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Preliminary communication

Reversible carbonylation of a rhodium(I) complex of *o*-(diphenylphosphino)-*N,N*-dimethylaniline involving displacement of the dimethylamino arm of the chelate

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SUMMARY

The coordinately unsaturated complex [Rh{(*o*-diphenylphosphino)-*N,N*-dimethylaniline}$_2$]PF$_6$ is described. This compound reversibly adds CO to form [Rh(PN)$_2$(CO)$_2$]PF$_6$ with the concomitant dissociation of the dimethylamino arms of the chelate.

Recently a number of cationic rhodium(I) complexes have been prepared where the univalent oxidation state is stabilized by phosphines, phosphites or chelating arsines[1-3] These complexes are coordinately unsaturated 16 electron molecules and are important in homogeneous catalysis. We wish now to report the synthesis of a 16 electron rhodium(I) compound which shows a novel reaction with carbon monoxide. In this reaction two molecules of CO coordinate to rhodium(I) by displacing the dimethylamino arms of the chelating ligands.

The ligand we have used in this work is *o*-(diphenylphosphino)-*N,N*-dimethylaniline, abbreviated to PN. This ligand can coordinate through the dimethylamino group and yet stabilize Rh^{I} because of the presence of a diphenylphosphino group. The use of a substituted nitrogen as one arm of the chelate is particularly important since it imparts a high nucleophilicity to the central metal atom. The complex [Rh(PN)$_2$]PF$_6$, designated compound I, ($\Lambda = 20.3$ ohm^{-1}·cm^{2}·equiv^{-1} in nitrobenzene) has been prepared by the reaction of Rh$_2$(C$_2$H$_4$)$_4$Cl$_2$ with 4 equivalents of PN in the presence of NH$_4$PF$_6$. This compound (I) is air sensitive in solution, but when isolated as orange crystals it is air stable for extended periods of time. This compound is the first complex of the PN ligand where two molecules of the bidentate are coordinated to the single metal[4,5]. The ^{1}H NMR spectrum of the compound shows a single resonance in the methyl region at τ 6.70, which represents a downfield shift of 40 ppm from the position of the methyl resonance in the free ligand. This shift is indicative of the nitrogen being coordinated. This spectrum has also been obtained at −27° and it is found that there is no change from the 35° spectrum. Although this shift difference on coordination is not as large as has been found with the complexes $Pt(PN)X_2$, this result is to be anticipated since Pt^{II} is more electron withdrawing than Rh^{I}.

When carbon monoxide is bubbled through a solution of (I) a new compound is formed with stoichiometry corresponding to $[Rh(PN)_2(CO)_2]PF_6$, designated compound II. The ^1H NMR spectrum of the complex again shows a single resonance due to the NMe_2 hydrogens, however the chemical shift is now at τ7.35. The position of this resonance corresponds exactly with that of the free ligand and is therefore consistent with the dimethylamino groups being uncoordinated*. This result is perfectly reasonable since the dimethylamino groups would not be expected to be good ligands for univalent rhodium(I), and the high nucleophilicity they confer to the metal would allow the ready attack by a good π-acceptor such as CO. The infrared spectrum of (II) shows a single band for the carbonyl at 1970 cm^{-1} which is consistent with a D_{2h} symmetry about the rhodium. This reaction involving coordination of CO with concomitant dissociation of the dimethylamino groups appears to be sterically unfavourable, however since the axial positions of complex (I) are vacant it can be envisaged that the CO can approach along this direction as shown diagrammatically in Fig. 1. An interesting feature of this carbonylation reaction is that it is readily reversible. When complex (II) is heated in boiling toluene the CO is eliminated from the complex to reform (I) where the dimethylamino groups are again coordinated.

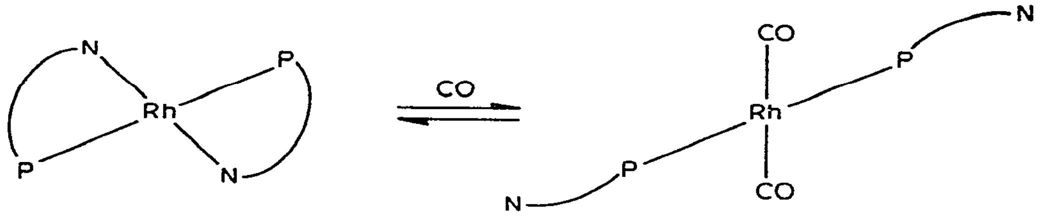

Fig.1. Diagrammatic representation of the carbonylation reaction of $[Rh(PN)_2]^+$.

An alternative approach to the synthesis of these complexes is possible from chlorodicarbonylrhodium dimer. Reaction of this compound with PN causes effervescence and formation of the air stable complex (PN)Rh(CO)Cl (ν(C=O) 1970 cm^{-1}). The ^1H NMR spectrum of this compound shows a singlet at τ6.70 characteristic of the coordinated dimethylamino group. This complex appears to be unreactive toward CO, however if the conditions are changed such that PN and NH_4PF_6 are also present, compound (II) is formed in high yield.

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* It has recently been reported[3] that the complex $[Rh(o\text{-vinylphenyldiphenylphosphine})_2]BPh_4$ will add a molecule of CO into the fifth coordination position. If the carbonylation of $Rh(PN)_2^+$ had occurred in a similar manner it would be expected that the π-acceptor ability of CO would further deshield the dimethylamino group and not shield it to coincidentally overlap the resonance of the free ligand.

We believe that the observation of a complex which will bond a π-acceptor ligand with simultaneous loss of one of the chelating arms gives support to the mechanistic ideas recently proposed for *syn/anti* exchange of allyls by palladium complexes[6], and a rather speculative mechanism for the polymerization of olefins by iron dipyridyl complexes[7]. Furthermore, kinetic studies on the substitution reactions of tetracarbonylchromium complexes of 2,4-dithiahexane[8], 2,2,7,7-tetramethyl-3,6-dithiaoctane[9] and 1,2-bis(diphenylarsino)-ethane[10] have produced evidence for the reversible dissociation of one end of the ligand. In each case a mechanism has been suggested which involves dissociation of one arm of a chelating ligand. Further studies on these and similar systems are presently being carried out and will be reported at a later date.

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