Reaction of Tetrafluoroethylene and Hexafluorobut-2-yne with Nitrosyltris(triphenylphosphine)iridium: *X*-Ray Diffraction Study of Di-μ-hexafluorobut-2-enylene-bis-[*cis*-triphenylphosphinenitrosyliridium(I)]

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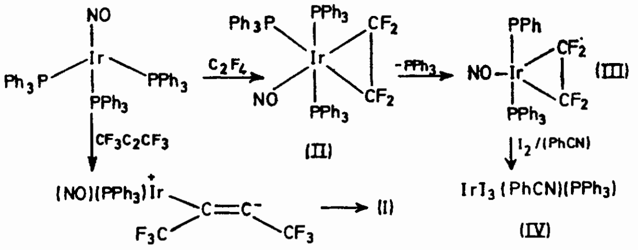
Summary Hexafluorobut-2-yne reacts with $Ir(NO)(PPh_3)_3$ to form a complex whose identity was established by *X*-ray crystallography as di-μ-hexafluorobut-2-enylene-bis-[*cis*-triphenylphosphinenitrosyliridium(I)]; tetrafluoroethylene reacts to form $Ir(NO)(C_2F_4)(PPh_3)_3$ which readily loses one molecule of PPh_3.

Recent studies[1-3] have shown that co-ordination of electronegatively substituted unsaturated molecules on to d^{10} Ni, Pd, and Pt systems can lead to interesting changes in the chemistry of the co-ordinated species. The report[4] of an improved synthesis of nitrosyltris(triphenylphosphine)-iridium and its oxidative-elimination reactions with acids, halogens, and alkyl halides provided an opportunity to study such effects in a system electronically similar to the d^{10} triad.

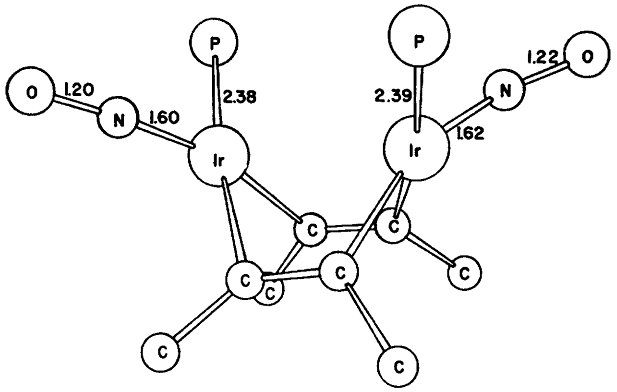
Hexafluorobut-2-yne, which reacts with Ni^0 complexes[5] to form hexakis(trifluoromethyl)benzene complexes and with Pd^0 and Pt^0 to form mono-acetylene and metallocyclopentadiene complexes,[6-8] reacts (20°; 3 days) with $Ir(NO)(PPh_3)_3$ to give the green crystalline complex (I) [m.p. 198—199°; ν_{NO}, 1780s cm^{-1}; ^{19}F n.m.r. resonances at 51·8 (q, J_{FF} 11·5 Hz) and 53·8 p.p.m. (m, J_{FF} 11·5 Hz)]. Molecular-weight measurements in solution indicated an unusual binuclear structure, and attempts at the oxidative displacement of $CF_3C_2CF_3$ from (I) with I_2–benzonitrile were unsuccessful. The crystal and molecular structure of (I) was therefore determined from three-dimensional *X*-ray data collected on a Picker, card-controlled, four-circle diffractometer using Zr-filtered Mo-K_α radiation.



The complex (I) crystallizes in space-group $P2_1/c$-$C_{2h}{}^5$ of the monoclinic system with four dimeric molecules in a unit cell of dimensions $a = 21{\cdot}852(9)$, $b = 10{\cdot}890(4)$, $c =$

20·318(8) Å, $\beta = 97{\cdot}51(2)°$. Using the 1891 observed reflections of the 3087 measured to a limiting 2θ of 35°, the co-ordinates of the two Ir atoms were obtained from a three-dimensional Patterson function. A heavy-atom structure-factor calculation followed by a series of difference Fourier syntheses and block-diagonal least-squares refinement revealed the remainder of the molecule. A difference map revealed partial occupation by methylene dichloride of some disordered sites close to a centre of symmetry. With account taken of this last feature, the refinement has converged at $R_1 = 0{\cdot}065$ and $R_2 = 0{\cdot}067$.

A perspective view of the co-ordination about iridium is shown in the Figure. The geometry about each Ir is essentially square planar with NO, P, and one carbon atom of each of the hexafluorobut-2-enylene ligands in this plane. The Ir–N–O angles are 157(2) and 171(2)° respectively. Although the first of these angles deviates considerably from 180°, it is only just outside the range previously found for complexes of NO$^+$.[9] Thus we feel that the best description of the complex is that it contains two NO$^+$ ligands. Average carbon-carbon distances in the hexafluorobut-2-enylene ligands are C–C = 1·52(5) Å and C=C = 1·27(3) Å. The latter distance is consistent with the bond order being reduced from three to essentially two. The average Ir–C distance is 2·05(3) Å.



Figure

The formation of a complex of this kind has not been previously observed. It is possible that (I) arises by dimerisation of an ionic dipolar intermediate,[10] *i.e.* $CF_3\text{-}\overset{-}{C}{=}C(CF_3)\overset{+}{Ir}(NO)(PPh_3)_2$, the so-called insertion mechanism not providing a rationale for the formation of (I).

Tetrafluoroethylene reacts slowly with $Ir(NO)(PPh_3)_3$ to form orange crystals of (II) [ν_{NO} 1600 cm^{-1}], which dissociate in solution to give the brown crystalline complex (III) [m.p. 163—164°, ν_{NO} 1680 cm^{-1}, ^{19}F n.m.r. resonance at 117·4 p.p.m. (t, J_{PF} 21·0 Hz)]. Reaction of (III) with I_2–benzonitrile led to the displacement of C_2F_4 and somewhat surprisingly to the loss of NO (possibly as NOI) with the formation of the five-co-ordinate iridium complex (IV) (m.p. 205—206°). The nitrosyl-stretching frequency of (III) is some 120 cm^{-1} higher than that found for the related complexes $IrX_2(NO)(PPh_3)_2$ (X = Cl or I) depicted as a tetragonal pyramid with a bent (NO$^-$) nitrosyl group at the apex. This suggests that in the C_2F_4 complex the nitrosyl group is linear, the high π-back-bonding capability of C_2F_4 restricting the transfer of electron density to the nitrosyl group which is necessary for a bent configuration.

The complex (III) does not react with more C_2F_4 to form a iridio-octafluorocyclopentane suggesting a correspondence to Pt rather than Ni chemistry.

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