 2. Proposed frontier orbital interactions for oxygen transfer from a peroxide to an organopalladium compound.

Acknowledgement

We thank the Innovation Oriented Research Program on Catalysis for financial support.

[#] TBHP has been estimated to be 10^7 - 10^9 x less reactive than mCPBA; ref. 2.

References

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