Tertiary Phosphine Palladium(0) Complexes

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Summary The co-ordination number of the phosphine complexes PdL_n may be 2, 3, or 4 depending on the steric hindrance of the phosphine and may change on going from the solid state into solution.

We have found that Pd^0 tertiary phosphine complexes of the type PdL_n ($n = 2,3,4$) can be prepared through displacement of the allyl ligand from $(2\text{-methylallylPdCl})_2$ by excess of phosphine. The behaviour of the Pd^0 complexes in solution has been studied by ^{13}C n.m.r.

The position of equilibrium $PdL_4 \rightleftharpoons PdL_3 + L$ lies well to the left for PdL_4 ($L = PMePh_2$) although ligand exchange occurs. The evidence is as follows: (a) the ^{13}C chemical shift separations of the PdL_4 complex do not vary on lowering the temperature; (b) the presence of undissociated PdL_4 at low temperatures is confirmed by the addition of free phosphine to the solution, when additional peaks from the free phosphine are observed; at room temperature exchange between co-ordinated and free phosphine occurs and the observed chemical shifts correspond to the appropriately weighted averages of PdL$_4$ and L. The ^{13}C chemical shifts (δ, p.p.m. ($\pm$0·1) downfield from Me$_4$Si, 22·62 MHz, CH$_2$Cl$_2$, 30°) obtained for CH$_3$, C-1, *o*-C, *m*-C, *p*-C are as follows: L, 12·6, 141·0, 132·5, *ca.* 128·6, *ca.* 128·6; PdL$_4$, 18·7, 144·1, 132·1, 127·9, 127·7; PdL$_4$ + L(1:1), 17·4, 143·3, 132·1, 127·9, 127·7.

A cryoscopic molecular weight determination provides further support that the tetrakis-PMePh$_2$ complex is practically undissociated in solution.† Similarly the tetrakis-complexes of PMe$_2$Ph (^{13}C n.m.r. and molecular weight) and PMe$_3$ (^{13}C n.m.r.) are not appreciably dissociated in solution.

For L = PEt$_3$ or PBu$^n_3$, PdL$_4$ complexes (white crystalline solids below 0°) are obtained in the preparative reaction; from them PdL$_3$ complexes (yellow oils) are obtained by pumping in high vacuum. The tetrakis-complexes of PEt$_3$ and PBu$^n_3$ are extensively dissociated to the tris-species in solution at room temperature. The ^{13}C chemical shifts of the PdL$_4$ complexes correspond to the weighted averages of those of PdL$_3$ and L in a 1:1 ratio [*e.g.* L = PEt$_3$, δ α–C and β–C: L, 19·5, 10·3; PdL$_3$ (THF) 23·4, 9·5; PdL$_4$ (THF) 22·6, 9·4]. Gerlach and his co-workers[2] have shown that Pt[PEt$_3$]$_4$ behaves similarly.

In the case of L = P(benzyl)$_3$, PdL$_3$ can be prepared and PdL$_4$ does not form in solution even in the presence of an excess of free phosphine; thus the ^{13}C spectrum of a 1:1 mixture of PdL$_3$ and L shows one set of signals at room temperature due to exchange average, but at low temperature it shows two sets of signals corresponding to PdL$_3$ and L [δ CH$_2$, C-1, *o*-C, *m*-C,*p*-C, 30°: L (CH$_2$Cl$_2$) 34·7, 138·3 129·5, 128·7, 126·1; PdL$_3$ (THF) 37·2, 137·9, 130·5, 128·2, 125·9; PdL$_3$ + L (1:1, THF) 36·6, 138·0, 130·2, 128·3, 125·9].

For L = PPr$^i_3$ the PdL$_3$ species, which is formed in the reaction, loses one molecule of L in high vacuum yielding the 14-electron PdL$_2$ complex and for L = P(cyclohexyl)$_3$ and PBu$^t_2$Ph, PdL$_2$‡ was isolated. The ^{13}C chemical shifts of a mixture of Pd[P(cyclohexyl)$_3$]$_2$ and P(cyclohexyl)$_3$ are weighted averages of the chemical shifts of the complex and of the free phosphine thus indicating that the equilibrium PdL$_2$ + L $\rightleftharpoons$ PdL$_3$ lies to the left [δ α–C, β–C, γ–C, δ–C (toluene) 30°: L, 32·2, 31·6, 28·0, 26·9; PdL$_2$, 34·9, 32·4, 28·1, 27·2; PdL$_2$ + L (1:1), 33·9, 32·2, *ca.* 28·2, *ca.* 27·2].

From the results given above the phosphines may be ordered according to their preference in forming complexes of low co-ordination numbers. PMe$_3$ $\sim$ PMe$_2$Ph $\sim$ PMePh$_2$ $<$ PPh$_3$[4] $\sim$ PEt$_3$ $\sim$ PBu$^n_3$ $<$ P(benzyl)$_3$ $<$ PPr$^i_3$ $<$ P(cyclohexyl)$_3$ $\sim$ PBu$^t_2$Ph. This order is clearly that of increasing steric hindrance and does not correlate well with the variation in the basicity of the phosphines. The 18 and 16 electron rule formulated by Tolman[5] requires a co-ordination number of 3 and 4 for Pd^0, but it is apparent from our results that if the ligands are too bulky then 14 electron two-co-ordinate complexes may be formed.

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† Clark and Itoh reached the same conclusion on the basis of a ^{1}H n.m.r. study,[1] although their evidence was less conclusive.

‡ The complex Pd[P(cyclohexyl)$_3$]$_2$ has been reported by other authors.[3] *X*-Ray structure determination has shown that this molecule is monomeric and has a bent geometry, the P–Pd–P angle being 158° (A. Immirzi, personal communication).

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