Internal Metallation of N- or P-Donor Bidentate Ligands to give Multidentate Organometallic Compounds

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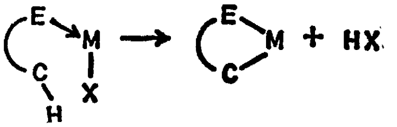
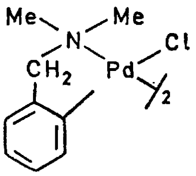
Summary Bidentate di-N- or di-P-donors are internally metallated by platinum or palladium very much less readily than analogous monodentate ligands but metallation can be promoted by increasing the chelate ring size from five to six and by using certain reagents.

There has been much interest in internal metallation of monodentate ligands by transition metals, as in equation (1), where M = Mn, Ru, Rh, Ir, Ni, Pd, Pt, *etc.*; E is generally N or P; X = halide, NO_3, H, Me, *etc.*, and the carbon atom metallated may be aliphatic, aromatic, or benzylic.[1–5] Some of the earliest work was by Cope and his co-workers with dialkylbenzylamines.[6] Thus, the internal palladation of dimethylbenzylamine occurs rapidly when Na_2PdCl_4 and $PhCH_2NMe_2$ are mixed in ethanol solution at 20° to give (I); an unmetallated intermediate has not been isolated. We find that, in contrast, the internal metallation of analogous chelating dibenzyldiamines to give multidentate organometallics normally proceeds only with great difficulty or not at all. We have, however, found that it is facilitated by increasing the size of the chelate rings from five- to six-membered and by the use of certain reagents. Thus, when Na_2PdCl_4 is treated with $PhCH_2(Me)NCH_2CH_2N(Me)CH_2Ph$ in methanol at 20° the chelate dichloride (II; $n = 2$, M = Pd, X = Cl) is formed as a mixture of ($\pm$)- and *meso*-isomers. Even on prolonged (several hours) heating in solvents such as ethanol this dichloride shows no tendency to undergo internal metallation. However, we have shown that acetate ion promotes internal metallation[5] and when heated with sodium acetate in ethanol for 30 min (II) is converted into (III; X = Cl). Attempts to effect further metallation and convert (III; $n = 2$, M = Pd, X = Cl) into (IV) have failed; *e.g.* (i) prolonged treatment with sodium acetate or (ii) heating the corresponding nitrate (II; X = NO_3), since nitrates are metallated more readily than chlorides. We have made analogous complexes with platinum (M = Pt, n = 2), but (III) resisted all attempts to effect further metallation to give (IV). It seems likely that the enormous difference between N-donor monodentates and analogous chelating diamines in their tendency to metallate is due to the rigidity of the chelate ring which restricts the approach of the *ortho*-carbon atom of the benzyl group towards the metal. We have studied the metallation of the corresponding substituted trimethylenediamine ligands (n = 3), expecting that the greater flexibility of the six-membered ring in (II) would enable the benzyl group to approach the metal and become metallated more easily. We have found this to be the case. Thus $PhCH_2(Me)NCH_2CH_2CH_2N(Me)CH_2Ph$ reacts with Na_2PdCl_4 to give (II) and after 16 h at 20° some (III). Compound (II; n = 3, M = Pd, X = Cl) was readily converted into (III) by sodium acetate. Similarly, the platinum complex (II; n = 3, X = Cl) on heating in xylene or 2-methoxyethanol gives (III), with some decomposition. Prolonged (10 days) reflux of (III; n = 3, M = Pt, X = Cl) in xylene gives some unchanged starting material and some of the dimetallated species (IV) as white plates, m.p. 293—300° (decomp.) in 20% yield. We often find that the complexes of types (II), (III), or (IV) occur as mixtures of the (±)- and *meso*-forms (n.m.r. evidence) which could be separated by t.l.c. on silica gel.

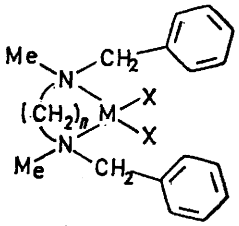


(1)

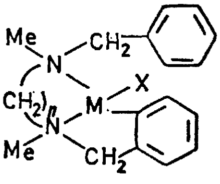
We have similarly found that chelating tertiary *o*-tolylphosphines undergo internal metallation much less readily than monodentate *o*-tolylphosphines: these are frequently metallated rapidly by platinum on the *o*-methyl group.[4] Thus the chelating phosphines $(o\text{-tolyl})_2P\,(CH_2)_nP(o\text{-tolyl})_2$ (n = 2 or 3), made from $(o\text{-tolyl})_2PLi$ and $Cl(CH_2)_2Cl$ or $Br(CH_2)_3Br$ are very resistant to internal metallation by Pd or Pt. Treatment of $[PtCl_2(Bu^tCN)_2]$ with the chelating diphosphines readily gives complexes of the type (V; X = Cl) but these are recovered essentially unchanged on heating in high boiling solvents (2-methoxyethanol, decalin, *etc.*) either alone or in the presence of sodium iodide or sodium acetate. Methyl groups on metals such as rhodium[7] or platinum[4] promote internal metallation of tertiary phosphine ligands. We prepared the dimethyl complexes (V; X = Me) for n = 2 and 3 by treating the dichlorides with methyl-lithium. On pyrolysis at 250° (V; n = 3, X = Me) loses 2 mol equiv. of methane and gives (VI), which is extremely stable thermally, melting without decomposition at 290—298°. We find that the five-membered ring chelate (V; n = 2, X = Me) requires a very high temperature (290°) before evolving methane and at this temperature blackening and decomposition occur.



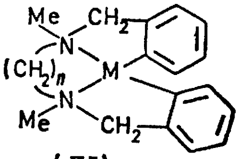
(I)



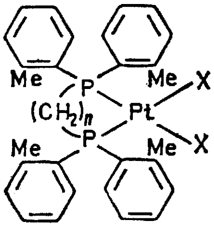
(II)



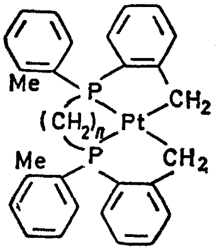
(III)



(IV)



(V)



(VI)

We were unable to isolate any internally metallated compounds with n = 2. This suggests that, as with the diamines, the greater flexibility of a six-membered ring chelate allows the metal to approach the *o*-methyl carbon atom more easily than with five-membered rings. We have prepared palladium analogues of (V) with X = Cl or Me but the chloride resisted attempts at internal metallation and the dimethyl complex went black on pyrolysis.

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