

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

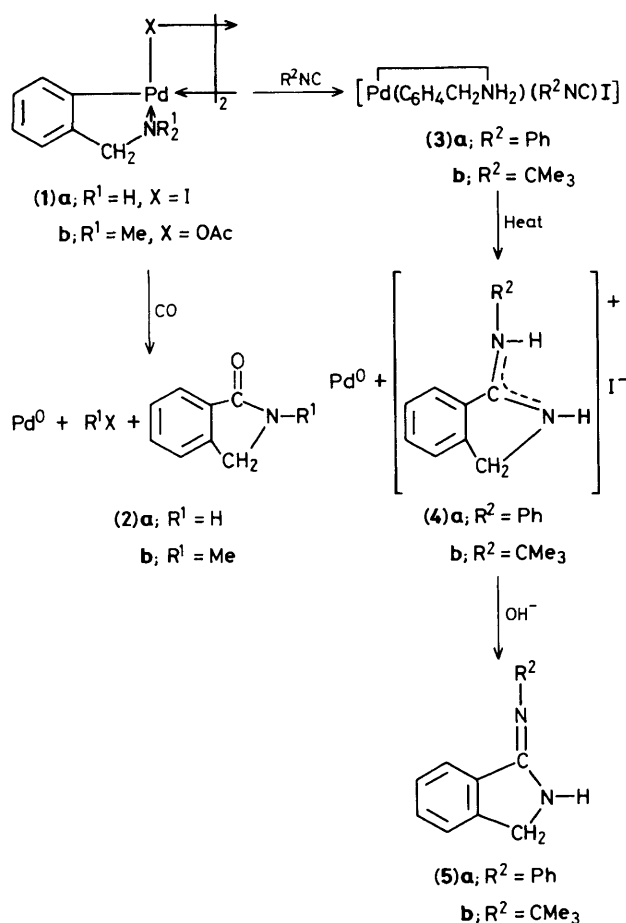
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The synthesis of the isoindolinimines (**5**) by the insertion of isocyanides into the metal-carbon bond of the *ortho*-palladated primary benzylamine complex (**1a**) is described; the novel oxidative addition and subsequent reductive elimination 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,<sup>1</sup> alkynes,<sup>2</sup> isocyanides,<sup>3</sup> and carbon monoxide.<sup>4</sup> Further reaction of these insertion products to yield cyclised organic compounds has been achieved in isolated cases only.<sup>4,5</sup> 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**)<sup>6</sup> 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<sup>4</sup> to give *N*-methylphthalimidine (**2b**), in which an *N*-methyl group is eliminated, as one of the organic products.

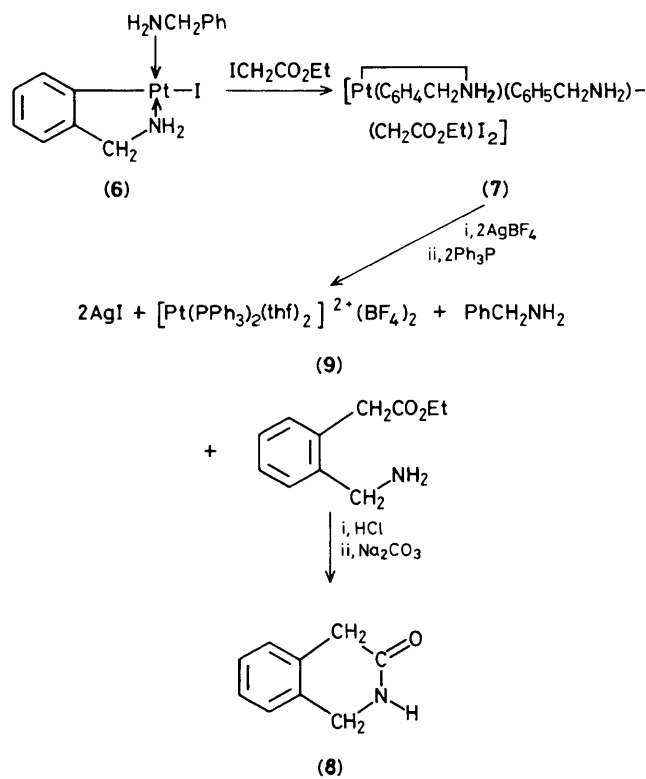


Scheme 1

On treatment of the *ortho*-metallated palladium complex (1a) with an isocyanide (2 equiv.), in CH<sub>2</sub>Cl<sub>2</sub> 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 <sup>1</sup>H n.m.r. spectroscopy. The compound 1-phenyliminoisoindoline (5a) was also prepared by condensation of aniline with (2a) using phosphorus oxychloride<sup>7</sup> 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.<sup>8</sup> 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<sub>3</sub>.

When (7) in dry tetrahydrofuran (thf) is treated first with AgBF<sub>4</sub> (2 equiv.) and then with Ph<sub>3</sub>P (2 equiv.), a white solid [Pt(Ph<sub>3</sub>P)<sub>2</sub>(thf)<sub>2</sub>]<sup>2+</sup>(BF<sub>4</sub>)<sub>2</sub> (9) is formed. The thf solution, on



Scheme 2

treatment first with dilute HCl and then with an excess of Na<sub>2</sub>CO<sub>3</sub> gives, as the major product, 3-oxo-1,2,3,4-tetrahydroisoquinoline (8) (Scheme 2), which was confirmed by comparison with an authentic sample.<sup>9</sup>

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.

We thank the S.E.R.C. for a Research Studentship (R. D. O.'S.) and Johnson Matthey plc for a loan of palladium and platinum salts.

Received, 17th May 1984; Com. 692

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