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Preliminary communication

AN ALKENE—ALKYNE METAL COMPLEX: THE PREPARATION AND CRYSTAL STRUCTURE OF CHLORO(CYCLOOCTA-1,5-DIENE)(HEXAFLUOROBUT-2-YNE)IRIDIUM(I) DIMER AND CHLORO(CYCLOOCTA-1,5-DIENYL)(HEXAFLUOROBUT-2-ENYL)IRIDIUM(III) DIMER

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Summary

Hexafluorobut-2-yne reacts with chloro(cycloocta-1,5-diene)iridium(I) dimer at 20 °C to give a complex $[IrCl(cod)(C_4F_6)]_2$ in which both the diene and the acetylene are π-coordinated to the same iridium atom; an isomeric product, $[IrCl(CCF_3{=}CHCF_3)(C_8H_{11})]_2$, is isolated from the same reactants at 90 °C.

Although there are many examples of complexes in which two alkenes are coordinated to the same metal atom, related complexes in which an alkene and an alkyne are coordinated to the same metal atom are unknown**. We now report that hexafluorobut-2-yne (C_4F_6) reacts, in diethyl ether, with chloro(cycloocta-1,5-diene)iridium(I) dimer at room temperature to give an adduct $\{IrCl(cod)(C_4F_6\}_2$ (I). The ^{19}F NMR spectrum of I exhibits two singlets at −6.45 and −11.54 ppm (relative to benzotrifluoride) and the IR spectrum shows a strong absorption at 1860 cm^{-1} (ν(C≡C)). These data are consistent with a rigidly bound π-complex of C_4F_6 with the metal. A single crystal X-ray structure determination shows the complex to be I, $C_{24}H_{24}Cl_2F_{12}Ir_2$ (mol. wt. 995.8) crystals of which are monoclinic, space group $P2_1/n$ with $a = 9.58$, $b = 12.61$, $c = 12.54$ Å, $\beta = 114.7°$, $U = 1376$ Å^3, $Z = 2$. Data were collected on a Stoe—Weissenberg diffractometer using monochromatic Mo-K_α radiation and were corrected for absorption. Block diagonal least-squares refinement reduced R to 0.048 for 2240 reflexions.

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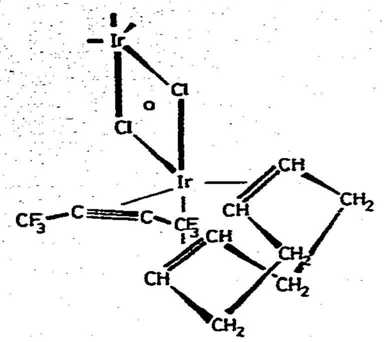
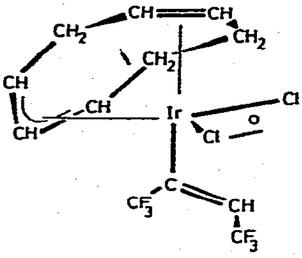
**The complex $Ru_4(CO)_{11}C_8H_{10}$ [1] contains coordinated cycloocta-1-ene-5-yne but the acetylenic carbon atoms are bonded to four metal atoms.



(I)



(II)

The dimer has a crystallographic centre of symmetry and the unique iridium atom exhibits approximate trigonal bipyramidal coordination (I). The detailed geometry of I is in excellent agreement with the recent conclusions of a theoretical treatment of pentacoordination in transition metal complexes [2]. The acetylenic bond and one of the olefinic bonds of cyclooctadiene lie approximately in the equatorial plane. The observed orientation of the cyclooctadiene ligand is geometrically favoured and is similar to that in other complexes [3] but there is no steric reason why the acetylene should lie in the equatorial plane. However, this orientation is in agreement with the prediction [2] that, for trigonal bipyramidal d^8 metal complexes, the π-interaction is strongest when the acceptor orbitals are in the equatorial plane (C_4F_6 is expected to be a good π-acceptor).

The axial Ir—Cl bond (2.438(3) Å) is shorter than the equatorial Ir—Cl bond (2.508(3) Å) following the predicted [2] greater strength of an axial σ-bond for a d^8 metal complex. The distances Ir—M_1 and Ir—M_2 * are equal with values of 2.066 and 2.062 Å, because in the case of π-acceptor ligands the relative preferences for strong σ- or π-interactions for axial and equatorial sites oppose each other. However, the Ir—M_3 distance is shorter (2.017 Å) suggesting that the C_4F_6 ligand is more strongly bound to iridium than the olefin.

We have recently investigated [4] the equivalent reaction with chloro(cycloocta-1,5-diene)rhodium(I) dimer and it seems likely that an intermediate in this reaction also contains a π-bonded C_4F_6 molecule. The corresponding reaction at room temperature with the iridium complex presumably proceeds no further because the acetylene is more strongly coordinated to iridium than to rhodium.

We have also investigated the reaction of hexafluorobut-2-yne with $[IrCl(C_8H_{12})]_2$ at 80-90 °C. A single crystal X-ray structure determination shows the product to be II, $C_{24}H_{24}Cl_2F_{12}Ir_2 \cdot 2C_6D_6$ (mol. wt. 1163.8) crystals of which are monoclinic, space group $P2_1/n$ with $a = 10.97$, $b = 17.96$, $c = 11.63$ Å, $\beta = 127.4°$, $U = 1820$ Å^3, $Z = 2$. The data were collected and

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*M_1 and M_2 are respectively the midpoints of the equatorial and axial olefinic bonds and M_3 is the midpoint of the acetylenic bond.

corrected as for I. *R* is 0.071 for 1755 reflexions. The acetylene has abstracted a hydrogen atom, possibly from the cyclooctadiene ligand, to form a *cis*-vinylic group σ-bonded to iridium. The original cyclooctadiene, having lost a hydrogen atom, remains coordinated as the cycloocta-1,5-dienyl ligand. Mean bond lengths are Ir—Cl 2.467, Ir—C(allyl) 2.17, Ir—C(olefin) 2.36 and Ir—C(vinylic) 2.09 Å.

Acknowledgement

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