

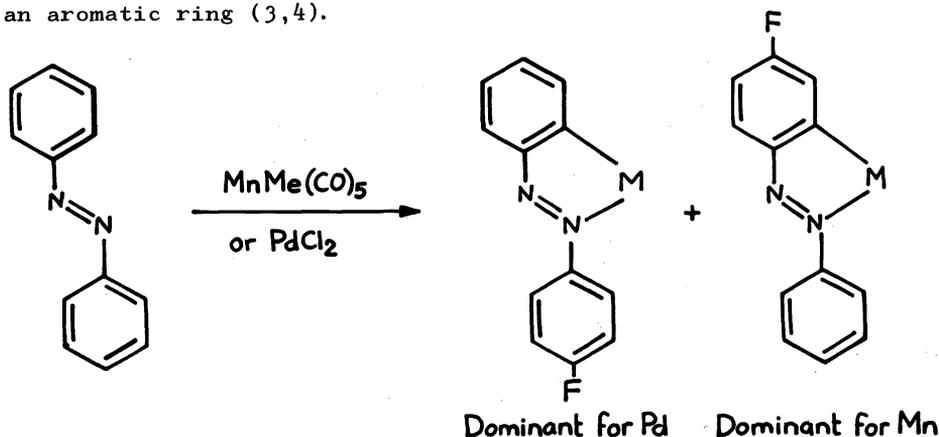
CARBON-HYDROGEN BOND ACTIVATION IN TRANSITION METAL COMPOUNDS

Antony J. Deeming and Ian P. Rothwell
Department of Chemistry, University College London,
20 Gordon Street, London WC1H 0AJ, U.K.

Abstract - Square-planar palladium and rhodium complexes of 8-methylquinoline and benzo[h]quinoline involve short CH...M interactions in an axial above-plane direction. Attempts to force the alkyl group into the coordination plane by use of bidentate ligands based on 8-alkyl-quinolines were unsuccessful. This is because gross distortions of the coordination, including unusual pyramidal geometries for the coordinated nitrogen atoms of the quinolines, allow the alkyl groups to move out of the coordination plane. Nevertheless, evidence is presented for cyclopalladation occurring via an in-plane interaction of metal with the hydrocarbon group, which is assisted by chelation.

INTRODUCTION

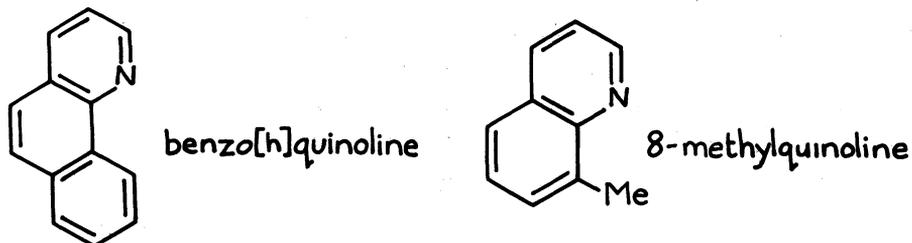
Cyclometallation is widely occurring class of reaction in which a C-H bond of a ligand is cleaved to give a chelate ring containing an M-C bond (1,2). With nitrogen-based ligands there is a preference for a tertiary nitrogen donor and for 5-membered ring formation. Cyclometallations undoubtedly occur by different mechanisms, but in general these have still to be elucidated. The metal centre may behave as an electrophile or as a nucleophile in its attack at an aromatic ring (3,4).



Nucleophilic reactions could occur by oxidative additions which may or may not be followed by reductive eliminations. With Fe^0 , Ru^0 , Os^0 , Rh^{I} and Ir^{I} the isolated cyclometallation product generally contains oxidised metal, while with Pt^{II} there is evidence for Pt^{IV} hydrido-intermediates in certain cases even where the isolated product contains Pt^{II} . Pt^{II} seems to be a borderline

case since oxidative addition occurs with tertiary phosphines, whereas cyclometallation of nitrogen ligands with $[\text{PtCl}_4]^{2-}$ probably involves an electrophilic metal centre as with $[\text{PdCl}_4]^{2-}$.

In this account we will describe some of our own work on cyclopalladation reactions which almost certainly involve electrophilic palladium. Our interest has centred on the two quinoline ligands below in which normal electrophilic aromatic substitution is impossible. Parshall suggested that



initial π -complexation of Pd with the aromatic ring of ligands such as dimethylbenzylamine would precede the formation of a σ -complex from which a proton is finally lost (5). Coordination of benzo[h]quinoline through nitrogen only allows the 10-H atom to approach the Pd atom so that direct attack at the 10-C atom, certainly by π -complexation, is prevented by the rigid structure of the ligand. Yet cyclopalladation occurs readily with this ligand and with 8-methylquinoline which is metallated at the 8-Me group (6).

We have directed our research towards the following:

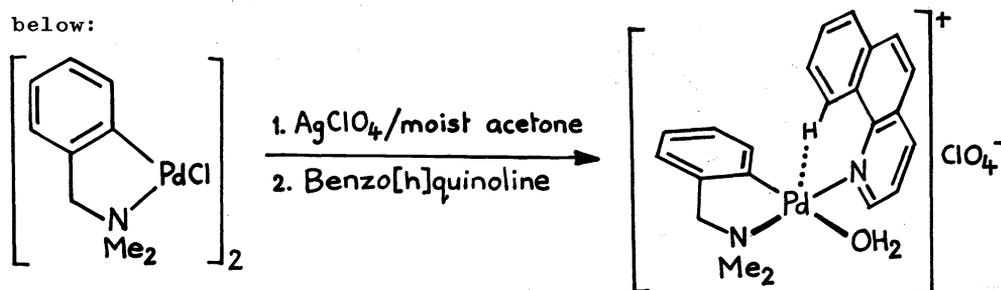
(1) To synthesise complexes of the two quinolines above, none being known at the start of our work, to see if any anomalies would result from close approach of hydrogen atoms of the unmetallated ligand to palladium.

(2) To study the coordination of 8-alkyl-quinolines which had been converted into bidentate ligands by the incorporation of coordinating groups into the 2-position. By chelation we hoped to force the 8-alkyl group into the square coordination plane of palladium.

(3) To establish geometric requirements for palladation. One would expect Pd^{II} to use the vacant $d_{x^2-y^2}$ orbital when acting as an electrophile and this would require cyclometallation in the coordination plane. Previously it was unknown whether the hydrocarbon group approached the metal axially or within the coordination plane during metallation.

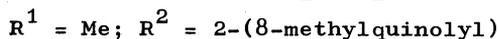
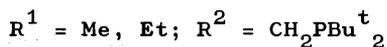
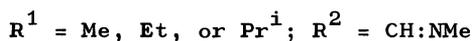
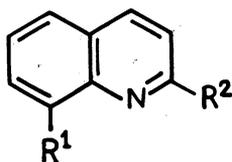
COORDINATION EFFECTS PRIOR TO METALLATION

We have synthesised a considerable number of square-planar complexes of Pd^{II} and Rh^{I} containing benzo[h]quinoline, 8-methyl-, ethyl-, or isopropyl-quinoline (7-9) which are easily prepared as long as there are no competing ligands in solution. A general route we have used is illustrated by the example below:



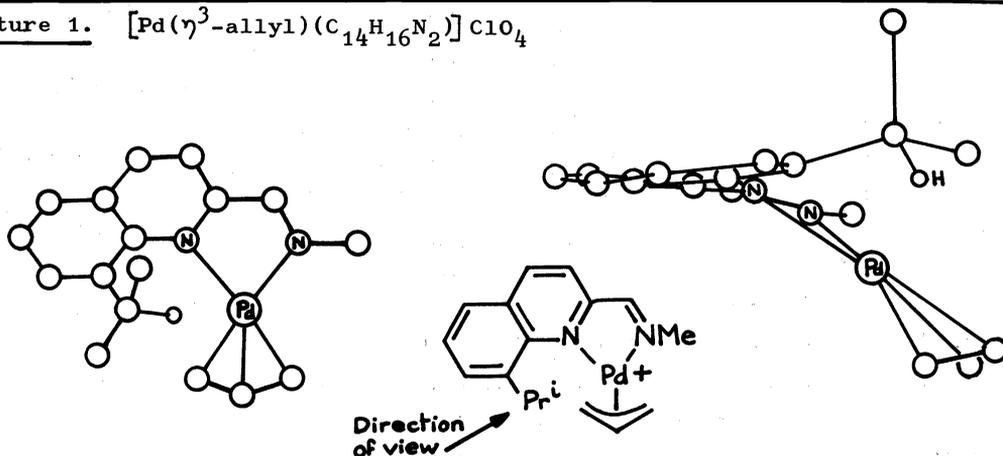
In all cases the closest approach of the hydrogen atoms of these monodentate ligands to the metal atoms is axial, established by X-ray diffraction for the compound shown and by large downfield ^1H n.m.r. shifts for the axially-positioned hydrogens. In the complex shown the 10-H...Pd distance is 2.09 Å, but although this is not very much greater than the sum of the covalent radii we believe that the interaction is repulsive. The ligand is tilted so as to increase this distance and equilibrium constants for the cleavage of chloro-bridged dimers of palladium are greater by a factor of 10^6 for 7-methylquinoline than for 8-methylquinoline (7). In other cases CH...M interactions (M = Mo, Fe, Os or Cu) appear to be stabilising (10-13).

Although axial CH...Pd interactions are destabilising, we felt that equatorial (in-plane) interactions of this sort might be stabilising. To test this we studied the coordination chemistry of some 2-substituted quinolines:

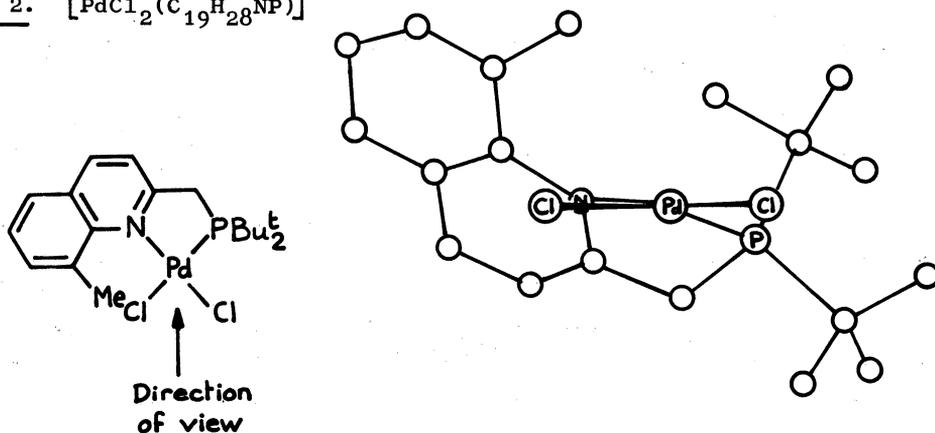


Three complexes containing these bidentate ligands have been shown to have structures 1-3 by X-ray diffraction (14-16).

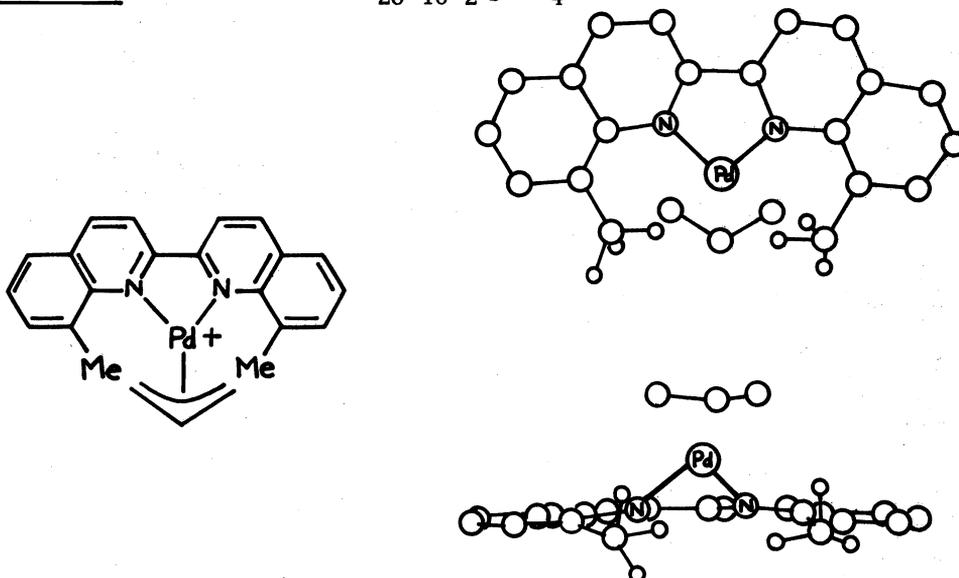
Structure 1. $[\text{Pd}(\eta^3\text{-allyl})(\text{C}_{14}\text{H}_{16}\text{N}_2)]\text{ClO}_4$



Structure 2. $[\text{PdCl}_2(\text{C}_{19}\text{H}_{28}\text{NP})]$



Structure 3. $[\text{Pd}(\eta^3\text{-allyl})(\text{C}_{20}\text{H}_{16}\text{N}_2)]\text{ClO}_4$

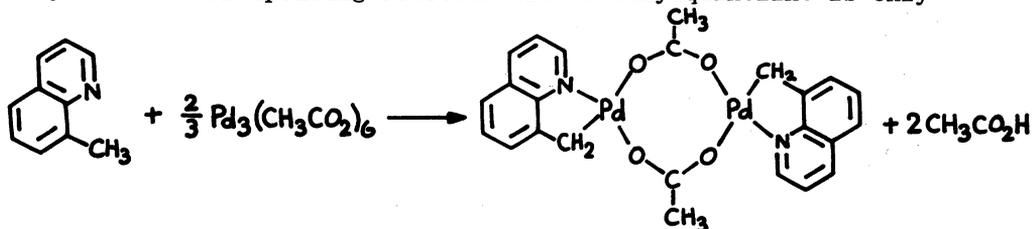


All three complexes (1-3 above) are essentially square-planar but show considerable distortions from idealised geometry so as to reduce the contact of the 8-alkyl groups with the Pd atoms and the cis-ligands. A notable feature is that the Pd atoms lie out of the planes of the quinoline ligands by as much as 1 Å or more, which is possible because of the pyramidal geometry at the nitrogen atoms. The only complex we isolated which indicated any 8-alkyl to metal bonding was $[\text{Rh}_2\text{Cl}_2(\text{CO})_3\text{L}]$ (where L is the phosphine ligand in compound 2 above) in which the 8-Me group showed coupling to ^{103}Rh and to ^{31}P in both the ^1H and ^{13}C spectra.

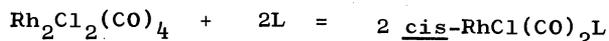
METALLATION REACTIONS

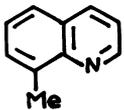
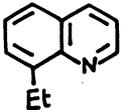
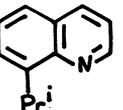
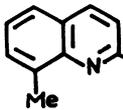
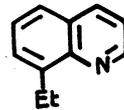
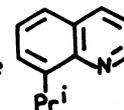
Effect of varying the 8-alkyl group

8-Methylquinoline metallates readily with palladium acetate in various solvents to give acetic acid and the acetato-bridged complex as a cis/trans mixture(13). The corresponding reaction with 8-ethylquinoline is only

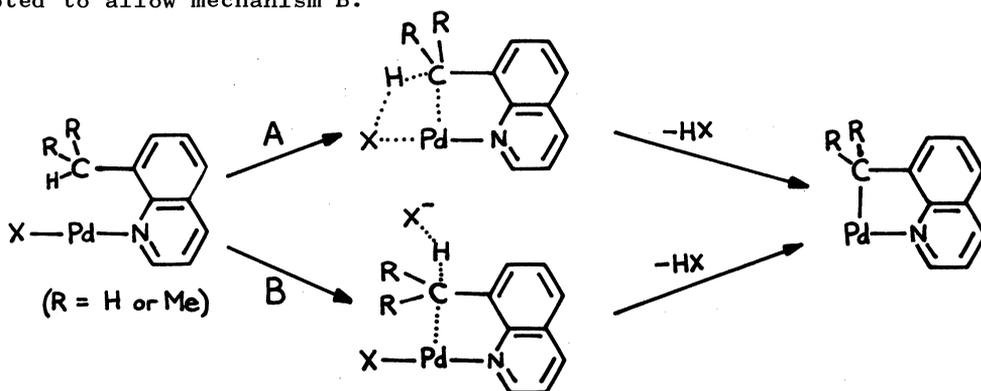


slightly slower, both reactions being complete within 2-3 hours at 30°C for 0.4 mol dm⁻³ solution in CDCl₃. 8-Isopropylquinoline is not palladated even under much more forcing conditions. This might reasonably reflect the relative coordinating abilities of these ligands which were assessed by measuring equilibrium constants for the reaction below at temperatures at which this reaction was slow enough to obtain separate ^1H n.m.r. signals for free and coordinated ligand L (Table 1).


 TABLE 1. Equilibrium constants /dm³mol⁻¹ (-25°C; CDCl₃)

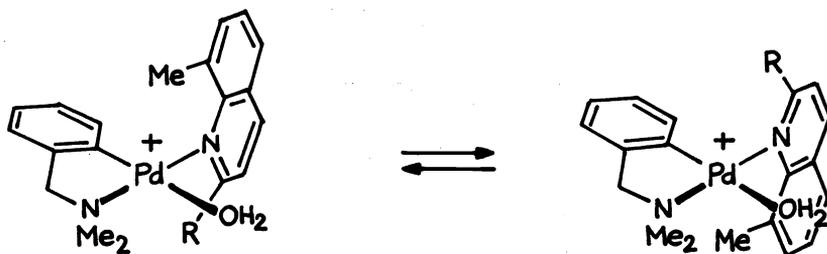
					
5.5x10 ⁴	2.7x10 ³	4.8x10 ²	90	15	0.8

It seems unlikely that differences of this order are sufficient to account for the total lack of metallation of 8-isopropylquinoline or any of the 2-Me substituted compounds. We have prepared complexes of 8-Prⁱ-quinoline and, although the CHMe₂ atom closely approaches Pd, there is no metallation. There is inadequate evidence to discuss intimate mechanisms at this stage, but while mechanism A (below) would be stereochemically possible or even favoured for isopropyl, the wrong conformation about the C-arene bond is adopted to allow mechanism B.

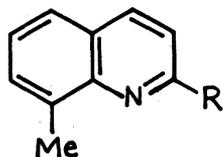


In-plane metallation

Whereas 8-methylquinoline metallates easily under mild conditions with tetrachloropalladate (II) or palladium acetate, 2,8-dimethylquinoline reacts with neither reagent even at elevated temperatures to give a cyclometallated product. One other important feature distinguishes these two ligands. From coalescence behaviour in the ¹H n.m.r. spectra we have shown that, when R = H, the process below is rapid at room temperature and involves the loss



of H_2O to allow the ligand to rotate into and through the coordination plane past the vacant cis site(8). When $R = Me$ the process is too slow to lead to n.m.r. coalescences even at $+60^\circ C$. Our interpretation is that the clash of the 2-Me group with the cis-ligand when the ligand and coordination planes are coincident makes movement into this spacial arrangement difficult, and that this arrangement is required for both the dynamic behaviour and cyclo-metallation(17). Furthermore, if the 2-substituent is a coordinating group, movement of the ligand into the coordination plane would be much more facile and we can indeed relate the ability to metallate at the 8-Me group with the coordinating ability of the 2-substituent.

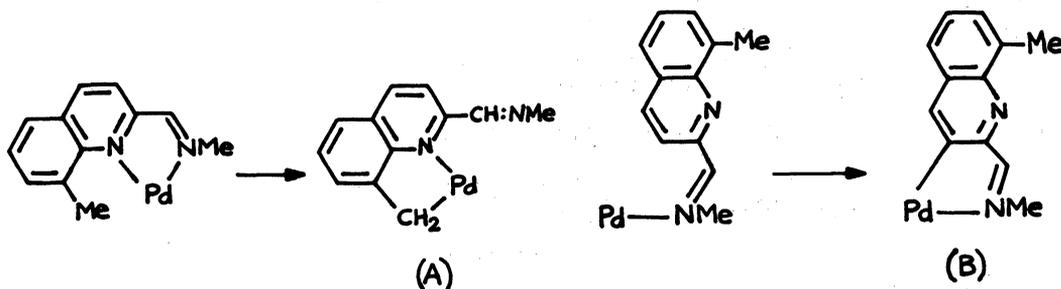


Ligands are readily metallated at 8-Me when
 $R = CH:NMe, CO_2H$ or CH_2OH .

Ligands not metallated at all at 8-Me when
 $R = Me, Br,$ or CHO .

Although the CHO group is potentially coordinating we believe that CO_2H and CH_2OH are much more strongly coordinating especially in their deprotonated forms.

The imine ligand ($R = CH:NMe$) can metallate either at the 8-Me group or at the 3-position of the heterocyclic ring depending upon whether the ligand is coordinated in a bidentate or monodentate manner when metallated.



With palladium acetate only the 8-Me-metallated product (A) is obtained, whereas with an excess of chloride more vigorous conditions are required but (B) is obtained. The dependence of the site of metallation on the nature of X (Cl or AcO) and on the X/Pd ratio is indicated in Table 2. We do not know whether in-plane metallation occurs in the formation of (B).

TABLE 2 Cyclometallation products when $R = CH:NMe$

X/Pd	Conditions	Isolated % yields		
		(A)	(B)	Other
2.0(AcO)	$CHCl_3$, 1 h, $40^\circ C$	95	0	0
2.0(Cl)	$CHCl_3$, 22h, reflux	0	0	83 ^(a)
2.0(Cl)	MeOH, 22h, reflux	37	16	0
4.0(Cl)	MeOH, 20h, reflux	17	23	0
5.5(Cl)	MeOH, 15h, reflux	0	52	16 ^(b)

(a) $PdCl_2L$, (b) $PdCl_2L_2$ (L = Unmetallated imine)

ACKNOWLEDGEMENTS

X-ray structures were determined by the group of Dr.M.B.Hursthouse at Queen Mary College London and Johnson Matthey Ltd loaned the PdCl₂ and RhCl₃ used in this work.

REFERENCES

1. J.Dehand and M.Pfeffer, Coordination Chem.Rev., **18**, 326 (1976).
2. M.I. Bruce, Angew.Chem.Int.Ed., **16**, 73 (1977).
3. M.I. Bruce, B.L. Goodall and F.G.A. Stone, J.C.S.Chem.Comm., 558 (1973) and J.C.S.Dalton, 687 (1978).
4. S. Hietkamp, D.J. Stufkins and K. Vrieze, J.Organometallic Chem., **168**, 351 (1979).
5. G.W. Parshall, Acc.Chem.Res., **3**, 139 (1970).
6. G.E. Hartwell, R.V. Lawrence and M.J. Smas, J.C.S.Chem.Comm., 912 (1970)
7. A.J. Deeming, I.P. Rothwell, M.B. Hursthouse and L. New, J.C.S.Dalton, 1490 (1978).
8. A.J. Deeming and I.P. Rothwell, J.C.S.Dalton, 1497 (1978).
9. A.J. Deeming and I.P. Rothwell, Inorg.Chim.Acta, 844 (1978).
10. F.A. Cotton, T.LaCour, and A.G. Stanislawski, J.Amer.Chem.Soc., **96**, 754 (1974).
11. J.M. Williams, R.K.Brown, A.J. Schultz, G.D. Stucky and S.D. Ittel, J.Amer.Chem.Soc., **100**, 7407 (1978).
12. R.B. Calvert and J.R. Shapley, J.Amer.Chem.Soc., **100**, 7726 (1978).
13. M. Pasquali, C. Floriani, A. Gaetani-Manfredotti and A. Chiesi-Villa, J.Amer.Chem.Soc., **100**, 4918 (1978).
14. A.J. Deeming, I.P. Rothwell, M.B. Hursthouse, K.M.A. Malik, J.C.S.Dalton, in press.
15. A.J. Deeming, I.P. Rothwell, M.B. Hursthouse, K.M.A. Malik, unpublished result.
16. A.J. Deeming, I.P. Rothwell, M.B. Hursthouse, J.D.J. Backer-Dirks, J.C.S.Chem.Comm., in press.
17. A.J. Deeming, and I.P. Rothwell, J.C.S.Chem.Comm., 344 (1978).