

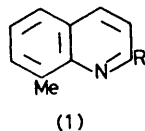
## Palladation of 8-Methylquinoline and Related 2-Substituted Derivatives: Evidence for In-plane Metallation of Methyl Groups†

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**Summary** 8-Methylquinoline reacts with palladium acetate to give palladation at the 8-methyl group and similar metallations occur for 2-substituted derivatives where one would expect the substituent R to allow chelate ring formation (R = CH:NMe, CO<sub>2</sub>H, or CH<sub>2</sub>OH) but not where R = Me, Br, or CHO; evidence is presented for metallation occurring when the ligand plane and the co-ordination plane are coincident.

THE tetrachloropalladate(II) ion reacts slowly in aqueous methanol with 8-methylquinoline (**1a**) with metallation at the methyl group to give the chloro-bridged dimer

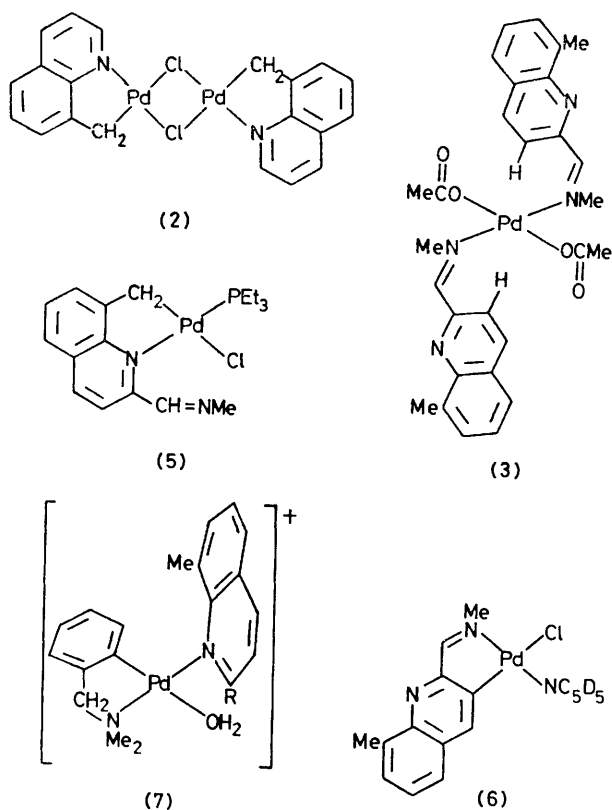


- |            |                           |
|------------|---------------------------|
| a; R = H   | e; R = CH:NMe             |
| b; R = Me  | f; R = CO <sub>2</sub> H  |
| c; R = Br  | g; R = CH <sub>2</sub> OH |
| d; R = CHO |                           |

[PdCl(C<sub>10</sub>H<sub>8</sub>N)]<sub>2</sub> (**2**).<sup>1</sup> We have found that the corresponding reaction with palladium acetate in chloroform to give the acetato-bridged analogue of (**2**) (as a mixture of

*cis*- and *trans*-isomers) is rather more rapid and complete, being complete within 90 min at 30 °C. In marked contrast the 2-substituted derivatives (**1b—d**) are not palladated with [PdCl<sub>4</sub>]<sup>2-</sup>, nor even with palladium acetate under a range of conditions; (**1b**) may be recovered, for example, after 2 h with palladium acetate in refluxing methanol (ligand: Pd = 1:1 or 2:1). Remarkably the other 2-substituted compounds (**1e—g**) readily undergo palladation with palladium acetate in chloroform at room temperature. For example, the di-imine (**1e**), derived from the aldehyde (**1d**) and rather similar to it sterically, reacts with palladium acetate in CDCl<sub>3</sub> (ligand: Pd = 2:1) almost instantaneously at room temperature to give [Pd(MeCO<sub>2</sub>)<sub>2</sub>(C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>)<sub>2</sub>] (**3**) which has monodentate imines co-ordinated in the configuration shown with the close approach of the 3-hydrogen atoms to palladium as indicated by the shift of their n.m.r. signals from δ8.07 to 11.16 on co-ordination. This species is moderately stable at room temperature and smooth metallation (2 h; 30 °C) only proceeds on doubling the palladium acetate concentration and a compound analysing as [Pd(MeCO<sub>2</sub>)(C<sub>12</sub>H<sub>11</sub>N<sub>2</sub>)(H<sub>2</sub>O)] (**4**) was isolated. As established by the <sup>1</sup>H and <sup>13</sup>C n.m.r. spectra of (**4**) and its derivative [PdCl(C<sub>12</sub>H<sub>11</sub>N<sub>2</sub>)(PEt<sub>3</sub>)] (**5**), formed by successive treatment with chloride ions and PEt<sub>3</sub>, palladation has occurred at the 8-Me group in spite of the structure of (**3**) which seems to suggest that metallation should occur at the 3-position. We propose

† No reprints available.



that palladation at the 8-Me group in these 2-substituted compounds (**1b–g**) only occurs when the substituent R is a sufficiently good ligand itself to form a five-membered chelate ring containing the quinoline nitrogen atom and thus forcing the 8-Me group close to the palladium atom in the co-ordination plane. It is probable that (**1e**), and (**1f** and **1g**) in their conjugate anionic forms, can form chelate rings, while (**1b** and **1c**) cannot, and the CHO group of (**1d**) is too weakly co-ordinating to participate in this way.

Using  $[\text{PdCl}_4]^{2-}$ , in which the co-ordination sites are much less readily available than in palladium acetate and bidentate bonding is presumably more difficult to achieve, metallation at the 3-position of (**1e**) as well as at the 8-Me group occurs. Thus treatment of  $[\text{PdCl}_4]^{2-}$  with (**1e**) (ligand: Pd = 1:1) in refluxing methanol (16 h) gave an almost insoluble product with the empirical formula  $[\text{PdCl}(\text{C}_{12}\text{H}_{11}\text{N}_2)]$  which was separated into the rather more soluble 8-Me-metallated isomer by Soxhlet extraction with  $\text{CH}_2\text{Cl}_2$  [this giving (**5**) on treatment with  $\text{PEt}_3$ ] and the 3-metallated isomer which was best characterised as the derivative  $[\text{PdCl}(\text{C}_{12}\text{H}_{11}\text{N}_2)(\text{C}_5\text{D}_5\text{N})]$  (**6**).

The lack of metallation of (**1b–d**), in contrast to (**1a**), is probably not due to any significant difference in their ability to co-ordinate, but rather to the inability of (**1b–d**) to rotate easily about the Pd–N bond to position

the Me-group in the co-ordination plane. In other work<sup>2,3</sup> we have shown that (**1a**) and (**1b**) (L) co-ordinate when  $[\text{PdCl}(2\text{-C}_6\text{H}_4\text{CH}_2\text{NMe}_2)]_2$  is treated with  $\text{AgClO}_4$  in undried acetone and then with L to give the complexes  $[\text{Pd}(2\text{-C}_6\text{H}_4\text{CH}_2\text{NMe}_2)(\text{L})(\text{H}_2\text{O})]\text{ClO}_4$  (**7**). When L = (**1a**) the complex is dynamic on an n.m.r. time scale giving rapid inversion by rotation of the ligand L from mainly above to mainly below the co-ordination plane *via* a site vacated by the co-ordinated  $\text{H}_2\text{O}$ , a process not observed at all for L = (**1b**). We believe that the inability of (**1b**) to pass into and through the co-ordination plane prevents its metallation and this is caused by steric hindrance of the group R with the adjacent *cis*-ligand. The Figure shows this schematically.

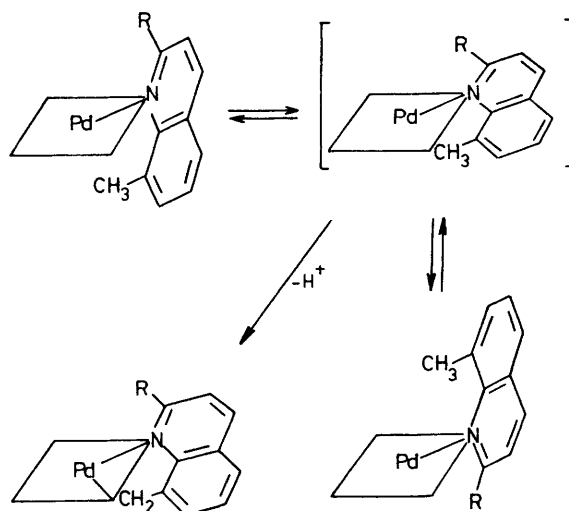


FIGURE. In-plane configuration required for inversion of (**7**) and proposed here to be required for metallation of (**1**).

Only for  $[\text{Pd}(\eta^3\text{-allyl})(\text{C}_{12}\text{H}_{12}\text{N}_2)]\text{ClO}_4$  ( $\text{C}_{12}\text{H}_{12}\text{N}_2 = \mathbf{1e}$ ) have we obtained a stable palladium complex with a non-metallated Me-group in the co-ordination plane, possibly here because of the small bite and flexibility of the  $\eta^3$ -allyl group. Metallation at Me is not therefore an immediate consequence of its entering the co-ordination plane and with the more common palladation of aromatic rings different conditions may apply altogether.

All new compounds were characterised by elemental analysis and in particular by  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r. spectra which provide unambiguous evidence for sites of metallation.

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<sup>1</sup> G. E. Hartwell, R. V. Lawrence, and M. J. Smas, *Chem. Comm.*, 1970, 912.

<sup>2</sup> A. J. Deeming, I. P. Rothwell, M. B. Hursthouse, and L. New, *J.C.S. Dalton*, in the press.

<sup>3</sup> A. J. Deeming and I. P. Rothwell, *J.C.S. Dalton*, in the press.