Bromination of 2-(Alkenyl)pyridine Complexes of Platinum(II)

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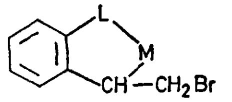
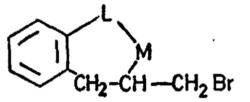
Summary Bromination of 2-(alkenyl)pyridine (L) complexes, *trans*-[$PtBr_2(PEt_3)L$], gives Pt^{IV}–C σ-bonded complexes and the mechanism of these and related reactions is discussed.

Bromination of platinum(II) and gold(I) complexes containing either *o*-styryldimethylarsine or *o*-styryldiphenylphosphine has been shown to give complexes containing group (**1**)[1–4] and bromination of analogous allylphenyl tertiary-phosphine and -arsine complexes gives related metal–carbon σ-bonded complexes containing group (**2**).[1,3,4]



(1)



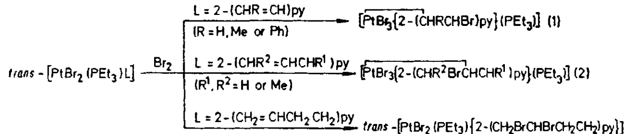
(2)

L = PPh2 or AsMe2
M = Au^{III} or Pt^{IV}

In an attempt to study the importance of steric–electronic factors controlling the site of metal–carbon σ-bond formation, we have studied the bromination of platinum(II) complexes containing 2-(alkenyl)pyridines and find that reactions (1)—(3) occur in benzene solution.†

It should be noted that in equation (1) when (a) R = H, only one conformer is obtained and metallation occurs at the β-carbon, [*cf.* group (**1**)], and (b), when R = Ph, the product is only obtained with the *cis*-olefin; the *trans*-olefin gives exclusively *trans*-[$PtBr_4(PEt_3)$ {*trans*-2($CHPh{=}CH$)py}]. Molecular models indicate that *trans*-addition of bromine and platinum to the olefin is only favourable for the *cis*-olefin.

We have prepared *trans*-[$PtBr_2(PEt_3)$ {2-($CH_2BrCHBr$)-py}] and *trans*-[$PtBr_4(PEt_3)$ {2-($CH_2{=}CH$)py}] and neither of these complexes react to give [$PtBr_3(PEt_3)$ {2-(CH_2-$CHBr$)py}]. Thus the brominations (1) and (2) probably involve a concerted mechanism similar to the one recently described by Bennett *et al.*[4] However, in order to rationalise the site of metallation we prefer to involve a conventional electrophilic addition of the polarised bromine molecule to the olefin with concomitant *trans*-nucleophilic attack by the metal on the incipient carbonium ion. Using these ideas the site of metallation is dependent on the stability of the carbonium ion and the results obtained for the bromination of 2-(alkenyl)pyridine and mono-olefinic-tertiary-phosphine and -arsine complexes can be rationalised. Thus, Markownikoff addition occurs except for complexes containing 2-(vinyl)- or 2-(substituted vinyl)-pyridines. In these cases, in keeping with results predicted[5] and found[6] for the free ligand, anti-Markownikoff addition occurs. However, where there is the possibility of the formation of 4- or 5-membered rings, it is always the sterically more favourable 5-membered ring that is formed and this may be as important as the carbonium ion stability discussed above. The ability of complexes containing these alkene ligands to undergo metallation on oxidation is a function of the proximity of the incipient carbonium ion to the nucleophilic metal. This is exemplified by the different products formed on oxidation of complexes containing *o*-allylphenyldiphenylphosphine (AP), *o*-allylphenyldimeth-



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† All the compounds have satisfactory analytical and molecular weight data and i.r. and Raman, and ^1H, ^{13}C, and ^{31}P n.m.r. data are completely in accord with the proposed formulations.

ylarsine (AA) and 2-($CH_2{=}CHCH_2CH_2$)py. The olefinic double bond in all these ligands is four carbon atoms removed from the other donor atom but only complexes containing (AP) and (AA) undergo metallation reactions on oxidation owing to the smaller degree of freedom enjoyed by the olefinic double bond in (AP) and (AA) compared to that in 2-($CH_2{=}CHCH_2CH_2$)py.

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[1] M. A. Bennett, J. Chatt, G. J. Erskine, J. Lewis, R. F. Long, and R. S. Nyholm, *J. Chem. Soc.* (*A*), **1967**, **501**.

[2] M. A. Bennett, G. J. Erskine, and R. S. Nyholm, *J. Chem. Soc.* (*A*), 1967, 1260.

[3] M. A. Bennett, W. R. Kneen, and R. S. Nyholm, *J. Organometallic Chem.*, 1971, **26**, 293.

[4] M. A. Bennett, K. Hoskins, W. R. Kneen, R. S. Nyholm, P. B. Hitchcock, R. Mason, G. B. Robertson, and A. D. C. Towl, *J. Amer. Chem. Soc.*, 1971, **93**, 293.

[5] Z. U. Kokoshko, V. G. Kitaeva, Z. V. Pushkareva, and V. E. Blokhin, *Zh. obshchei Khim.*, 1967, **37**, 58.

[6] I. E. Il'echev, V. S. Etlis, and A. P. Terent'ev, *Doklady Akad. Nauk S.S.S.R.*, 1969, **185**, 832.