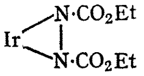
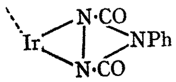
A Mononuclear Iridium Nitrene Complex

By J. ASHLEY-SMITH, M. GREEN, N. MAYNE, and F. G. A. STONE*
(*Department of Inorganic Chemistry, University of Bristol, Bristol* BS8 1TS)

Summary Hexafluoroazomethane reacts with *trans*-chlorocarbonylbis(methyldiphenylphosphine)iridium(I) to yield stable nitrene complexes, *cis*- and *trans*-$(Ph_2PMe)_2Ir(CO)(Cl)(NCF_3)$.

WHILE investigating oxidative-addition reactions of d^8 complexes, Collman and his co-workers[1] treated $(Ph_3P)_2Ir(CO)(Cl)$ with organic azides in the expectation that the adducts formed would extrude nitrogen and form nitrene complexes. Instead, the novel complex $(Ph_3P)_2Ir(N_2)(Cl)$ was obtained. Similarly, reactions between chlorocarbonylbis(methyldiphenylphosphine)iridium(I) and diethyl azodicarboxylate or 4-phenyl-1,2,4-triazoline-3,5-dione fail to break the nitrogen–nitrogen bonds in these ligands.[2] Instead, stable complexes are obtained in which the iridium–ligand bonding may, in valence-bond terminology, be depicted as the three-membered ring systems:





However, a localized molecular-orbital scheme involving three centres is more satisfactory and serves to emphasize the connection between metal-to-ligand back-bonding and interatomic distances between ligand atoms in complexes of this type.[3]

Treatment of a benzene solution of $(Ph_2PMe)_2Ir(CO)(Cl)$ with hexafluoroazomethane, a ligand with highly electronegative groups bonded to the nitrogen atoms, affords two complexes (I) and (II). The complex (I), m.p. 210°, which crystallises directly from the reaction solution with one molecule of benzene of crystallisation, is formulated as a trifluoromethylnitrene complex $CF_3NIr(CO)(Cl)(PPh_2Me)_2$. The i.r. spectrum shows a single sharp terminal carbonyl band at 2071·5 vs cm.$^{-1}$ (chloroform). The ^{19}F and ^1H n.m.r. spectra show, respectively, absorptions at 77·6 (s) p.p.m, (rel. CCl_3F), and τ 2·62 [20H (m), C_6H_5P], 2·72 [6H(s), C_6H_6], and 7·86 [6H(d), CH_3P, J_{HP} 11·0 c./sec.]. The appearance of the CH_3P ^1H n.m.r. signal as an apparent doublet suggests[4] a relative *cis*-configuration for the phosphine ligands.

The product obtained on removal of solvent, after separation of (I), gave on recrystallisation a white crystalline isomeric complex (II), $CF_3NIr(CO)(Cl)(PPh_2Me)_2$, m.p. 136—139°, which showed $\nu_{max}(CO)$ 2071·5 cm.$^{-1}$ (chloroform), a ^{19}F n.m.r. resonance at 76·0(s) p.p.m., and ^1H n.m.r. absorptions at τ 2·62 [20H(m), C_6H_5P] and 7·75 [6H(t), CH_3P, J_{HP} 4·5 c./sec.]. The apparent triplet at τ 7·75 indicates a relative *trans*-configuration for the phosphine ligands.

It is suggested that in (I) the benzene is incorporated in the crystal lattice and is not co-ordinated on to the iridium atom.[5] Thus (I) and (II) may be formulated as pentacoordinate iridium(I) nitrene complexes, and may have either trigonal bipyramidal or tetragonal pyramidal structures. The bonding between the iridium and the CF_3N ligand will involve donation of an electron pair from nitrogen to iridium with concomitant back-bonding from filled iridium *d*-orbitals to an empty *p*-type orbital of nitrogen, the electronegative trifluoromethyl group serving to enhance π-bonding.

In the formation of (I) and (II) from CF_3NNCF_3 the N–N bond is broken. Other experiments suggest that an adduct $(CF_3N_2CF_3)Ir(PPh_2Me)_2(CO)(Cl)$ is formed initially. Hence, under the reaction conditions back-bonding by iridium *d*-electrons into the empty azomethane π^*-antibonding orbitals apparently weakens and ultimately cleaves the N–N bond.

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