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Preliminary communication

CYCLOPALLADATED PRIMARY, SECONDARY AND TERTIARY BENZYLAMINES, AND BENZALIMINES. A NEW METHOD OF SYNTHESIS

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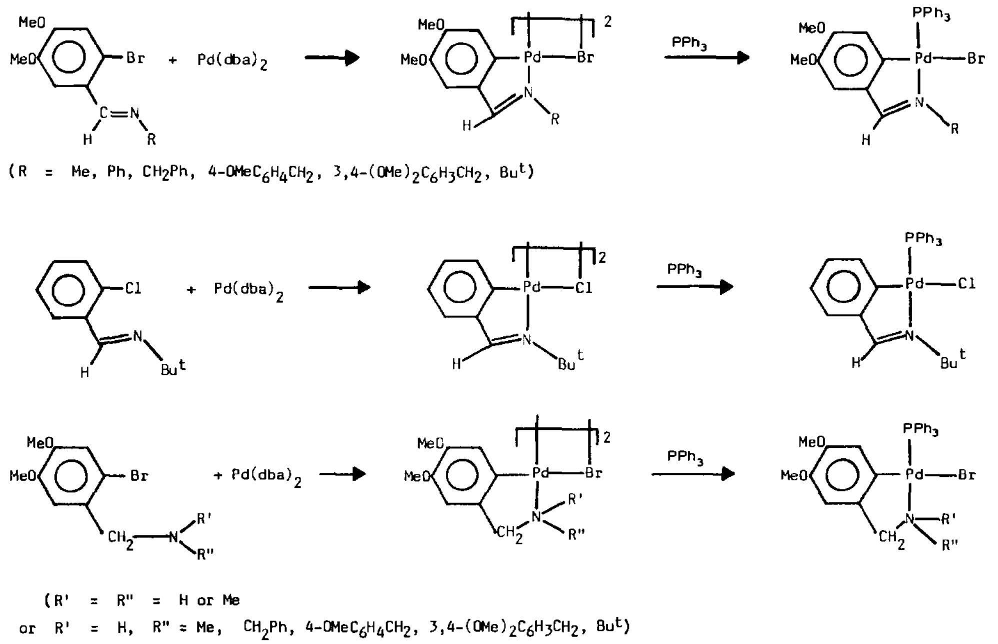
Summary

Cyclopalladated complexes of primary, secondary and tertiary benzylamines and of benzalimines have been prepared by the oxidative addition of the corresponding *ortho*-bromobenzylamine and *ortho*-halobenzalimine to bis(dibenzylideneacetone)palladium(0). The complexes have been characterised fully as the monomeric triphenylphosphine derivatives.

During the past twenty years, since the discovery that transition metals will form cyclometallated complexes [1], cyclometallation has become an integral part of organometallic chemistry [2—4]. Since the earlier days of its conception, the delineation of the bounds of cyclometallation has largely remained unchanged from that outlined by Cope and Friedrich [5]. Except for one isolated case [6] involving the sterically hindered amines *N*-methyltriphenylmethylamine and triphenylmethylamine, cyclometallation has, for nitrogen-base ligands, been restricted to tertiary amines, benzalimines and azo compounds. As a consequence, this has severely limited the scope of any further reaction involving an "insertion" into the metal—carbon bond. We have actively been investigating "insertion" reactions into the metal—carbon bond involving cyclopalladated nitrogen-base ligands [7]. In order to overcome the above limitation, we have devised a new method of synthesis to produce cyclopalladated primary, secondary and tertiary amines, and benzalimines.

The new method of synthesis involves the coordination and subsequent oxidative-addition of *ortho*-halogenated amines and benzalimines to either of the palladium(0) complexes, $Pd(Ph_3P)_4$ or $Pd(dba)_2$, dba = dibenzylideneacetone. For our purposes in considering subsequent "insertion" reactions, we have concentrated our investigations mainly on the reactions of $Pd(dba)_2$.

It has been shown that the attempted cyclometallation of benzalimines by dichlorobis(benzonitrile)palladium(II) in methanol often results in the methanol-



(R = Me, Ph, CH_2Ph, $4\text{-}OMeC_6H_4CH_2$, $3,4\text{-}(OMe)_2C_6H_3CH_2$, Bu^t)

(R' = R" = H or Me
or R' = H, R" = Me, CH_2Ph, $4\text{-}OMeC_6H_4CH_2$, $3,4\text{-}(OMe)_2C_6H_3CH_2$, Bu^t)

SCHEME 1

ysis of the imine [8], and that a method of forming the desired cyclopalladated imines is to react the imine with palladium acetate in acetic acid [8,9]. In our method of synthesis, we have shown that a series of 3,4-dimethoxy-6-bromobenzalimines and *N*-t-butyl-6-chlorobenzalimine react smoothly and in high yield (68—98%) with bis(dibenzylideneacetone)palladium(0) to form the corresponding cyclopalladated benzalimine dimeric complexes (see Scheme 1). As all of the 3,4-dimethoxybenzalimine dimer complexes were very insoluble, they were cleaved with triphenylphosphine to give the corresponding monomeric complexes for ease of ^1H and ^{13}C NMR studies. The reaction of *N*-methyl(3,4-dimethoxy-6-bromo)benzalimine with tetrakis(triphenylphosphine)palladium(0) gave the same monomeric palladium(II) product as above.

Similarly, the series of primary, secondary and tertiary 3,4-dimethoxy-6-bromobenzylamines (Scheme 1) reacted with bis(dibenzylideneacetone)-palladium(0) to give the corresponding amine complexes. These dimeric complexes were then split with triphenylphosphine to give the monomeric species for ease of characterisation. The acetylacetonate monomer of the primary amine complex was also prepared to give further characterisation, and the reaction of *N*-methyl(3,4-dimethoxy-6-bromo)benzylamine with tetrakis(triphenylphosphine)palladium(0) gave the same monomeric complex as above.

The monomeric complexes were characterised by ^1H and ^{13}C NMR spectral studies, infrared spectral and elemental analyses. Elemental analyses were found to be satisfactory.

Investigations are presently being pursued into the "insertion" reactions of the primary and secondary amine complexes.

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References

1 J.P. Kleinmann and M. Dubeck, J. Amer. Chem. Soc., 85 (1963) 1544.
2 M.I. Bruce, Angew. Chem. Int. Ed. Engl., 16 (1977) 73.
3 J. Dehand and M. Pfeffer, Coordination Chem. Rev., 18 (1976) 327.
4 I. Omae, Chem. Rev., 79 (1979) 287.
5 A.C. Cope and E.C. Friedrich, J. Amer. Chem. Soc., 90 (1968) 909.
6 B.N. Cockburn, D.V. Howe, T. Keating, B.F.G. Johnson and J. Lewis, J. Chem. Soc., Dalton Trans., (1973) 404.
7 P.W. Clark, H.J. Dyke, S.F. Dyke and G. Perry, J. Organomet. Chem., 253 (1983) 399 and references cited therein.
8 I.R. Girling and D.A. Widdowson, Tetrahedron Lett., (1982) 1957.
9 H. Onoue and I. Moritani, J. Organomet. Chem., 43 (1972) 431.