Carbonyl Insertion at Chloro(alkyl or aryl)(methyldiphenylphosphine)-carbonylplatinum: Critical Effects of Stereochemistry and the Nature of the Alkyl or Aryl Group

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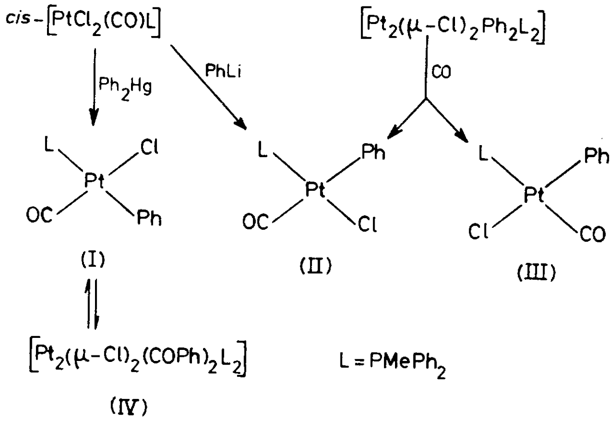
Summary The chloride-bridged acyl complexes $[Pt_2(\mu\text{-}Cl)_2(COR)_2(PMePh_2)_2]$ equilibrate with one isomer of $[PtClR(CO)(PMePh_2)]$ in solution, and the equilibrium position is critically dependent on the nature of R.

EARLY studies by Booth and Chatt[1] on the action of CO on *trans*-$[PtXR(PEt_3)_2]$ (X = halogen; R = Me, Et, or Ph) showed that carbonyl insertion into Pt–C bonds proceeded readily to give acyl complexes of the type *trans*-$[PtX(COR)(PEt_3)_2]$. Kinetic studies by Mawby,[2] Heck,[3] and their co-workers later established that the predominant reaction pathway involved acyl formation at a four-co-ordinate carbonyl complex $[PtXR(CO)(PR'_3)]$.

Previously we reported the formation of the bridged acyl complexes $[Pt_2(\mu\text{-}Cl)_2(COPh)_2(PR_3)_2]$ from the reaction between *cis*-$[PtCl_2(CO)(PR_3)]$ and diphenylmercury.[4] The reaction between *cis*-$[PtCl_2(CO)(PR_3)]$ and phenyl-lithium gave no insertion products. We now report that in chloroform solution the complex $[Pt_2(\mu\text{-}Cl)_2(COPh)_2(PMePh_2)_2]$ (IV) is in equilibrium with one isomer of $[PtClPh(CO)(PMePh_2)]$. The small phosphorus–platinum coupling constant (1402 Hz) confirms it to be isomer (I) (Scheme) with the phosphine and phenyl groups in mutually *trans* positions.[5]



SCHEME

The reaction between *cis*-$[PtCl_2(CO)(PMePh_2)]$ and phenyl-lithium, on the other hand, produces isomer (II), and treating $[Pt_2(\mu\text{-}Cl)_2Ph_2(PMePh_2)_2]$† with carbon monoxide yields a mixture of isomers (II) and (III) (Scheme). Attempts to promote carbonyl insertion at (II) and (III) by adding tertiary phosphine to their chloroform solution,

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† This material, produced from the reaction between $[Pt_2Cl_4(PMePh_2)_2]$ and Ph_2Hg, exists in solution as a mixture of *cis*- and *trans*-isomers.

or oxidising the platinum with Cl_2 failed. Carbon monoxide was eliminated in each case to give $[PtClPh(PMePh_2)_2]$ and the novel chloride-bridged phenylplatinum(IV) complex $[Pt_2Cl_6Ph_2(PMePh_2)_2]$ respectively. Heating solutions of (II) and (III) also led predominantly to CO loss, though small amounts of (I) and (IV) were produced. Slightly more of the acyl complex is formed when solutions of (II) and (III) are allowed to stand at room temperature for several days, and a slow isomerisation process may be responsible. It thus appears that isomer (I) is the principal reactive intermediate in the insertion scheme proposed by Heck,[3] and isomers (II) and/or (III), if they participate at all, do so either very slowly or *via* isomerisation to (I).

The key step in nucleophile-assisted CO insertion into manganese–carbon bonds involves migration of the organic group to a neighbouring carbonyl ligand.[6] If a similar mechanism operates at our square-planar platinum complexes, the critical dependence on the geometry of the isomers might be explained by the high *trans*-influence of the tertiary phosphine.[7] In isomer (I), $PMePh_2$ is *trans* to Ph and would labilise the Pt–C bond, allowing easy migration. In isomer (III), despite the favourable *cis* arrangement of CO and Ph, no such effect will operate.

When mercurials other than Ph_2Hg are allowed to react with *cis*-$[PtCl_2(CO)(PMePh_2)]$, the effect of the organic group on the equilibrium position between the acyl and the carbonyl complex analogous to (I) is critical. The amount of the acyl complex present decreases in the order R = Et (*ca.* 95%) > Ph > Me > CH_2Ph (*ca.* 0%). For R = CH_2Ph, only the terminal carbonyl complex $[PtCl(CH_2Ph)CO(PMePh_2)]$ could be detected spectroscopically or isolated as a solid, but slow addition to the solution of 1 mol equiv. of $PMePh_2$ produced the acyl complex *trans*-$[PtCl(COCH_2Ph)(PMePh_2)_2]$. We have no explanation at present for the order of the effects of the R groups on the equilibrium position. Similar sequences have emerged, however, from kinetic studies on carbonyl insertions and decarbonylations at other metals.[6]

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