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Reaction of Trifluoroacetonitrile with π-Allylic-iridium Complexes; the Crystal Structure of an Iridium(I) Six-membered Ring Chelate Complex

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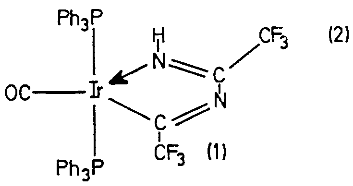
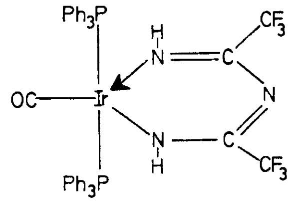
Summary $[Ir(\pi\text{-}2\text{-}Me\text{-}C_3H_4)(CO)(PPh_3)_2]$ reacts with CF_3CN to afford an iridium(I) six-membered chelate complex, identified by *X*-ray crystallography; whereas, with $[Ir(\pi\text{-}1\text{-}MeC_3H_4)(CO)(PPh_3)_2]$ C_4H_6 is displaced and a five-membered ring system is formed from two CF_3CN molecules joined head to tail.

THE reaction of charged[1] and uncharged electrophiles[2] with unsaturated organic molecules, which are co-ordinated to low-valent transition metal species, is a subject of current interest. Although the conversion on protonation of a co-ordinated π-allyl ligand into an olefin is well known, the related reactions with unchanged electrophiles have received little attention. In investigating the reaction of trifluoroacetonitrile with π-allylic iridium(I) complexes, we have discovered two unusual insertion reactions.

Treatment of a solution of carbonyl-(π-2-methylallyl)bis-(triphenylphosphine)iridium[3] in benzene with an excess of trifluoroacetonitrile resulted in the formation (room temperature; 2 days) of the complex (I) [orange crystals, m.p. 195—197°, ν_{CO}(Nujol) 1973 cm^{-1}; ^1H n.m.r. resonances ($CDCl_3$) at τ −0·27 br (s, 1H, NH), 2·12 br (s, 1H, NH), 2·4 (m, 5H, Ph), 4·66 (s, 1H, $C{=}CH_2$), 5·07 (s, 1H, $C{=}CH_2$), and 8·12 (s, 3H, Me); ^{19}F resonances (CH_2Cl_2) at 63·9 p.p.m. (s, 3F, CF_3) and 69·3 (s, 3F, CF_3)] characterised as a 1 : 2 adduct by elemental analysis and mass spectroscopy. The absence of absorption in the i.r. spectrum attributable to ν_{CN} discounted the possibility of co-ordinated ($CF_3C{\equiv}N \rightarrow Ir$) trifluoroacetonitrile; moreover, the n.m.r. data suggested the possibility that (I) had an unusual chelate structure.



(II)



(III)

An *X*-ray crystallographic study was therefore undertaken, establishing the illustrated structure (Figure). *Crystal data:* $C_{27}H_{22}F_6IrN_2OP$, $M = 727{\cdot}7$, orange monoclinic crystals, space group $P2_1/c$, $a = 15{\cdot}615(9)$, $b = 10418(6)$, $c = 17{\cdot}816(11)$ Å, $\beta = 113{\cdot}68(5)°$, $U = 2654{\cdot}3$ Å^3, $D_m = 1805$, $Z = 4$, $D_c = 1812$ kg m^{-3}; Mo-K_α radiation, $\lambda = 0{\cdot}71069$ Å, μ(Mo-K_α) $= 548$ m^{-1}. Monochromated data for 3277 planes were measured on a linear diffractometer, corrected for absorption, and refined to an *R* of 0·045.

The central iridium atom exhibits square-planar coordination with Ir–P = 2·271(3), Ir–Cl(1) = 1·831(13), Ir–N(1) = 2·028(10), and Ir–N(2) = 2·023(9) Å. All atoms, except fluorine, hydrogen, C(26), C(27), and the carbons of the phenyl groups lie close to the co-ordination plane. Bonds of the same type in the heterocyclic ring have the same lengths, within the error limits of the analysis, N–C = 1·321(16), C–C = 1·410(17)Å. The CH_3–C=CH_2 group is inclined at nearly 90° to the plane of the heterocyclic ring, presumably because of repulsions from the bulky CF_3 groups.

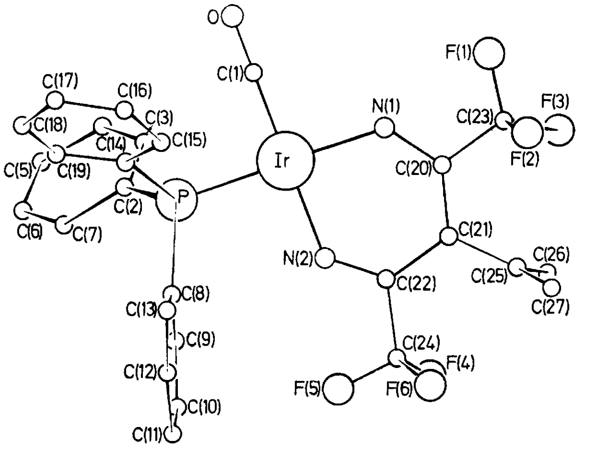


FIGURE. Structure of complex (I)

Thus, in this unusual reaction two CF_3CN groups have each become bonded to the same terminal carbon atom of the original π-2-methylallyl ligand, displacing it from the iridium, while themselves becoming co-ordinated to the metal through their nitrogen atoms, forming a six-membered chelate ring.

In contrast, reaction of carbonyl-(π-1-methylallyl)bis(triphenylphosphine)iridium with trifluoroacetonitrile afforded orange crystals of (II) [m.p. 241—243°, ν_{CO}(hexane) 1990, ν_{CN}(Nujol) 1500 cm^{-1}; ^1H resonances ($CDCl_3$) at τ 2·5 br (s, 1H, NH) and 2·9 (m, 5H, Ph); ^{19}F resonances (CH_2Cl_2) at 62·8 p.p.m. [t, 3F, CF_3(1), J_{PF} 14·0 Hz] and 67·7 [t, CF_3(2), J_{PF} 8·5 Hz], where the couplings were established by $^{19}F\{^{31}P\}$ decoupling experiments]. Elemental analysis and mass spectroscopy confirmed that the reaction involved loss of C_4H_6, a process which can be understood in terms of the reverse of the addition of Ir–H to buta-1,3-diene.[3] These observations suggested the structure shown for (II), in which head-to-tail dimerisation of CF_3CN affords a five-membered chelate ring, the transfer of hydrogen from iridium to nitrogen completing the reaction.

The corresponding reaction of carbonyl-(π-allyl)bis(triphenylphosphine)iridium with CF_3CN affords an analogue of (I) together with a variable low yield of a yellow crystalline complex (III) (m.p. 164—165°), which on the basis of analytical and spectroscopic evidence is formulated as shown, and is clearly related to the product of the reaction of CF_3CN with $[Pt(PPh_3)_4]$.[4]

The formation in (I) and (II) of chelate ring systems has also led us to reconsider the identity of the product of the reaction of CF_3CN with $[FeMe(CO)_2(\pi\text{-}C_5H_5)]$, formulated by King and Pannell as $[Fe\{C(CF_3)=NH\}(CF_3CN)(\pi\text{-}C_5H_5)]$.[5] A preliminary crystal structure determination, shows that in fact this species contains the five-membered chelate structure present in (II).

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