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Preliminary communication

CONVERSION OF A CYCLOPALLADATED BENZYLAMINE COMPLEX TO A SALICYLALDAMINE COMPLEX

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Summary

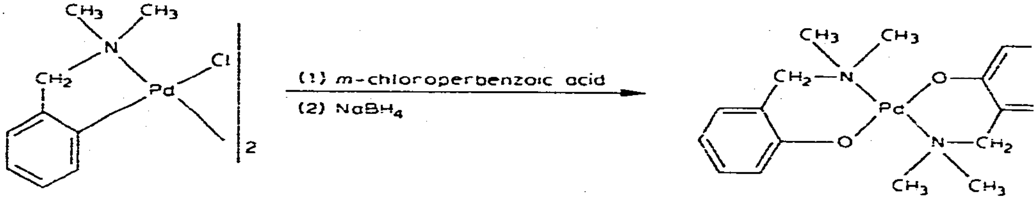
Bis(*N*,*N*-dimethylsalicylaldaminato)palladium(II) may be prepared from the reaction of *m*-chloroperbenzoic acid with di-μ-chlorobis[α-(dimethylamine)-2-tolyl]-dipalladium followed by treatment with $NaBH_4$.

In the reaction of peracids with metal carbon σ-bonds, Russian workers have reported the isolation of *o*-hydroxyazobenzene from an azobenzene cyclometallated compound of nickel [1]. More recently reaction of *m*-chloroperbenzoic acid with σ-benzyl complexes of platinum and palladium has given benzyl *m*-chlorobenzoate and benzyl alcohol [2].

During our investigations of similar oxidations of cyclometallated complexes, we were able to isolate the salicylaldaminepalladium complex (II) from the cyclopalladated *N*,*N*-dimethylbenzylamine complex (I) [3].

Experimental

Bis(N,N-dimethylsalicylaldaminato)palladium (II). *m*-Chloroperbenzoic acid (0.13 g, 0.75 mmol) in methylene dichloride (4 ml) was added slowly to a solution of di-μ-chlorobis[α-(dimethylamine)-2-tolyl]dipalladium (0.2 g, 0.36 mmol) in methylene dichloride (10 ml) maintained at ice temperature. The solution was stirred for 30 minutes followed by addition of methanol (2 drops) and excess solid $NaBH_4$. Removal of solvent and preparative TLC gave the complex as a yellow air-sensitive solid (yield 35%). Mass spectrum: $M^{+\cdot}$ found 404, $M^{+\cdot}$ calcd. 404. Others: 360, 299, 253, 211, 150 ($C_9H_{12}NO$), 58, 44. IR ($CDCl_3$): 1595 (C=C aromatic), 1270 (C–O). ^1H NMR ($CDCl_3$): δ 2.63 (s, 6H, 2Me), 3.22 (s, 2H, $-CH_2$), 6.40–7.18 ppm (m, 4H, aromatics).



(I) (II)

Early attempts to obtain *o*-hydroxy compounds were hindered by poor cleavage of the peracid reaction product from the metal, by cyanide or acid, and our attention turned to reducing palladium to the metallic state. While $LiAlH_4$ reduces C=N and N=N groups readily [4, 5] it was found that $NaBH_4$ reduced known cyclopalladated complexes to palladium metal and the free ligand in high yield. Reaction of complex I with peracid gave a red solution which, on treatment with sodium borohydride, led to only 20% of the theoretical palladium black. Preparative TLC of the residue afforded a small amount of the free ligand and complex II as a yellow solid which proved difficult to handle in air. The structure was determined by spectroscopic methods. ^1H NMR indicated 4 aromatic protons, a methylene and two methyl groups and a strong new band in the IR at 1270 cm^{-1} (ν(C–O)) was present. The mass spectrum had the correct molecular ion (404 based on palladium-104), an abundant ion for the ligand $C_9H_{12}NO$, and other characteristic fragments.

Work on the general applicability of the reaction is presently in progress.

References

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