# An Oxidative Addition Reaction of *trans*-$[IrCl(N_2)(Ph_3)_2]$ in which the Dinitrogen Ligand is Retained in the Co-ordination Sphere of the Product

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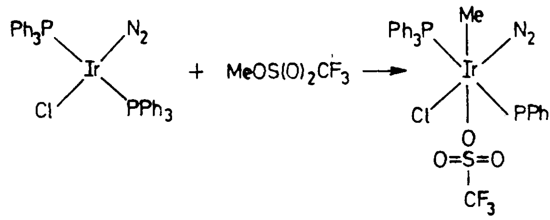
*Summary* *trans*-Chlorodinitrogenbis(triphenylphosphine) iridium(I) undergoes an oxidative addition reaction with methyl trifluoromethane-sulphonate to give a new dinitrogen complex of iridium(III) with a very high $\nu(N \equiv N)$ stretching frequency.

In general, transition metal dinitrogen complexes have been found to undergo reactions with loss of dinitrogen.[1] The iridium complex, $[IrCl(N_2)(PPh_3)_2]$, has been found to undergo the oxidative addition reaction with a wide range of reagents such as acyl halides,[2] sulphonyl halides,[3] hydrogen halides,[4] carboxylic acids[5] and anhydrides,[6] and carbon disulphide.[7] In only one case has a product been isolated that retained the dinitrogen as a ligand, namely in the reaction with diethyl maleate to give [IrCl$(N_2)(PPh_3)_2$(EtO$_2$CCH=CHCO$_2$Et)].[8] Upon addition of the diethyl maleate there is a shift of $\nu(N \equiv N)$ from 2095 to 2190 cm$^{-1}$. Presumably the general loss of dinitrogen upon oxidation of the metal indicates a decline in stability of the M–N$_2$ bond which parallels the decrease in M–N$_2$ $\pi$-bonding in complexes of higher oxidation states.[1]



(1)

The iridium dinitrogen complex has been found to react [see equation (1)] with a slight excess of methyl trifluoromethanesulphonate in benzene solution to give a cream product which contains 1 mole of benzene of solvation (decomp. 153—155 °C).† Its i.r. spectrum shows $\nu(N \equiv N)$ 2215s, $\nu$(Ir–Cl) 320w (Cl *trans* to N$_2$) and bands at 1328, 1230, and 1010 cm$^{-1}$ characteristic of the $CF_3SO_3^-$ anion. The i.r. spectrum in the region 2000—400 cm$^{-1}$ is nearly identical to that of the carbon monoxide analogue [$\nu(C \equiv O)$ 2065 and $\nu$ (Ir–Cl) 300 cm$^{-1}$] prepared from Vaska's complex, [IrCl$(O_3SCF_3)$(Me)$(PPh_3)_2$(CO)]. Preparation of the carbon monoxide analogue has been previously reported along with analogous adducts of methyl fluorosulphonate but no details were given.[9] The large shift ($\Delta\nu$ 120 cm$^{-1}$) in $\nu(N \equiv N)$ upon reaction gives this complex one of the highest values of the $\nu(N \equiv N)$ stretching frequency yet observed in a transition metal dinitrogen complex.[1] The shift is larger than that observed in $\nu(C \equiv O)$ for the carbonyl analogue ($\Delta\nu$ 100 cm$^{-1}$). The relative *trans* addition of the Me–OS(O)$_2$CF$_3$ is supported by the value of $\nu$(Ir–Cl) which is near that for Cl *trans* to N$_2$ in the iridium(I) complex (320 cm$^{-1}$). By analogy with oxidative addition reactions of Vaska's complex, the phosphines are assumed to remain *trans* in the octahedral complex.[10]

The complex loses dinitrogen in hot benzene to yield a transient red solution which turns light yellow during 3—4 min. The red colour is characteristic of five-coordinated complexes of iridium(III)[2] but the nature of the final product in solution has not yet been determined.

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† Satisfactory elemental analyses (C, H, Cl, and N) were obtained.

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