The Synthesis of N-Heterocycles using *ortho*-Metallated Primary Benzylamine Complexes of Palladium(II) and Platinum(II)

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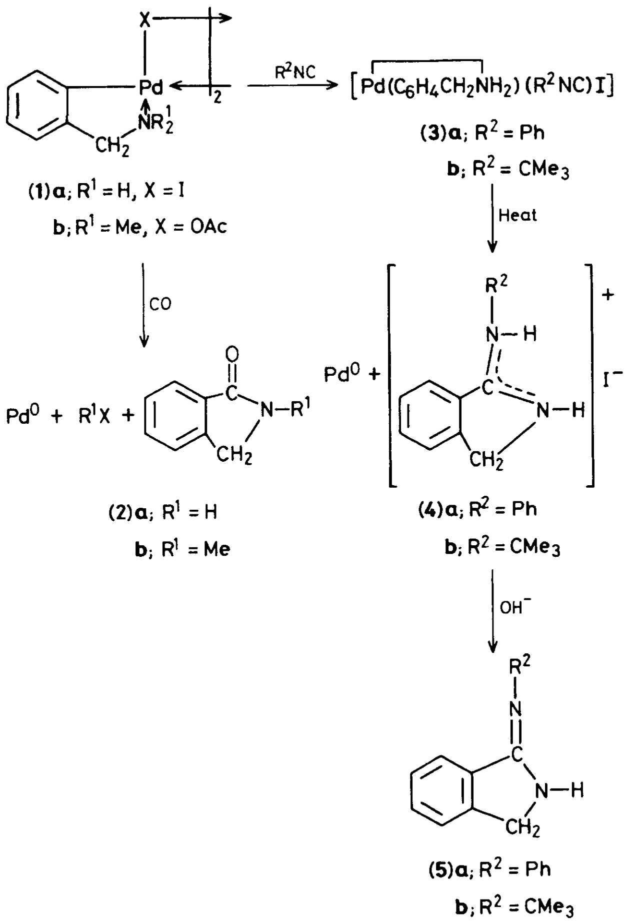
The synthesis of the isoindolinimines (**5**) by the insertion of isocyanides into the metal–carbon bond of the *ortho*-palladated primary benzylamine complex (**1a**) is described; the novel oxidative addition and subsequent reductive elimination of the *ortho*-metallated primary benzylamine–platinum complex (**6**) yields 3-oxo-1,2,3,4-tetrahydroisoquinoline (**8**).

It has been observed that the metal–carbon bond of *ortho*-metallated complexes of palladium undergoes insertions of unsaturated molecules, such as alkenes,[1] alkynes,[2] isocyanides,[3] and carbon monoxide.[4] Further reaction of these insertion products to yield cyclised organic compounds has been achieved in isolated cases only.[4,5] This has been due to the use of *N*-trisubstituted nitrogen ligands and the subsequent low reactivity at the nitrogen centres.

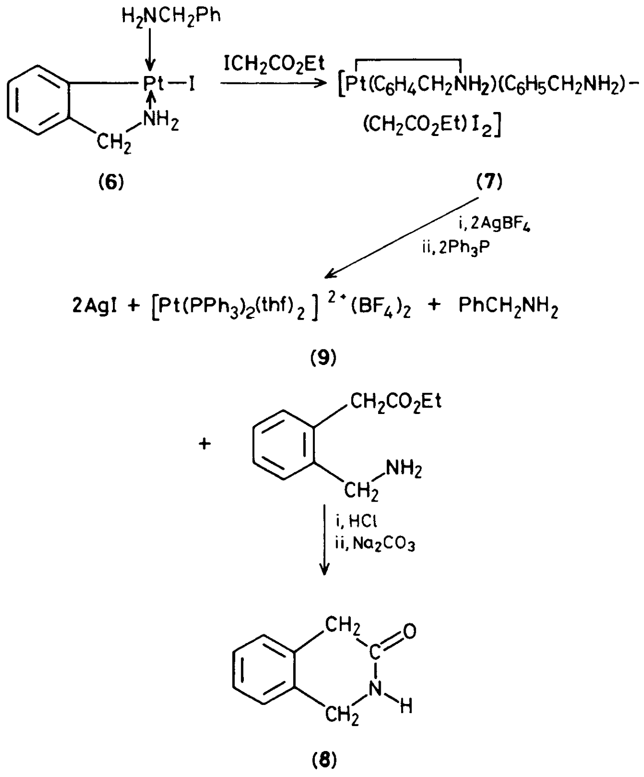
The palladium complex (**1a**)[6] reacts with carbon monoxide in methanol at room temperature and pressure to give phthalimidine (**2a**) and palladium metal (Scheme 1). These mild reaction conditions may be compared with the carbonylation of *N*,*N*-dimethylbenzylamine–palladium acetate dimer (**1b**) which is carried out at 100 °C in xylene[4] to give *N*-methylphthalimidine (**2b**), in which an *N*-methyl group is eliminated, as one of the organic products.



Scheme 1

On treatment of the *ortho*-metallated palladium complex (**1a**) with an isocyanide (2 equiv.), in CH_2Cl_2 at room temperature, a bridge splitting reaction takes place and the complex (**3**) is formed. If this is then refluxed in toluene for 3 h the corresponding isoindolinimine is deposited as the hydroiodide salt (**4**) in good yield, together with palladium metal (Scheme 1). The salts (**4**) and the free bases (**5**) have been characterised by i.r. and ^1H n.m.r. spectroscopy. The compound 1-phenyliminoisoindoline (**5a**) was also prepared by condensation of aniline with (**2a**) using phosphorus oxychloride[7] and the spectra of samples from both preparations agreed closely.

The *ortho*-metallated benzylamine–platinum complexes undergo different reactions compared with those compounds of palladium. The complex (**6**) reacts readily with ethyl iodoacetate at room temperature in acetone to give (**7**) by oxidative addition. The reaction in which methyl iodide adds to a platinum(II) complex to yield a six co-ordinate platinum(IV) species has been studied.[8] Under certain conditions this type of platinum(IV) complex, with more than one metal–carbon σ-bond, has been found to undergo reductive elimination to yield a dialkyl or a mixed alkyl–aryl molecule and a platinum(II) complex. It was shown that cations of platinum(IV) complexes undergo reductive elimination more readily than do the neutral species. This process is also facilitated if the ligands to be eliminated are *trans* to ligands of high *trans* influence such as PR_3.



Scheme 2

When (**7**) in dry tetrahydrofuran (thf) is treated first with $AgBF_4$ (2 equiv.) and then with Ph_3P (2 equiv.), a white solid $[Pt(Ph_3P)_2(thf)_2]^{2+}(BF_4)_2$ (**9**) is formed. The thf solution, on treatment first with dilute HCl and then with an excess of Na_2CO_3 gives, as the major product, 3-oxo-1,2,3,4-tetrahydroisoquinoline (**8**) (Scheme 2), which was confirmed by comparison with an authentic sample.[9]

Although the reactions described are not as yet catalytic, they show how platinum and palladium can be used to direct substituents into the *ortho*-position of benzylamine and provide routes to N-heterocycles using readily available starting materials.

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References

1 B. J. Brisdon, P. Nair, and S. F. Dyke, *Tetrahedron*, 1981, **37**, 173.

2 C. Arlen, M. Pfeffer, O. Bars, and D. Grandjean, *J. Chem. Soc., Dalton Trans.*, 1983, 1535.

3 Y. Yamamoto and H. Yamazaki, *Inorg. Chim. Acta*, 1980, **41**, 229.

4 J. M. Thompson and R. F. Heck, *J. Org. Chem.*, 1975, **40**, 2667.

5 H. Takahashi and J. Tsuji, *J. Organomet. Chem.*, 1967, **10**, 511; A. Bahsoun, J. Dehand, M. Pfeffer, M. Zinsius, S. E. Bouaoud, and G. Le Borgne, *J. Chem. Soc., Dalton Trans.*, 1979, 547; P. W. Clark, H. J. Dyke, S. F. Dyke, and G. Perry, *J. Organomet. Chem.*, 1983, **253**, 399; Y. Yamamoto and H. Yamazaki, *Synthesis*, 1976, 750; N. Barr, S. F. Dyke, and S. N. Quessy, *J. Organomet. Chem.*, 1983, **253**, 391.

6 A. Avshu, R. D. O'Sullivan, A. W. Parkins, N. W. Alcock, and R. M. Countryman, *J. Chem. Soc., Dalton Trans.*, 1983, 1619.

7 I. G. Hinton, F. G. Mann, and A. Vanterpool, *J. Chem. Soc.*, 1959, 610.

8 T. G. Appleton, H. C. Clark, and L. E. Manzer, *J. Organomet. Chem.*, 1974, **65**, 275.

9 R. Huisgen and J. Reinertshofer, *Liebigs Ann. Chem.*, 1952, **575**, 197.