Aromatic Hydroxylation: the Direct Oxidation of C–Pd into C–OPd

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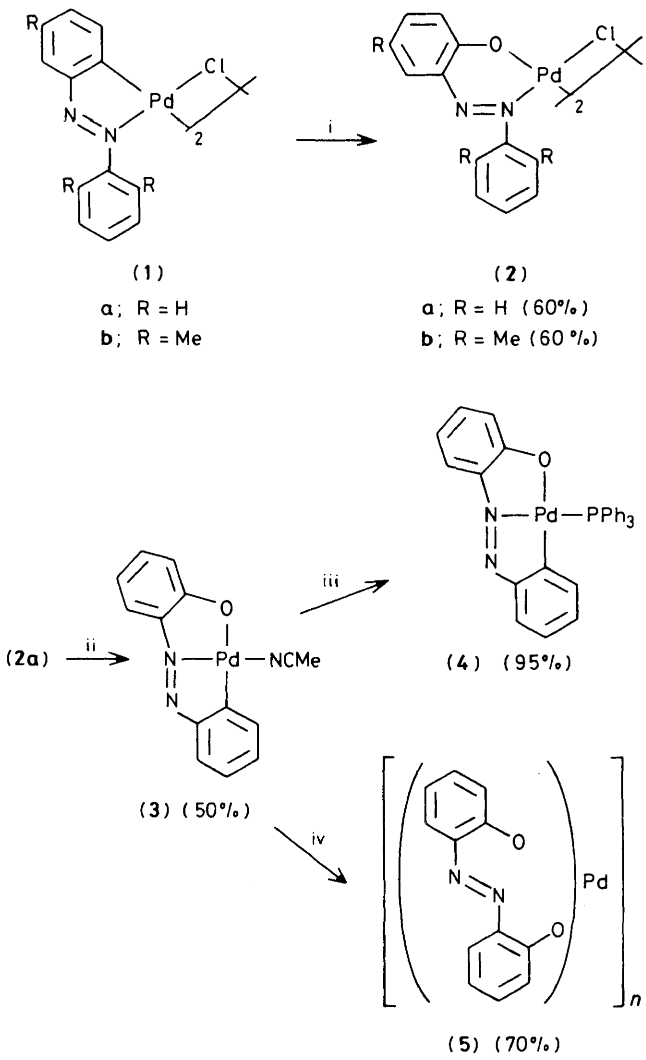
The C–Pd bond in cyclopalladated azobenzenes [(**1**) and (**3**)] is converted into the C–OPd function [(**2**) and (**5**)] in good yield by stoicheiometric reactions with *m*-chloroperbenzoic acid; in effect azobenzene is successively oxidised to 2-hydroxyazobenzene and 2,2′-dihydroxyazobenzene.

The hydroxylation of aromatic carbon atoms (C–H → C–OH) is a reaction of current interest.[1] We report here that the oxidation C–Pd → C–OPd can be directly achieved in palladated azobenzenes[2] (**1**) using *m*-chloroperbenzoic acid (*m*-CPBA) as the oxidant, Scheme 1. The details given for the conversion (**1b**) → (**2b**) are representative.

To an acetonitrile solution of (**1b**) (1 mmol) a solution of *m*-CPBA (3 mmol) in the same solvent was added dropwise at room temperature. After stirring for 3 h, the solvent was removed under reduced pressure and the residue was washed with aqueous ethanol and cold diethyl ether to remove excess of acid. Chromatography of a chloroform solution of the residue on a silica gel column with acetonitrile–benzene (5:95) as eluant gave complex (**2b**) which was isolated by evaporation under reduced pressure.

The various species shown in Scheme 1 are formed in good yields, and all except (**3**) have been isolated in pure solid form by simple crystallisation or by column chromatography on silica gel using benzene, acetonitrile, or a mixture of both as eluants. These compounds have been characterized by elemental analysis, spectra, and, where possible, by unambiguous synthesis [(**2b**) and (**5**), see below] from preformed azophenols. Species (**2**) and (**4**) have ν(CO) *ca.* 1140 cm^{-1}; (**5**) 1140 and 1120 cm^{-1}; $\lambda_{max.}$ (CH_2Cl_2): (**2a**), 495 (ε 2 900 dm^3 mol^{-1} cm^{-1}); (**2b**), 495 (3 400); (**4**), 660 (6 000) and 625 (6 600); (**5**), 495 (9 800) and 450 (9 000) nm. The ^{1}H n.m.r. spectrum of (**4**) shows a doublet (1H, *J* 7.0 Hz) at δ 5.88; the remaining aromatic signals occur as a complex pattern in the range δ 6.3—7.7. As in the case[3] of the PPh_3 adduct of *ortho*-palladated azobenzenes, the unique high-field signal is assigned to the proton *ortho* to the metallated carbon in (**4**). This proton lies close to the phenyl groups of PPh_3 and the shift to high field arises owing to the shielding effect of these phenyl groups. In the pyridine analogue of (**4**) [synthesised as for (**4**), Scheme 1, but using pyridine in place of PPh_3] all aromatic proton signals occur above δ 6.2.

Palladium(II) chloride reacts with 2′,5,6′-trimethyl-2-hydroxyazobenzene in anhydrous ethanol to yield a reddish-



Scheme 1. *Reagents and conditions*: i, MeCN, *m*-CPBA; ii, adsorption on silica gel, 348 K, 2 h, MeCN; iii, CH_2Cl_2, PPh_3; iv, MeCN, *m*-CPBA. Yields are based on the immediate precursors.

brown complex that is identical in all respects with (**2b**). This confirms that the C–OPd bond in (**2b**) arises directly from the C–Pd bond of (**1b**). Similarly, the reaction of 2,2′-dihydroxyazobenzene with Na_2PdCl_4 in ethanol affords an orange-red complex that is identical to (**5**). Owing to its insolubility the molecular weight of (**5**) could not be determined; to date we have not been able to grow single crystals.

The *ortho*-metallation of (**2a**) (ii, Scheme 1) is achieved by adsorbing the complex on silica gel followed by mild heating of the dry material. On subsequent elution with MeCN a green solution of (**3**) is obtained from which MeCN can be displaced by donors such as PPh_3 [as in (**4**)], pyridine, *etc.* In this novel surface-induced *ortho*-metallation reaction the Si–OH groups[4] of the silica are thought to be active.

The mechanism and more general applicability of the C–Pd → C–OPd reaction are under study. The existing information[5] on oxidative cleavage of aliphatic M–C (M = Pd or Pt) species suggests that co-ordination of the oxidising agent is a possible initial step.

Financial support provided by Department of Science and Technology, Government of India, is gratefully acknowledged.

Received, 4th April 1984; Com. 480

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