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Conversion of the Carbonyl Group in Chlorocarbonyl((*o*-diphenylphosphino)-*N*,*N*-dimethylaniline)iridium(I) and Chlorocarbonyl((*o*-diphenylphosphino)-*N*, *N*-dimethylbenzylamine)iridium(I) into Carbon Dioxide by Reaction with Molecular Oxygen

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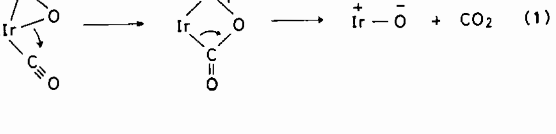
Recently we showed by a single crystal structure determination that the complex chlorocarbonyl((*o*-diphenylphosphino)-*N*,*N*-dimethylaniline)iridium(I), IrCl(CO)PN has a planar geometry and a stereochemistry with mutually *trans* dimethylamino and carbonyl ligands [1]. Furthermore, from spectroscopic comparisons we concluded that the same stereochemistry was adopted for the complex chlorocarbonyl ((*o*-diphenylphosphino)-*N*,*N*-dimethylbenzylamine)iridium(I), IrCl(CO)PCN. We now report that these complexes react with oxygen under ambient conditions with complete loss of carbonyl ligand. The reaction is not reversible and yields carbon dioxide and a blue hydroxy-bridged iridium complex. Previous reports of the oxidation of a coordinated carbonyl group are rather few, especially under conditions where water or hydroxide ions are absent [2–4].

When oxygen is passed through a yellow solution of IrCl(CO)PCN or IrCl(CO)PN in benzene or dichloromethane solvent a bule-green compound is gradually formed over a period of 3–6 hours in 90% yield. The complexes precipitate from benzene solution, or they can be isolated from dichloromethane solvent by addition of diethyl ether. The following data have been found for compounds $[Ir(OH)O_2(PCN)]_2Cl_2$ (I) and $[Ir(OH)O_2(PN)]_2Cl_2$(II): *Anal.* (I); Found: C, 42.2; H, 4.09; N, 2.02; Cl, 6.56%; Calcd. C, 42.3; H, 3.89; N, 2.35; Cl, 5.95%. ν(OH) 3550 cm^{-1}, δ(OH) 1650 cm^{-1}. M. pt. Decomposes at 140 °C. *Anal.* (II); Found: C, 39.6; H, 3.65; N, 2.37; Cl, 5.95; O, 9.17%; Calcd. C 41.3; H, 3.64; N, 2.41; Cl, 6.09; O, 8.25%. ν(OH) 3450 cm^{-1}, δ(OH) 1650 cm^{-1}. M.pt. Decomposes at 190 °C. λ(max.) = 650 nm ($\epsilon = 10^4$). The products are formed even in benzene dried by distillation from $LiAlH_4$. Indeed, addition of water causes no apparent acceleration of the reaction and introduction of D_2O does not lead to changes in the infrared spectra of the products. The compounds show zero magnetic moment and the solids show no EPR signal. Purification of the complexes can be effected by precipitation from a dichloromethane solution upon addition of diethyl ether, but we have been unable to obtain the complex in crystalline form. The compounds are stable in the solid state and dichloromethane solutions do not oxidize triphenylphosphine.

The blue-green color of the complexes is a consequence of an absorption bond at 650 nm. This low energy charge transfer band resembles those found for complexes having more than one metal center, and we believe this transition is also likely to be an intermetallic charge transfer absorption. The complexes are soluble in dichloromethane, but solutions will change to a pale yellow compound after a few hours even in an atmosphere free of oxygen and water. The infrared spectrum of this fawn compound is indistinguishable from its precursor, and we interpret this behavior in terms of a dissociation reaction to maybe a monomeric species.

Loss of coordinated carbonyl and halide ligand by reaction with molecular oxygen is rather unexpected in iridium chemistry. The products show no band due to ν(IrCl), and the CO_2 formed has been identified by gas chromatography using a Supelco Carbosieve S. column. This reaction does not occur with $IrCl(CO)(PPh_3)_2$, since we find that oxygen adduct $IrCl(CO)(PPh_3)_2O_2$ remains unchanged even after 3 days' reaction with oxygen under ambient conditions. We believe that the difference in chemistry of IrCl(CO)PN and IrCl(CO)PCN from that of $IrCl(CO)(PPh_3)_2$ is caused by the electronic and stereochemical effects induced by the aminophosphine ligands. The bond distance IrC for the carbonyl *trans* to the amine is unusually short because of π-backbonding, and possibly susceptible to nucleophilic attack. Since the reaction between IrCl(CO)(L–L) (L–L = PCN, PN) and O_2 occurs in the absence of protolytic medium we propose that the coordinated oxygen acts as a nucleophile to the coordinated carbonyl. Decarboxylation will yield an intermediate oxoiridium compound which will be unusually basic and susceptible to protonation and bridge formation (1).



This bridge formation will occur by a substitution reaction leading to chloride displacement by hydroxide ion. Compounds I and II show no infrared absorption due to ν(IrCl) and the respective conductivities (λ_M) for II in CH_2Cl_2 and CH_3NO_2 solvents are 17 and 75 ohm^{-1} cm^2 mol^{-1} for 10^{-3} *M* solutions. Because of the instability of II in solution we believe these values correspond to the conductivity of the dissociated product [5].

The reactivity pattern of IrCl(CO)PCN and IrCl(CO)PN with O_2 resembles the protolytic conversion of $PtO_2(PPh_3)_2$ into $Pt_2(\mu\text{-}O_2)(\mu\text{-}OH)(PPh_3)_4$ [6]. Furthermore, we and others [7] have observed that a blue solution is formed if oxygen is admitted during the preparation of $Li[IrCl_2(CO)_2]$. We believe it likely that this product is a similar one, and that its formation is a consequence of the reactivity of a coordinated O_2 to an electron-rich anionic carbonyl iridium(I) complex.

Acknowledgements

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