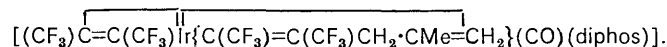


## Reactions of Co-ordinated Ligands. Part IX.<sup>1</sup> Insertion Reactions of $\pi$ -Allylic Iridium(I) Complexes with Hexafluorobut-2-yne †

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Reaction of hexafluorobut-2-yne (HFB) with  $[\text{Ir}(\pi\text{-allyl})(\text{CO})(\text{PPh}_3)_2]$  ( $\pi\text{-allyl} = \text{C}_3\text{H}_5$  or  $2\text{-MeC}_3\text{H}_4$ ) in toluene solution affords the *cis*-insertion products  $[\text{IrC}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{CH}_2\cdot\text{CR}=\text{CH}_2(\text{CO})_x(\text{PPh}_3)_y]$  ( $x = 1, y = 2; x = 2, y = 1; \text{R} = \text{H}$  or  $\text{Me}$ ) together with the *trans*-insertion 1:1 adduct  $[\text{Ir}\{\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{CH}_2\cdot\text{CR}=\text{CH}_2\}(\text{CO})\text{-}(\text{PPh}_3)_2]$ . When the reaction is carried out in a solvent mixture of toluene-methanol the complexes  $[\text{IrC}(\text{CF}_3)=\text{C}(\text{CF}_3)(\pi\text{-allyl})(\text{CO})(\text{PPh}_3)]$  are formed, the 2-methylallyl complex being transformed into a mixture of the *cis*- and *trans*-insertion products on treatment with triphenylphosphine. In toluene at  $-30^\circ\text{C}$ ,  $[\text{Ir}(\pi\text{-1-MeC}_3\text{H}_4)(\text{CO})(\text{PPh}_3)]$  reacts with HFB to give a very low yield of a *trans*-insertion product, whereas from a prolonged reaction in benzene the complexes  $[\text{Ir}\{\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{H}\}(1\text{-}4\eta\text{-C}_4\text{H}_6)(\text{CO})(\text{PPh}_3)]$  and  $[\text{IrC}(\text{CF}_3)=\text{C}(\text{CF}_3)\cdot\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)(\pi\text{-1-MeC}_3\text{H}_4)(\text{CO})(\text{PPh}_3)]$  were obtained. The corresponding reaction of  $[\text{Ir}(2\text{-MeC}_3\text{H}_4)(\text{CO})(\text{diphos})]$  affords a *cis*-insertion product together with the complex



The n.m.r. spectra of the complexes and possible mechanisms for their formation are discussed.

THE reaction of the electrophilic acetylene, hexafluorobut-2-yne (HFB), with a wide range of low-valent transition-metal species had led to a great deal of interesting chemistry. However, there has been relatively little work done on systems in which the acetylene becomes bonded to a co-ordinated organic molecule as is illustrated by the reaction of HFB or  $\text{C}_2(\text{CO}_2\text{Me})_2$  with nickelocene.<sup>2</sup> More recently, the complexes  $[\text{Co}(\pi\text{-2-MeC}_3\text{H}_4)(\text{CO})_3]$ <sup>3</sup> and  $[\text{PdCl}(\pi\text{-2-MeC}_3\text{H}_4)(\text{PMe}_2\text{Ph})]$ <sup>4</sup> have been shown to form respectively 1:2 and 1:1 adducts with HFB, reactions which formally correspond to the insertion of the acetylene into a carbon-to-metal bond. The reaction of HFB with acetylacetonato(cyclo-octa-1,5-diene)rhodium has been shown<sup>5</sup> to lead to the 1,4-addition of the acetylene to the acetylacetonato-ring, and the replacement of the  $1,5\text{-C}_8\text{H}_{12}$  by hexakis-trifluoromethylbenzene. A similar 1,4-addition of HFB occurs with acetylacetonato(norbornadiene)rhodium, but

† No reprints available.

<sup>1</sup> Part VIII, M. Green and B. Lewis, *J.C.S. Dalton*, 1975, preceding paper.

<sup>2</sup> D. W. McBride, E. Dudek, and F. G. A. Stone, *J. Chem. Soc.*, 1964, 1752; L. F. Dahl and C. H. Wei, *Inorg. Chem.*, 1963, 2, 713.

<sup>3</sup> A. Greco, M. Green, and F. G. A. Stone, *J. Chem. Soc. (A)*, 1971, 3476.

also one HFB molecule links the diene to the rhodium *via* a rhodacyclopentene ring. In this paper we describe an investigation of the reaction of HFB with  $\pi$ -allylic iridium(I) complexes. The new compounds obtained have been characterised by elemental analysis, and i.r., mass, and n.m.r. spectroscopy.

In investigating the reaction of HFB with triphenylphosphine-substituted  $\pi$ -allylic iridium(I) complexes a major difficulty is that the displaced triphenylphosphine initiates the polymerisation of the acetylene.<sup>6</sup> However, by carrying out the reactions at low temperatures it was possible to minimise this side reaction, and thus isolate organometallic species from the reaction mixtures, although often only in low yield.

Treatment ( $-30^\circ\text{C}$ ) of carbonyl( $\pi$ -2-methylallyl)bis-(triphenylphosphine)iridium<sup>7</sup> with hexafluorobut-2-yne in toluene solution led to the formation of the com-

<sup>4</sup> T. G. Appleton, H. C. Clark, R. C. Potter, and R. J. Puddephatt, *J. Organometallic Chem.*, 1972, 39, C13.

<sup>5</sup> D. M. Barlex, J. A. Evans, D. R. Russell, and R. D. W. Kemmitt, *Chem. Comm.*, 1971, 331; D. M. Barlex, A. C. Jarvis, B. Y. Kimura, and R. D. W. Kemmitt, *J.C.S. Dalton*, 1972, 2549.

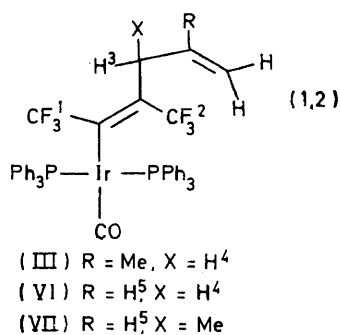
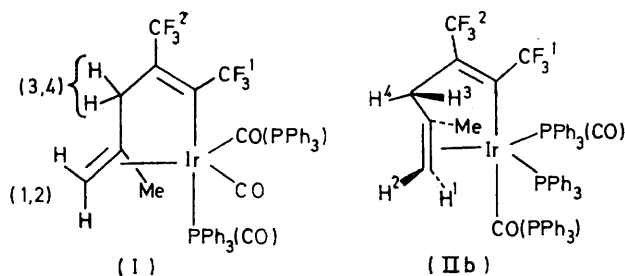
<sup>6</sup> W. R. Cullen and D. S. Dawson, *Canad. J. Chem.*, 1967, 45, 2887.

<sup>7</sup> C. K. Brown, M. Mowat, G. Yagupsky, and G. Wilkinson, *J. Chem. Soc. (A)*, 1971, 850.

plexes (I), (II), and (III), which were separated by column chromatography. Elemental analysis showed that, whereas (II) and (III) are 1:1 adducts of HFB and the  $\pi$ -allyl complex, the analytical results suggested that (I) was a dicarbonyl species, structurally similar to (II) but with only one triphenylphosphine ligand. In agreement the i.r. spectra of (II) and (III) showed a single terminal carbonyl band, whereas (I) showed bands at 2062 and 2014  $\text{cm}^{-1}$ . The absence in the spectra of all three complexes of a medium intensity band in the 1800–1700  $\text{cm}^{-1}$  region assignable to  $\text{IrC}(\text{CF}_3)=\text{C}(\text{CF}_3)$  implied that insertion reactions had occurred. Examination of the n.m.r. spectra confirmed this and suggested the illustrated structures.

The  $^{19}\text{F}$  n.m.r. spectra of (I) showed two resonances of equal intensity at 53.2 and 58.2 p.p.m., which were assigned to  $\text{CF}_3^1$  and  $\text{CF}_3^2$  respectively. In addition to the  $^{19}\text{F}$ – $^{19}\text{F}$  coupling of 15 Hz characteristic of *cis*-orientated  $\text{CF}_3$  groups, the high-field resonance had a doublet splitting of 5.5 Hz, which was shown by a heteronuclear decoupling experiment to arise from coupling with the  $^{31}\text{P}$  nucleus of the triphenylphosphine ligand. In the  $^1\text{H}$  n.m.r. spectrum the  $\text{H}^1$  and  $\text{H}^2$  protons appeared at  $\tau$  6.89 and 7.08, respectively, indicating that the terminal olefin is co-ordinated to the iridium. In general the  $^1\text{H}$  spectrum showed a similarity to that exhibited by the related  $^8\text{C}_2\text{F}_4$  insertion product, and was temperature invariant.

In contrast, the n.m.r. spectra of (II) were temperature



dependent. At  $-30^\circ\text{C}$  the  $^{19}\text{F}$  spectrum showed two resonances at 45.5 and 58.8 p.p.m. In addition to the quartet coupling [ $J(\text{FF})$  14.0 Hz] both resonances showed phosphorus coupling [ $J(\text{CF}_3^1\text{P})$  22.0 Hz and  $J(\text{CF}_3^2\text{P})$  5.0 Hz]. On warming to room temperature the fine structure was lost giving two broad signals. In the corresponding  $^1\text{H}$  spectrum measured at  $-30^\circ\text{C}$

the methyl protons appeared as a doublet due to  $^{31}\text{P}$  coupling; such a coupling has been established<sup>8</sup> in the related tetrafluoroethylene adducts. At ambient temperature and up to  $80^\circ\text{C}$  the doublet splitting was lost giving a single sharp resonance. Of the remaining four resonances attributable to  $\text{H}^1$ ,  $\text{H}^2$ ,  $\text{H}^3$ , and  $\text{H}^4$  none have chemical shifts below  $\tau$  7.3, either at  $-30^\circ\text{C}$  or at higher temperatures, suggesting that the terminal olefin remains co-ordinated to the iridium.

The two resonances at  $\tau$  7.7 and 7.8, which show an early loss of fine structure at  $0^\circ\text{C}$ , are assigned to the olefinic protons  $\text{H}^1$  and  $\text{H}^2$ , since geminal coupling of 1.0 Hz is observable between them in the expanded spectra at 60 and  $80^\circ\text{C}$ . The resonances at  $\tau$  7.3 and 9.0 (at  $-30^\circ\text{C}$ ) can hence be assigned to the methylene protons  $\text{H}^4$  and  $\text{H}^3$ , respectively, showing a geminal coupling of 18 Hz. On raising the temperature, the  $\text{H}^3$  and  $\text{H}^4$  signals collapse and reappear in the spectrum measured at  $80^\circ\text{C}$  close to the  $\text{H}^1$  and  $\text{H}^2$  signals. Since the solvent effect on these changes is negligible, and no change in the spectrum was observed on addition of triphenylphosphine, it is suggested that the complex exists as a single isomer in solution at room temperature, but intramolecular isomerisation, caused by rotation about the olefin–iridium bonding axis, occurs at higher temperatures resulting in an averaged spectrum being observed.

Of the two possible isomers, (IIb), with the olefin lying perpendicular to the equatorial plane, is proposed to be the structure preferred at low temperatures. Examination of molecular models shows the environment of  $\text{H}^3$  and  $\text{H}^4$  to differ considerably in this structure, and greater shielding of  $\text{H}^3$  by the metal might be expected. Such a separation of chemical shifts cannot be explained by structure (IIa) in which the olefin is lying in the equatorial plane as in (I), and where  $\text{H}^3$  and  $\text{H}^4$  appear to be in closely similar environments, experiencing only relatively slight shielding by the iridium, as is reflected in the similar shifts for  $\text{H}^3$  and  $\text{H}^4$ . That ready isomerisation occurs with complex (II) and not with (I) is not easily explained, although it is interesting that a similar effect was found<sup>8</sup> with the related  $\text{C}_2\text{F}_4$  insertion products on introduction of an additional triphenylphosphine ligand.

Examination of the n.m.r. spectra of the complex (III), which as noted above is a 1:1 adduct of HFB and  $[\text{Ir}(\pi\text{-2-MeC}_3\text{H}_4)(\text{CO})(\text{PPh}_3)_2]$ , showed that a *trans*-insertion had occurred and that the complex had the illustrated structure. The  $^{19}\text{F}$  n.m.r. spectrum of (III) showed resonances at 46.9 and 58.9 p.p.m., assigned to  $\text{CF}_3^1$  and  $\text{CF}_3^2$  respectively. However, the largest coupling observable is 3.5 Hz indicating that the two trifluoromethyl groups have a relative *trans*-configuration.<sup>9,10</sup> Such an arrangement would require that the olefin of the allyl group is not co-ordinated onto the iridium, and in agreement the i.r. spectrum shows, in

<sup>8</sup> M. Green and S. H. Taylor, *J.C.S. Dalton*, 1975, 1128.

<sup>9</sup> J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution N.M.R. Spectroscopy,' Pergamon Press, Oxford, 1966, vol. 2.

<sup>10</sup> G. V. D. Tiers, *J. Phys. Chem.*, 1962, **66**, 1192.

addition to one terminal carbonyl band, a band at  $1645\text{ cm}^{-1}$  assignable to  $\nu_{\text{C}=\text{C}}$  of a free double bond. The  $^1\text{H}$  n.m.r. spectrum confirmed this conclusion showing resonances at  $\tau$  5.64 and 6.16 assignable to the olefinic protons  $\text{H}^1$  and  $\text{H}^2$ ; the  $\text{H}^3$  and  $\text{H}^4$  resonances at  $\tau$  7.7 are coincident owing to the unrestricted rotation about a C-C bond.

The corresponding reaction of  $[\text{Ir}(\pi\text{-C}_3\text{H}_5)(\text{CO})(\text{PPh}_3)_2]$  with hexafluorobut-2-yne in toluene gave a low yield (5%) of only the one product (VI), a 1:1 adduct, which by comparison of spectroscopic data was established as the *trans*-insertion product.

The formation of both *cis*- and *trans*-insertion products in the same reaction is particularly interesting, and suggested that HFB can react with  $\pi$ -allylic iridium(I) complexes by at least two different reaction paths. In examining this question further it was found that there was a considerable solvent effect on the reaction.

Reaction of  $[\text{Ir}(2\text{-MeC}_3\text{H}_4)(\text{CO})(\text{PPh}_3)_2]$  with HFB in toluene-methanol\* (9:1) afforded only one product (34%), the crystalline complex (IV). The i.r. spectrum exhibited carbonyl absorptions at 2015, 2005, and 2002  $\text{cm}^{-1}$  and two weak  $\nu_{\text{C}=\text{C}}$  bands at 1839 and 1822  $\text{cm}^{-1}$  together with a third medium intensity band at 1797  $\text{cm}^{-1}$ , characteristic of an isomeric mixture of complexes

containing the system  $\text{IrC}(\text{CF}_3)=\text{C}(\text{CF}_3)$ . Analysis indicated a formula  $[\text{Ir}(\text{HFB})(\text{C}_4\text{H}_7)(\text{CO})(\text{PPh}_3)]$ , which was confirmed by the evidence of the mass spectrum. Examination of the n.m.r. spectra showed bands corresponding to the major isomer, the signals due to the other isomers being of too low intensity (<10%) for detailed study, and suggested the illustrated structure for the major isomer.

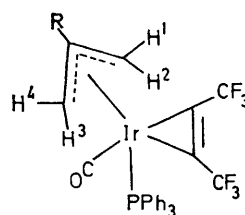
Both the  $^1\text{H}$  and  $^{19}\text{F}$  spectra of (IV) were temperature dependent. At  $-60^\circ\text{C}$ , two inequivalent  $\text{CF}_3$  resonances were apparent in the  $^{19}\text{F}$  spectrum at 50.9 and 55.6 p.p.m., assigned to  $\text{CF}_3^1$  and  $\text{CF}_3^2$ . The observed  $\text{CF}_3^1\text{-CF}_3^2$  coupling constant of 4.5 Hz is small for trifluoromethyl groups with an approximate relative *cis*-configuration, however, very similar coupling constants were recorded<sup>11</sup> between the inequivalent  $\text{CF}_3$

groups of the complexes  $[(\text{NO})\text{RuC}(\text{CF}_3)=\text{C}(\text{CF}_3)(\text{Cl}_2)\text{L}_2]$  ( $\text{L} = \text{PPh}_3, \text{PMe}_2\text{Ph}, \text{or PMe}_2\text{Ph}$ ). The small  $^{31}\text{P}\text{-}^{19}\text{F}$  couplings [ $J(\text{CF}_3^1\text{P})$  1.5 Hz,  $J(\text{CF}_3^2\text{P})$  2.0 Hz] imply a *cis*-orientation between each end of the co-ordinated acetylene and the triphenylphosphine ligand. As the temperature is raised to  $-20^\circ\text{C}$ , ambient, and  $60^\circ\text{C}$ , the two resonances progressively lose all resolution and are reduced in intensity. At  $60^\circ\text{C}$  (in  $\text{C}_6\text{H}_5\text{Cl}$  solution) irradiation of the  $\text{CF}_3^1$  signal causes complete disappearance of the  $\text{CF}_3^2$  signal, indicating that the two sites are undergoing exchange at a rate faster than their spin-lattice relaxation times.

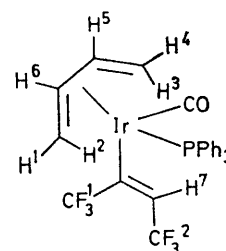
The low-temperature  $^1\text{H}$  n.m.r. spectrum was characteristic of the AGKPX<sub>3</sub> spin system of an asymmetric  $\pi$ -allyl complex, values of  $^{31}\text{P}\text{-}^1\text{H}$  coupling constants for

\* In the presence of MeOH the  $\text{PPh}_3$  initiated polymerisation of HFB is inhibited.

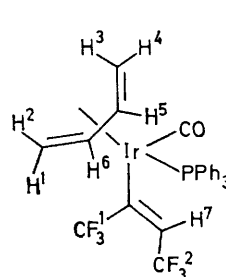
$\text{H}^1$  and  $\text{H}^2$  [ $J(\text{H}^1\text{P})$  3.0 Hz,  $J(\text{H}^2\text{P})$  10.0 Hz] agree well with those usually observed for the *syn*- and *anti*-protons *trans* to phosphine ligands. However, it is interesting that the chemical shifts of  $\text{H}^1$  and  $\text{H}^2$  ( $\tau$  6.89 and 8.74) are to high field of those of  $\text{H}^3$  and  $\text{H}^4$  ( $\tau$  6.47 and 6.13), since the Ir-C<sup>1</sup> bond, *trans* to  $\text{PPh}_3$ , would be expected to be weakened by the latter's strong *trans*-influence. Hence an increase in the C<sup>1</sup>-C<sup>2</sup> bond order relative to that of the C<sup>2</sup>-C<sup>3</sup> bond would be expected. It is possible that the orbitals used in back-bonding to the acetylene and  $\pi$ -allyl ligands are sufficiently compatible in this case for the acetylene to cause considerable



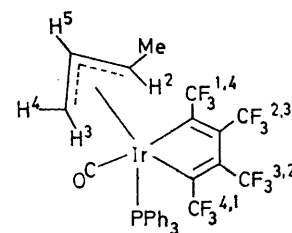
(IV) R = Me

(V) R = H<sup>5</sup>

(VIII)



(VIIIa)



(IX)

weakening of the Ir-C<sup>3</sup> bond, thus reversing the above order of bond strengths. This suggestion is consistent with the observed  $^1\text{H}$  n.m.r. temperature-dependent behaviour.

Irradiation of the  $\text{H}^1$  resonance at  $-60^\circ\text{C}$  caused a decrease in intensity of the  $\text{H}^2$  resonance, indicating that  $\text{H}^1$  and  $\text{H}^2$  are still undergoing site exchange even at this temperature. At ambient temperatures all peaks show a loss of resolution and the  $\text{H}^1$  and  $\text{H}^2$  resonances can be seen to approach one another. However, the high-temperature limiting spectrum could not be obtained due to decomposition becoming important. These observations suggest that fission of the weak Ir-C<sup>3</sup> bond leads to the formation of a formally five-co-ordinate  $\sigma$ -allyl intermediate with *syn-anti* exchange. Re-co-ordination of the olefinic bond can then occur at two possible faces leading to the effective site exchange of the  $\text{CF}_3^1$  and  $\text{CF}_3^2$  groups.

The corresponding reaction of  $[\text{Ir}(\pi\text{-C}_3\text{H}_5)(\text{CO})(\text{PPh}_3)_2]$  with HFB in the presence of dry methanol proceeded similarly, and afforded the analogous crystalline com-

<sup>11</sup> J. Clemens, M. Green, and F. G. A. Stone, *J.C.S. Dalton*, 1973, 375.

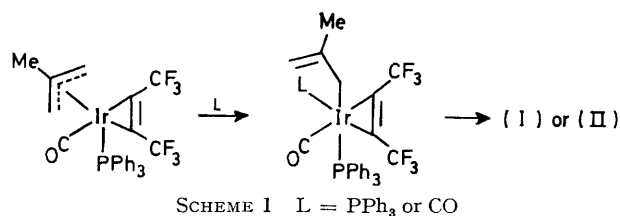
plex (V). The low-temperature ( $-60\text{ }^{\circ}\text{C}$ )  $^{19}\text{F}$  spectrum again showed inequivalent  $\text{CF}_3$  groups, which undergo site exchange at higher temperatures. The  $^1\text{H}$  spectrum ( $-60\text{ }^{\circ}\text{C}$ ) was typical of an AGKPX spin system of an asymmetric  $\pi$ -allyl complex, and *syn*- and *anti*-proton assignments suggested for (IV) could be confirmed for (V) by the magnitude of their couplings with the central allylic proton  $\text{H}^5$  (established by spin decoupling). A  $^{31}\text{P}$ - $^1\text{H}$  decoupling experiment established the values of  $J(\text{H}^1\text{P}) = 5.0\text{ Hz}$ , and  $J(\text{H}^2\text{P}) = 10.0\text{ Hz}$  assigned to coupling with a  $\text{PPh}_3$  ligand in a relative *trans*-position.

At higher temperatures all resolution was lost from the spectrum and at  $60\text{ }^{\circ}\text{C}$  (in  $\text{C}_6\text{H}_5\text{Cl}$  solution) only the  $\text{H}^5$  resonance was visible. Its appearance as a symmetrical quintet suggested that not only was *syn-anti* exchange occurring, but also left to right exchange (probably by a polytopal rearrangement of the five-coordinate  $\sigma$ -allyl intermediate), thus causing averaging of all four terminal allyl protons.

The complexes (IV) and (V) are clearly possible precursors of the *cis*-insertion products (I) and (II), since Clark and Puddephatt have shown<sup>12</sup> that the platinum

complex  $[\text{PtC}(\text{CF}_3)=\text{C}(\text{CF}_3)(\text{Cl})(\text{Me})\text{L}_2]$  can be converted into the *cis*-insertion product  $[\text{Pt}\{\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{Me}\}(\text{Cl})\text{L}_2]$  ( $\text{L} = \text{AsMe}_2\text{Ph}$ ), and further studies<sup>13</sup> on the reaction of  $[\text{Pt}(\text{Me})\text{Cl}(\text{PMe}_2\text{Ph})_2]$  with  $\text{C}_2(\text{CO}_2\text{Me})_2$  have shown that the conversion of the acetylene into the *cis*-insertion product involves a radical process.

When complex (IV) and an equimolar proportion of triphenylphosphine were refluxed together in benzene, examination of the spectra of the reaction mixture (after  $1\frac{1}{2}$  h) showed the presence of complexes (I) and (II), and also the *trans*-insertion product (III). Hence the entering carbon monoxide ligand (derived from a disproportionation reaction) or triphenylphosphine may occupy the vacant co-ordination site of the  $\sigma$ -allyl intermediate. Migration of the  $\sigma$ -bonded carbon atom of the allyl group on to the HFB ligand, possibly promoted by the co-ordination of the allyl olefinic group, would then lead to the formation of the insertion products (Scheme 1).



SCHEME 1  $\text{L} = \text{PPh}_3$  or CO

Further work will be required, however, to understand the details of the migration reaction.

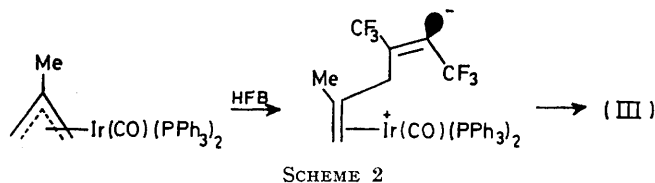
It is most unlikely that the *trans*-insertion adducts (III) and (VI) are formed directly from (IV) or (V) via an intramolecular process, and it is suggested that reaction of  $\text{PPh}_3$  with, for example, (IV) results in

<sup>12</sup> H. C. Clark and R. J. Puddephatt, *Inorg. Chem.*, 1971, **10**, 18.

<sup>13</sup> T. G. Appleton, M. H. Chisholm, and H. C. Clark, *J. Amer. Chem. Soc.*, 1972, **94**, 8912.

<sup>14</sup> W. P. Giering and M. Rosenblum, *J. Amer. Chem. Soc.*, 1971, **93**, 5299.

complete displacement of HFB to regenerate  $[\text{Ir}(\pi\text{-2-MeC}_3\text{H}_4)(\text{CO})(\text{PPh}_3)_2]$  which then reacts by an alternative reaction path with the liberated acetylene. Such an alternative pathway could involve either *exo*- or *endo*-attack by the acetylene on a carbon atom of the co-ordinated allyl group, followed by charge collapse (Scheme 2). Mechanisms of this kind have been con-



SCHEME 2

sidered for the reaction of tetracyanoethylene (TCNE) with  $[\text{Fe}(\text{CO})_2(\sigma\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{H}_5)]$ .<sup>14</sup> A further alternative, analogous to that proposed<sup>15,16</sup> for the *trans*-insertion of acetylenes into metal-hydrogen bonds, would involve nucleophilic attack by the iridium(i) species on the acetylene to give a *trans*-dipolar intermediate collapsing via bimolecular allyl transfer. Clearly, further studies will be required to establish the relative importance of these different reaction paths.

Reaction of  $[\text{Ir}(\pi\text{-1-MeC}_3\text{H}_4)(\text{CO})(\text{PPh}_3)_2]$  with HFB in toluene at  $-30\text{ }^{\circ}\text{C}$  again led to the *trans*-insertion adduct, (VII), this being the only product which could be isolated from the reaction mixture. However, analytical results were not obtained because the low yield (1%) prevented the isolation of sufficient crystalline material. The *trans*-insertion structure was, however, supported by the mass and i.r. spectra. Also both the  $^1\text{H}$  and  $^{19}\text{F}$  n.m.r. spectra of (VII) closely resembled those of (VI), except for the replacement of  $\text{H}^4$  by a methyl group. Thus insertion has occurred at the substituted end of the  $\pi$ -allyl ligand, in contrast to *cis*-insertion reactions, which usually occur at the unsubstituted end.<sup>4,17</sup> Hence a change in mechanism between *cis*- and *trans*-insertion reactions is emphasised, although the result does not enable a distinction to be made between the various mechanisms discussed.

In contrast, when  $[\text{Ir}(\pi\text{-1-MeC}_3\text{H}_4)(\text{CO})(\text{PPh}_3)_2]$  was allowed to react with HFB at room temperature in benzene over a prolonged period, two complexes (VIII) (6%) and (IX) (9%) were isolated in low yield by use of column chromatography. The crystalline complex (VIII) had an analysis consistent with its formulation as  $[\text{Ir}(\text{HFB})(\text{C}_4\text{H}_7)(\text{CO})(\text{PPh}_3)]$ , and showed a single terminal carbonyl band at  $2022\text{ cm}^{-1}$ . There was no evidence for a  $\nu_{\text{C}=\text{O}}$  absorption in the i.r. spectrum suggesting that some form of insertion reaction had occurred, this also being indicated by the presence of a band at  $1607\text{ cm}^{-1}$  characteristic of  $\text{MC}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{R}$ . This was confirmed by the n.m.r. spectra which were consistent with the illustrated vinyl structure.

<sup>15</sup> B. L. Booth and R. G. Hargreaves, *J. Chem. Soc. (A)*, 1969, 2766.

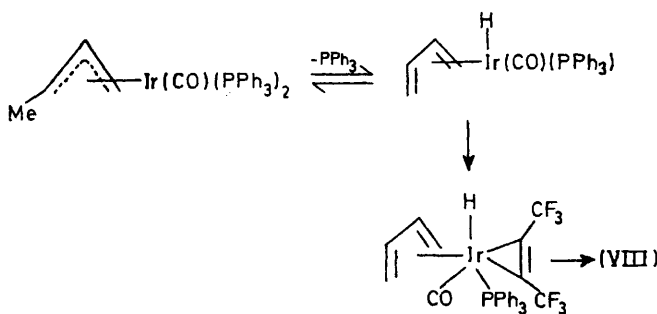
<sup>16</sup> J. A. Ibers and R. M. Kirchner, *J. Amer. Chem. Soc.*, 1973, **95**, 1095.

<sup>17</sup> R. P. Hughes and J. Powell, *J. Organometallic Chem.*, 1971, **30**, C45.

The  $^{19}\text{F}$  spectrum exhibited two inequivalent  $\text{CF}_3$  resonances at 56.6 and 58.0 p.p.m., of which the former is assigned to  $\text{CF}_3^1$  in the position  $\alpha$  to the metal. The  $\text{CF}_3^1$ - $\text{CF}_3^2$  coupling constant of 13.0 Hz establishes a *cis*-configuration between the two groups, while  $\text{CF}_3^2$  has an additional coupling of 10.0 Hz assignable to the geminal proton  $\text{H}^7$ . Both chemical shifts and coupling constants agree well with those reported<sup>18</sup> for  $[\text{Pt}\{\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{H}\}_2(\text{cod})]$  (cod = cyclo-octadiene), and evidence for the loss of a  $\text{C}_4\text{H}_6\text{F}_6$  fragment from the parent ion in the mass spectrum confirms the proposed vinylic structure.

The  $^1\text{H}$  spectrum exhibits resonances over a wide range of chemical shift. Although all six diene protons are inequivalent due to the overall asymmetry of the molecule, their resonances fall into three groups,  $\text{H}^5$  and  $\text{H}^6$ ,  $\text{H}^4$  and  $\text{H}^1$ , and  $\text{H}^3$  and  $\text{H}^2$ , for which the shifts compare well with those observed<sup>19,20</sup> for symmetric diene complexes.  $^{31}\text{P}$ -Decoupling experiments showed that all the diene protons except  $\text{H}^1$  and  $\text{H}^4$  are coupled to the  $^{31}\text{P}$  nucleus of the triphenylphosphine ligand. This has been interpreted in terms of structure (VIII) by a close approach between the  $\text{PPh}_3$  and  $\text{H}^2$  and  $\text{H}^3$ , involving 'through-space' couplings of  $J_{2,P}$  10.0 Hz and  $J_{3,P}$  7.5 Hz. This seems more likely than co-ordination of  $\text{PPh}_3$  *trans* to one olefinic bond since  $J_{2,P}$  and  $J_{3,P}$  are of the same order of magnitude. Co-ordination by the alternative face of the diene as in (VIIIa) is, however, possible when the vicinal dihedral angles between the  $^{31}\text{P}$  and  $^1\text{H}$  nuclei may explain the magnitude of their couplings.

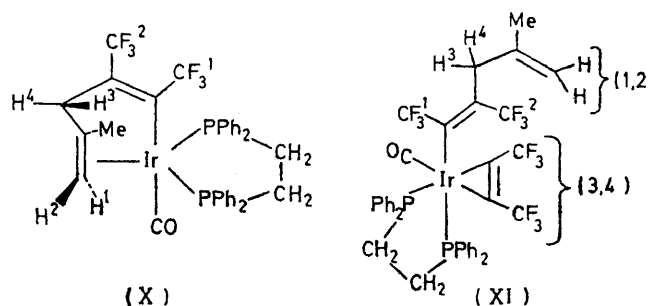
The formation of (VIII) is interesting in that it may be explained by postulating that an intermediate of the type frequently suggested to explain the isomerisation of  $\pi$ -allyl complexes<sup>21</sup> is intercepted by reaction with HFB (Scheme 3).



SCHEME 3

The second product, (IX), of the reaction analysed as  $[\text{Ir}(\text{HFB})_2(\text{C}_4\text{H}_7)(\text{CO})(\text{PPh}_3)]$ , and showed in the i.r. spectrum a terminal carbonyl band at  $2059\text{ cm}^{-1}$  and weak  $\nu_{\text{C}=\text{C}}$  bands at  $1572$  and  $1522\text{ cm}^{-1}$ . Analysis of

the n.m.r. spectra suggested that (IX) had the illustrated iridacyclopentadiene structure.



The  $^1\text{H}$  spectrum was typical of an  $\text{AGKPX}_3$  spin system of a methyl-substituted  $\pi$ -allyl complex, however, the shifts are at lower field than those of the related

tetrafluoroethylene complex,  $[\text{IrCF}_2\text{CF}_2(\pi\text{-1-MeC}_3\text{H}_4)(\text{CO})(\text{PPh}_3)]$ .<sup>8</sup> A  $^{31}\text{P}$ -decoupling experiment established that only  $\text{H}^2$  and the methyl group exhibit significant  $^{31}\text{P}$  coupling, and hence the triphenylphosphine ligand is assumed to occupy the position *trans* to one end ( $\text{CH}^2\text{Me}$ ) of the  $\pi$ -allyl ligand. The  $^{31}\text{P}$ -decoupled  $\text{H}^2$  resonance approximates to a sextet, which can be rationalised as an overlapping doublet ( $J_{2,5}$  11.0 Hz) of quartets ( $J_{2,\text{Me}}$  5.5 Hz). Hence the proposed structure is that of the *syn*-methyl isomer.

Four inequivalent  $\text{CF}_3$  resonances were apparent in the  $^{19}\text{F}$  spectrum. Two quartets at lower field (49.1 and 51.5 p.p.m.) were assigned to the  $\alpha$ -groups  $\text{CF}_3^1$  and  $\text{CF}_3^4$ , and two septets at higher field (56.4 and 57.5 p.p.m.) were characteristic of the  $\beta$ -groups  $\text{CF}_3^2$  and  $\text{CF}_3^3$ , respectively. Irradiation of the  $\text{CF}_3^1$  resonance collapsed the  $\text{CF}_3^2$  septet to a quartet, establishing that the two groups are attached to adjacent carbon atoms. Similarly, irradiation of  $\text{CF}_3^4$  collapsed  $\text{CF}_3^3$  to a quartet. The magnitude of the coupling constants involved,  $J(\text{CF}_3^1\text{-CF}_3^2) = J(\text{CF}_3^2\text{-CF}_3^3) = 15\text{ Hz}$ , and  $J(\text{CF}_3^3\text{-CF}_3^4) = 16\text{ Hz}$ , confirm a mutual *cis*-configuration for all adjacent groups.

The formation of iridacyclopentadienes in the reaction of electronegatively substituted acetylenes with iridium(I) complexes has been previously observed<sup>22</sup> and possible mechanisms discussed,<sup>23</sup> which are equally applicable to the formation of (IX). The complex (IX) is, however, the first example of such a system, which also contains a  $\pi$ -allylic ligand, and the possibility of a ring-opening reaction, involving migration of the allyl group from iridium to a carbon atom of the cyclopentadiene ring, is being examined.

When  $[\text{Ir}(\pi\text{-2-MeC}_3\text{H}_4)(\text{CO})(\text{diphos})]$  was allowed to react with HFB in the absence of methanol, no polymerisation of the acetylene was observed and the products (X) and (XI) were isolated in reasonable yield. The

<sup>18</sup> J. Browning, H. D. Empsall, M. Green, and F. G. A. Stone, *J.C.S. Dalton*, 1973, 381.

<sup>19</sup> M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1959, 3753.

<sup>20</sup> J. C. Davis, jun., and H. G. Preston, *J. Amer. Chem. Soc.*, 1966, **88**, 1585.

<sup>21</sup> M. A. Cairns, J. F. Nixon, and B. Wilkins, *J.C.S. Chem. Comm.*, 1973, 86.

<sup>22</sup> J. P. Collman, J. W. Kang, W. F. Little, and M. F. Sullivan, *Inorg. Chem.*, 1968, **7**, 1298.

<sup>23</sup> R. Burt, M. Cooke, and M. Green, *J. Chem. Soc. (A)*, 1970, 2981.

complex (X) is tentatively characterised as an analogue of the *cis*-insertion product, (II), the low solubility of the complex limiting n.m.r. measurements. The occurrence of the H<sup>3</sup> resonance in the <sup>1</sup>H spectrum at  $\tau$  9.54 is interpreted as evidence that (X) exists as a single isomer in solution at ambient temperature of similar structure to that adopted by (II) in solution at  $-30^\circ\text{C}$ . Whether fluxional behaviour is displayed by (X) at higher temperatures is unknown, since the low solubility and thermal decomposition prevented variable-temperature studies.

The second product (XI) isolated was characterised as a 1:2 adduct, and the presence of a  $\nu_{\text{C}=\text{O}}$  band at  $1756\text{ cm}^{-1}$  together with a terminal carbonyl band at  $2020\text{ cm}^{-1}$  suggested the presence of a  $\pi$ -co-ordinated hexafluorobut-2-yne ligand. This was confirmed by the n.m.r. spectra, which established a structure in which both  $\pi$ -bonding of the HFB, and insertion of the acetylene into a carbon-iridium bond has occurred.

Three resonances were observed in the <sup>19</sup>F n.m.r. spectrum at 42.6, 52.7, and 54.2 p.p.m. with relative intensities 1:1:2, and are assigned respectively to CF<sub>3</sub><sup>1</sup>, CF<sub>3</sub><sup>3</sup>, and coincident CF<sub>3</sub><sup>2</sup> and CF<sub>3</sub><sup>4</sup>; no <sup>19</sup>F-<sup>19</sup>F couplings greater than 5.0 Hz were observed. The presence of a large <sup>31</sup>P-<sup>19</sup>F coupling of 19.0 Hz in the CF<sub>3</sub><sup>1</sup> resonance suggests that the IrC(CF<sub>3</sub>)=C(CF<sub>3</sub>)R (R = allyl) group is *trans* to one end of the diphos ligand.

The formation of (XI) resembles the reaction of tetra-cyanoethylene or HFB with iridium(I) hydrides where both oxidative  $\pi$ -bonding of TCNE or HFB, and insertion into the Ir-H bond occurs.<sup>24-26</sup>

#### EXPERIMENTAL

The spectroscopic data were obtained by the methods outlined in Part V of this series. The <sup>1</sup>H{<sup>31</sup>P} and <sup>19</sup>F{<sup>31</sup>P} decoupling experiments were carried out by the INDOR technique. All reactions were carried out in an oxygen-free nitrogen atmosphere or in Carius tubes *in vacuo*.

**Reactions of Hexafluorobut-2-yne.**—(a) *With carbonyl( $\pi$ -methylallyl)bis(triphenylphosphine)iridium.* An excess of hexafluorobut-2-yne (3 mmol) was condensed ( $-196^\circ\text{C}$ ) into a Carius tube containing a solution of carbonyl( $\pi$ -methylallyl)bis(triphenylphosphine)iridium (0.5 g, 0.63 mmol) in toluene (30 ml). The tube and contents were kept at  $-30^\circ\text{C}$  for 3 days, although immediate polymerisation of the acetylene was evident. The solvent was removed *in vacuo* and the benzene-hexane (1:1)-soluble material chromatographed on an alumina-packed column. Elution with benzene-hexane (1:9) gave a fraction, which, on recrystallisation from methylene chloride-hexane, afforded colourless crystals of (I) (0.017 g, 4%), m.p.  $157-159^\circ\text{C}$  (decomp.) (Found: C, 46.2; H, 3.1; F, 15.8; P, 4.5). C<sub>28</sub>H<sub>22</sub>F<sub>6</sub>IrO<sub>2</sub>P requires C, 46.2; H, 3.0; F, 15.7; P, 4.3%),  $\nu_{\text{CO}}$  (hexane) 2062s and 2014s cm<sup>-1</sup>;  $\nu$  (Nujol) 3042w, 2067vs, 2013vs, 1601m, 1583w, 1569w, 1479m, 1432s, 1311m, 1272s, 1249s, 1219m, 1180w, 1151s, 1125s, 1100m, 1090m, 1047m, 966m, 932m, 840w, 751m, 747m, 739m, 695s, and 689m cm<sup>-1</sup>. The mass spectrum showed peaks at  $m/e$  700 (*P* - CO) and 672 (*P* - 2CO). The <sup>1</sup>H n.m.r.

spectrum (CDCl<sub>3</sub>) showed resonances at  $\tau$  2.60 (m, 15H, C<sub>6</sub>H<sub>5</sub>P), 6.89 (br, s, 1H, H<sup>1</sup>), 7.08 (br, s, 1H, H<sup>2</sup>), 7.57 (d, 1H, H<sup>3</sup>,  $J_{3,4}$  7.0 Hz), 7.96 (d, 1H, H<sup>4</sup>,  $J_{3,4}$  7.0 Hz), and 8.12 (s, 3H, Me). The <sup>19</sup>F n.m.r. spectrum (CH<sub>2</sub>Cl<sub>2</sub>) showed resonances at 53.2 p.p.m. [q, 3F, CF<sub>3</sub><sup>1</sup>,  $J(\text{CF}_3^1-\text{CF}_3^2)$  15 Hz] and 58.2 [qd, 3F, CF<sub>3</sub><sup>2</sup>,  $J(\text{CF}_3^1-\text{CF}_3^2)$  15 Hz,  $J(\text{CF}_3^2-\text{P})$  5.5 Hz].

Further elution with benzene-hexane (1:9) afforded a second fraction, which on recrystallisation from methylene chloride-hexane gave colourless crystals of (II) (0.07 g, 12%), m.p.  $192-194^\circ\text{C}$  (decomp.) (Found: C, 56.5; H, 3.9; F, 11.8; P, 6.4). C<sub>45</sub>H<sub>37</sub>F<sub>6</sub>IrOP requires C, 56.3; H, 3.9; F, 11.9; P, 6.5%),  $\nu_{\text{CO}}$  (hexane) 2011s;  $\nu$  (Nujol) 3055w, 3040w, 2010vs (CO), 1588w, 1577w, 1480m, 1434s, 1323w, 1275s, 1248s, 1219m, 1180m, 1154s, 1147s, 1122s, 1098s, 1087m, 1067w, 1045m, 1026w, 1000w, 929m, 748m, 735m, 725m, 698s, 681m, and 674 cm<sup>-1</sup>. The mass spectrum showed peaks at  $m/e$  700 (*P* - PPh<sub>3</sub>) and 672 (*P* - CO - PPh<sub>3</sub>). The <sup>1</sup>H n.m.r. spectrum (CD<sub>2</sub>Cl<sub>2</sub>,  $-30^\circ\text{C}$ ) showed resonances at  $\tau$  2.6 (m, 30H, C<sub>6</sub>H<sub>5</sub>P), 7.3 (m, 1H, H<sup>4</sup>,  $J_{3,4}$  18.0 Hz), 7.7-7.8 (m, 2H, H<sup>1</sup> and H<sup>2</sup>,  $J_{1,2}$  1.0 Hz), 8.24 [d, 3H, Me,  $J(\text{Me}-\text{P})$  9.0 Hz], and 9.0 (d, 1H, H<sup>3</sup>,  $J_{3,4}$  18.0 Hz). The <sup>19</sup>F n.m.r. spectrum (CH<sub>2</sub>Cl<sub>2</sub>,  $-30^\circ\text{C}$ ) showed resonances at 45.5 p.p.m. [qd, 3F, CF<sub>3</sub><sup>1</sup>,  $J(\text{CF}_3^1-\text{CF}_3^2)$  14 Hz,  $J(\text{CF}_3^1-\text{P})$  22 Hz], and 58.8 [qd, 3F, CF<sub>3</sub><sup>2</sup>,  $J(\text{CF}_3^1-\text{CF}_3^2)$  14 Hz,  $J(\text{CF}_3^2-\text{P})$  5.0 Hz].

Further elution afforded a third fraction, which was recrystallised ( $-30^\circ\text{C}$ ) from hexane to give yellow crystals of (III) (0.017 g, 3%), m.p.  $90-92^\circ\text{C}$  (Found: C, 56.6; H, 3.9). C<sub>45</sub>H<sub>37</sub>F<sub>6</sub>IrOP<sub>2</sub> requires C, 56.3; H, 3.9%),  $\nu_{\text{CO}}$  (hexane) 1979s;  $\nu$  (Nujol) 1960vs, 1645w, 1588w, 1573w, 1420m, 1435s, 1310m, 1229s, 1205s, 1149s, 1112s, 1095s, 1070s, 1029m, 1000m, 925w, 896w, 880w, 823w, 755m, 744m, 701s, 691s, and 684m. The mass spectrum showed peaks at  $m/e$  700 (*P* - PPh<sub>3</sub>) and 672 (*P* - CO - PPh<sub>3</sub>). The <sup>1</sup>H n.m.r. spectrum (CDCl<sub>3</sub>) showed resonances at  $\tau$  2.70 (m, 30H, C<sub>6</sub>H<sub>5</sub>P), 5.64 (br, s, 1H, H<sup>1</sup>), 6.16 (br, s, 1H, H<sup>2</sup>), 7.70 (br, s, 2H, H<sup>3</sup>, H<sup>4</sup>), and 8.62 (s, 3H, Me). The <sup>19</sup>F n.m.r. spectrum (CH<sub>2</sub>Cl<sub>2</sub>) showed resonances at 46.9 p.p.m. (br, s, 3F, CF<sub>3</sub><sup>1</sup>) and 58.9 [sx, 3F, CF<sub>3</sub><sup>2</sup>,  $J(\text{CF}_3^1-\text{CF}_3^2)$  3.5 Hz,  $J(\text{CF}_3^2-\text{P})$  3.5 Hz].

The above reaction was repeated, using toluene (18 ml) and dry methanol (2 ml) as solvent. No polymerisation of the excess of hexafluorobut-2-yne occurred. After 3 days at room temperature the reaction mixture was chromatographed on an alumina-packed column. Elution with benzene-hexane (1:9) gave a yellow product, which, on recrystallisation ( $0^\circ\text{C}$ ) from methylene chloride-hexane, afforded yellow crystals of (IV) (0.15 g, 34%), m.p.  $128-131^\circ\text{C}$  (decomp.) (Found: C, 46.6; H, 3.2; F, 16.2; P, 4.2). C<sub>27</sub>H<sub>22</sub>F<sub>6</sub>IrOP requires C, 46.3; H, 3.2; F, 16.3; P, 4.4%),  $\nu_{\text{CO}}$  (hexane) 2015m, 2005s, and 2002s;  $\nu$  (Nujol) 2022s, 1980vs, 1839w, 1822w, 1797m, 1481m, 1438m, 1383m, 1261s, 1243m, 1228s, 1125s, 1120s, 1098s, 1072w, 1035w, 1028w, 1000w, 951m, 911m, 838m, 810m, 752m, 741m, 707m, 694s, 624m, and 602m cm<sup>-1</sup>. The mass spectrum showed peaks at  $m/e$  700 (*P*), 672 (*P* - CO), 681 (*P* - F), 670 (*P* - C<sub>2</sub>H<sub>6</sub>), 645 (*P* - C<sub>4</sub>H<sub>7</sub>), 617 (*P* - CO - C<sub>4</sub>H<sub>7</sub>), 538 (*P* - C<sub>4</sub>F<sub>6</sub>), and 510 (*P* - C<sub>4</sub>F<sub>6</sub> - CO). The <sup>1</sup>H n.m.r. spectrum (CDCl<sub>3</sub>,  $-60^\circ\text{C}$ ) showed resonances at  $\tau$  2.60 (m, 15H, C<sub>6</sub>H<sub>5</sub>P), 6.13 (s, 1H, H<sup>4</sup>), 6.47 (br, s, 1H,

<sup>25</sup> W. H. Baddeley and M. S. Fraser, *J. Amer. Chem. Soc.*, **1969**, **91**, 3661.

<sup>26</sup> H. C. Clark and R. K. Mittal, *Canad. J. Chem.*, **1973**, **51**, 1511.

<sup>24</sup> W. H. Baddeley and G. L. McClure, *J. Organometallic Chem.*, **1971**, **27**, 155.

H<sup>3</sup>), 6.89 [m, 1H, H<sup>1</sup>,  $J(\text{H}^1\text{-P})$  3.0 Hz], 7.43 (s, 3H, Me), and 8.74 [d, 1H, H<sup>2</sup>,  $J(\text{H}^2\text{-P})$  10.0 Hz]. The <sup>19</sup>F n.m.r. spectrum (CH<sub>2</sub>Cl<sub>2</sub>, -60 °C) showed resonances at 50.9 [qd, 3F, CF<sub>3</sub><sup>1</sup>,  $J(\text{CF}_3^1\text{-CF}_3^2)$  4.5 Hz,  $J(\text{CF}_3^1\text{-P})$  1.5 Hz] and 55.6 [qd, 3F, CF<sub>3</sub><sup>2</sup>,  $J(\text{CF}_3^1\text{-CF}_3^2)$  4.5 Hz,  $J(\text{CF}_3^2\text{-P})$  2.0 Hz]. Irradiation of the CF<sub>3</sub><sup>1</sup> resonance at 60 °C (in C<sub>6</sub>H<sub>5</sub>Cl) caused the disappearance of the CF<sub>3</sub><sup>2</sup> resonance.

(b) *With (π-allyl)carbonylbis(triphenylphosphine)iridium.* A solution of π-allyl(carbonyl)bis(triphenylphosphine)iridium (0.50 g, 0.64 mmol) and hexafluorobut-2-yne (6 mmol) in toluene (18 ml) and dry methanol (2 ml) were sealed together in a Carius tube. The reaction mixture was kept at -30 °C for 5 days; no polymerisation of the acetylene occurred and a yellow solution remained. Volatile material was removed *in vacuo* and the residue chromatographed on an alumina-packed column. Elution with benzene-hexane (1 : 4) gave first a yellow material. Recrystallisation (0 °C) from methylene chloride-hexane gave pale yellow crystals of (V) (0.19 g, 44%), m.p. 114–117 °C [Found: C, 45.9; H, 2.9; F, 16.5; P, 4.9%;  $M(\text{C}_6\text{H}_6)$ , 684. C<sub>26</sub>H<sub>20</sub>F<sub>6</sub>IrOP requires C, 45.5; H, 2.9; F, 16.6; P, 4.5%;  $M$ , 675],  $\nu_{\text{CO}}$  (hexane) 2019s;  $\nu$  (Nujol) 2015vs, 1834w, 1797m, 1482m, 1435m, 1253s, 1240m, 1223s, 1186m, 1143m, 1125sh, 1115s, 1100m, 946w, 902w, 803m, 752m, 745m, 706m, 699m, 694m, and 674m cm<sup>-1</sup>. The mass spectrum showed peaks at  $m/e$  686 (P), 658 (P-CO), 645 (P-C<sub>3</sub>H<sub>5</sub>), 639 (P-CO-F), 617 (P-CO-C<sub>3</sub>H<sub>5</sub>), 524 (P-C<sub>4</sub>F<sub>6</sub>), 496 (P-C<sub>4</sub>F<sub>6</sub>-CO), 455 (P-C<sub>4</sub>F<sub>6</sub>-C<sub>3</sub>H<sub>5</sub>), 424 (P-PPh<sub>3</sub>), and 396 (P-CO-PPh<sub>3</sub>). The <sup>1</sup>H n.m.r. spectrum (CDCl<sub>3</sub>, -60 °C) showed resonances at  $\tau$  2.60 (m, 15H, C<sub>6</sub>H<sub>5</sub>P), 4.43 (m, 1H, H<sup>5</sup>,  $J_{1.5}$  5.0 Hz,  $J_{2.5}$  10 Hz,  $J_{3.5}$  11.5 Hz,  $J_{4.5}$  6.0 Hz), 6.33 [d, 1H, H<sup>4</sup>,  $J_{4.5}$  6.0 Hz), 6.90 (d, 1H, H<sup>3</sup>,  $J_{3.5}$  11.5 Hz), 7.81 [t, 1H, H<sup>1</sup>,  $J_{1.5}$  5.0 Hz,  $J(\text{HP})$  5.0 Hz], and 7.89 [t, 1H, H<sup>2</sup>,  $J_{2.5}$  10.0 Hz,  $J(\text{HP})$  10.0 Hz]. Coupling constants were established by <sup>1</sup>H{H} and <sup>1</sup>H{<sup>31</sup>P} spin-decoupling experiments. The <sup>19</sup>F n.m.r. spectrum (CH<sub>2</sub>Cl<sub>2</sub>, -60 °C) showed resonances at 52.7 p.p.m. [q, 3F, CF<sub>3</sub><sup>1</sup>,  $J(\text{CF}_3^1\text{-CF}_3^2)$  4.5 Hz] and 56.0 [qd, 3F, CF<sub>3</sub><sup>2</sup>,  $J(\text{CF}_3^1\text{-CF}_3^2)$  4.5 Hz,  $J(\text{CF}_3^2\text{-P})$  1.5 Hz].

The above reaction was repeated using a solution of π-allyl(carbonyl)bis(triphenylphosphine)iridium (0.60 g, 0.77 mmol) and hexafluorobut-2-yne (3 mmol) in toluene (30 ml). Extensive polymerisation of the acetylene occurred, and the polymer was removed by filtering the reaction mixture through a short column of alumina. The solvent was removed and the residue chromatographed. Elution with benzene-hexane (1 : 4) gave a yellow band. Removal of solvent and recrystallisation (0 °C) from methylene chloride-hexane gave yellow crystals of (VI) (0.038 g, 5%), m.p. 211–212 °C (decomp.) (Found: C, 55.7; H, 3.8; F, 11.9; P, 6.7. C<sub>44</sub>H<sub>35</sub>F<sub>6</sub>IrOP<sub>2</sub> requires C, 55.7; H, 3.7; F, 12.0; P, 6.6%),  $\nu_{\text{CO}}$  (hexane) 1997s;  $\nu$  (Nujol) 3050w, 1968vs, 1638w, 1586w, 1571w, 1479m, 1433s, 1310m, 1233m, 1204s, 1182m, 1150s, 1112sh, 1098s, 1070sh, 1025w, 997w, 947w, 919w, 909w, 751m, 742s, 701sh, 693s, and 683m cm<sup>-1</sup>. The mass spectrum showed peaks at  $m/e$  948 (P), 920 (P-CO), 764 (P-C<sub>3</sub>H<sub>5</sub>C<sub>4</sub>F<sub>6</sub>), 745 (P-C<sub>3</sub>H<sub>5</sub>C<sub>4</sub>F<sub>6</sub>), 736 (P-CO-C<sub>3</sub>H<sub>5</sub>C<sub>4</sub>F<sub>6</sub>), 717 (P-CO-C<sub>3</sub>H<sub>5</sub>C<sub>4</sub>F<sub>6</sub>), and 686 (P-PPh<sub>3</sub>). The <sup>1</sup>H n.m.r. spectrum (CDCl<sub>3</sub>) showed resonances at  $\tau$  2.50 (m, 30H, C<sub>6</sub>H<sub>5</sub>P), 4.83 (m, 1H, H<sup>5</sup>,  $J_{1.5}$  10 Hz,  $J_{2.5}$  18 Hz,  $J_{3.5}$  =  $J_{4.5}$  5.0 Hz), 5.29 (dd, 1H, H<sup>1</sup>,  $J_{1.5}$  10 Hz,  $J_{1.2}$  2.0 Hz), 5.32 (dd, 1H, H<sup>2</sup>,  $J_{2.5}$  18.0 Hz,  $J_{1.2}$  2.0 Hz), and 7.60 (br, d, 2H, H<sup>3</sup>, H<sup>4</sup>,  $J_{3.5}$  =  $J_{4.5}$  5.0 Hz,  $J_{1.3}$  =  $J_{1.4}$  < 1 Hz,  $J_{2.3}$  =  $J_{2.4}$  < 1 Hz). Coupling constants were established by <sup>1</sup>H{<sup>1</sup>H} spin-decoupling experiments. The <sup>19</sup>F

n.m.r. spectrum (CH<sub>2</sub>Cl<sub>2</sub>) showed resonances at 46.5 p.p.m. [br, s, 3F, CF<sub>3</sub><sup>1</sup>,  $J(\text{CF}_3^1\text{-CF}_3^2)$  4.0 Hz] and 59.5 [sx, 3F, CF<sub>3</sub><sup>2</sup>,  $J(\text{CF}_3^1\text{-CF}_3^2)$  4.0 Hz,  $J(\text{CF}_3^2\text{-P})$  4.5 Hz]. Irradiation of the CF<sub>3</sub><sup>1</sup> resonance collapsed CF<sub>3</sub><sup>2</sup> to a triplet ( $J$  4.5 Hz).

(c) *With carbonyl(π-1-methylallyl)bis(triphenylphosphine)iridium.* A solution of carbonyl(π-1-methylallyl)bis(triphenylphosphine)iridium (0.50 g, 0.63 mmol) and hexafluorobut-2-yne (3 mmol) in toluene (30 ml) contained in a sealed Carius tube was kept at -30 °C for 7 days. The resultant polymer was removed by filtration through alumina, the solvent removed, and the residue chromatographed. Elution with benzene-hexane (1 : 9) gave a yellow band. Removal of the solvent and recrystallisation (0 °C) from hexane gave yellow crystals of (VII) (0.004 g, 1%), m.p. 184–185 °C,  $\nu_{\text{CO}}$  (hexane) 1977s;  $\nu$  (Nujol) 3060w, 1971vs, 1637w, 1588w, 1570w, 1478m, 1435s, 1218s, 1183w, 1145m, 1103sh, 1097s, 1074m, 1037m, 998w, 742m, 701m, 693s, and 683m cm<sup>-1</sup>. The mass spectrum showed peaks at  $m/e$  962 (P), 948 (P-CH<sub>2</sub>), 764 (P-C<sub>4</sub>H<sub>7</sub>C<sub>4</sub>F<sub>6</sub>), 745 (P-C<sub>4</sub>H<sub>7</sub>C<sub>4</sub>F<sub>6</sub>), 736 (P-C<sub>4</sub>H<sub>7</sub>C<sub>4</sub>F<sub>6</sub>-CO), 700 (P-PPh<sub>3</sub>), 672 (P-PPh<sub>3</sub>-CO), 502 (P-PPh<sub>3</sub>-C<sub>4</sub>H<sub>7</sub>C<sub>4</sub>F<sub>6</sub>), and 474 (P-PPh<sub>3</sub>-C<sub>4</sub>H<sub>7</sub>C<sub>4</sub>F<sub>6</sub>-CO). The <sup>1</sup>H n.m.r. spectrum (CDCl<sub>3</sub>, CAT) showed resonances at  $\tau$  2.62 (m, 30H, C<sub>6</sub>H<sub>5</sub>P), 4.62 (m, 1H, H<sup>5</sup>), 5.24 (dd, 1H, H<sup>1</sup>,  $J_{1.5}$  9.0 Hz,  $J_{1.2}$  2.0 Hz), 5.29 (dd, 1H, H<sup>2</sup>,  $J_{2.5}$  18 Hz,  $J_{1.2}$  2.0 Hz), 6.91 [m, 1H, H<sup>3</sup>,  $J_{3.5}$  6.0 Hz,  $J(\text{H}^3\text{-Me})$  7.0 Hz], and 9.29 [d, 3H, Me,  $J(\text{H}^3\text{-Me})$  7.0 Hz]. The <sup>19</sup>F n.m.r. spectrum (CH<sub>2</sub>Cl<sub>2</sub>, CAT) showed resonances at 45.7 [q, 3F, CF<sub>3</sub><sup>1</sup>,  $J(\text{CF}_3^1\text{-CF}_3^2)$  4.0 Hz] and 54.0 [sx, 3F, CF<sub>3</sub><sup>2</sup>,  $J(\text{CF}_3^1\text{-CF}_3^2)$  4.0 Hz,  $J(\text{CF}_3^2\text{-P})$  4.0 Hz].

The above reaction of carbonyl(π-1-methylallyl)bis(triphenylphosphine)iridium (0.40 g, 0.5 mmol) and hexafluorobut-2-yne (2 mmol) was repeated but in benzene (30 ml). After 3 weeks at room temperature the polymer was removed and the involatile material chromatographed. Elution with benzene-hexane (1 : 4) gave an orange fraction, which was discarded, followed by the product. Recrystallisation (0 °C) from hexane gave colourless plates of (VIII) (0.02 g, 6%), m.p. 164–166 °C (decomp.) (Found: C, 46.4; H, 3.3; F, 16.1; P, 4.2. C<sub>27</sub>H<sub>22</sub>F<sub>6</sub>IrOP requires C, 46.3; H, 3.2; F, 16.3; P, 4.4%),  $\nu_{\text{CO}}$  (hexane) 2022s;  $\nu$  (Nujol) 2013vs, 2008vs, 1607w, 1479w, 1437m, 1432m, 1344w, 1254s, 1211m, 1189w, 1181w, 1133s, 1110s, 1094m, 1088m, 1037w, 753m, 744m, 740m, 701m, and 692s cm<sup>-1</sup>. The mass spectrum showed peaks at  $m/e$  700 (P), 672 (P-CO), 646 (P-C<sub>4</sub>H<sub>6</sub>), 618 (P-C<sub>4</sub>H<sub>6</sub>-CO), and 537 (P-C<sub>4</sub>HF<sub>6</sub>). The <sup>1</sup>H n.m.r. spectrum (CDCl<sub>3</sub>) showed resonances at  $\tau$  2.61 (m, 15H, C<sub>6</sub>H<sub>5</sub>P), 4.29 [m, 1H, H<sup>5</sup>,  $J_{3.5}$  7.5 Hz,  $J_{4.5}$  6.5 Hz,  $J_{5.6}$  3.5 Hz,  $J(\text{HP})$  4.0 Hz], 4.80 [m, 1H, H<sup>6</sup>,  $J_{1.6}$  6.5 Hz,  $J_{2.6}$  8.0 Hz,  $J_{5.6}$  3.5 Hz,  $J(\text{HP})$  4.0 Hz], 4.94 [q, 1H, H<sup>7</sup>,  $J(\text{H}^7\text{-CF}_3^2)$  10.0 Hz], 7.83 [dd, 1H, H<sup>4</sup>,  $J_{3.4}$  3.0 Hz,  $J_{4.5}$  6.5 Hz,  $J(\text{HP})$  < 1 Hz], 8.21 [dd, 1H, H<sup>1</sup>,  $J_{1.2}$  3.0 Hz,  $J_{1.6}$  6.5 Hz,  $J(\text{HP})$  < 1 Hz], 9.91 [td, 1H, H<sup>3</sup>,  $J_{3.4}$  3.0 Hz,  $J_{3.5}$  7.5 Hz,  $J(\text{HP})$  7.5 Hz], and 10.37 [td, 1H, H<sup>2</sup>,  $J_{1.2}$  3.0 Hz,  $J_{2.6}$  8.0 Hz,  $J(\text{HP})$  10.0 Hz]. Coupling constants were established by <sup>1</sup>H{<sup>1</sup>H}, <sup>1</sup>H{<sup>31</sup>P}, and <sup>1</sup>H{<sup>19</sup>F} spin-decoupling experiments. The <sup>19</sup>F n.m.r. spectrum (CH<sub>2</sub>Cl<sub>2</sub>) showed resonances at 56.6 p.p.m. [q, 3F, CF<sub>3</sub><sup>1</sup>,  $J(\text{CF}_3^1\text{-CF}_3^2)$  13.0 Hz] and 58.0 [qn, 3F, CF<sub>3</sub><sup>2</sup>,  $J(\text{CF}_3^1\text{-CF}_3^2)$  13.0 Hz,  $J(\text{CF}_3^2\text{-H}^7)$  10.0 Hz].

Further elution with benzene-hexane (1 : 4) gave a third fraction. Recrystallisation (0 °C) from methylene chloride-hexane afforded pale pink crystals of (IX) (0.04 g, 9%), m.p. 156–159 °C (decomp.) (Found: C, 43.2; H, 2.6; F, 26.7; P, 3.7. C<sub>31</sub>H<sub>22</sub>F<sub>12</sub>IrOP requires C, 43.2; H, 2.7;

F, 26.5; P, 3.6%),  $\nu_{\text{CO}}$  (hexane) 2059s;  $\nu$  (Nujol) 3058w, 2072vs, 2065vs, 1572w, 1522w, 1482w, 1329m, 1258w, 1220vs, 1196vs, 1185vs, 1150vs, 1137sh, 1125sh, 1110sh, 1089s, 1035m, 1000w, 982w, 958w, 902w, 798w, 753w, 747m, 740m, 718w, 713w, 708m, 698s, and 643s  $\text{cm}^{-1}$ . The mass spectrum showed peaks at  $m/e$  862 (*P*), 834 (*P* - CO), and 815 (*P* - CO - F). The  $^1\text{H}$  n.m.r. spectrum ( $\text{CDCl}_3$ ) showed resonances at  $\tau$  2.60 (m, 15H,  $\text{C}_6\text{H}_5\text{P}$ ), 5.02 (td, 1H,  $\text{H}^5$ ,  $J_{2,5}$  11.0 Hz,  $J_{3,5}$  11.5 Hz,  $J_{4,5}$  7.0 Hz), 6.09 (d, 1H,  $\text{H}^4$ ,  $J_{4,5}$  7.0 Hz), 6.77 [sp, 1H,  $\text{H}^2$ ,  $J_{2,5}$  11.0 Hz,  $J(\text{H}^2\text{-Me})$  5.5 Hz,  $J(\text{HP})$  5.5 Hz], 7.39 (d, 1H,  $\text{H}^3$ ,  $J_{3,5}$  11.5 Hz), and 8.87 [t, 3H, Me,  $J(\text{HP})$  5.5 Hz,  $J(\text{H}^2\text{-Me})$  5.5 Hz]. Coupling constants were established by  $^1\text{H}\{^1\text{H}\}$  and  $^1\text{H}\{^{31}\text{P}\}$  spin-decoupling experiments. The  $^{19}\text{F}$  n.m.r. spectrum ( $\text{CH}_2\text{Cl}_2$ ) showed resonances at 49.1 p.p.m. [q, 3F,  $\text{CF}_3^1$ ,  $J(\text{CF}_3^1\text{-CF}_3^2)$  15 Hz], 51.5 [q, 3F,  $\text{CF}_3^4$ ,  $J(\text{CF}_3^4\text{-CF}_3^3)$  16 Hz], 56.4 [sp, 3F,  $\text{CF}_3^3$ ,  $J(\text{CF}_3^1\text{-CF}_3^2) = J(\text{CF}_3^2\text{-CF}_3^3)$  15.0 Hz], and 57.6 [sp, 3F,  $\text{CF}_3^3$ ,  $J(\text{CF}_3^3\text{-CF}_3^2)$ , 15 Hz,  $J(\text{CF}_3^3\text{-CF}_3^4)$  15 Hz]. Irradiation of  $\text{CF}_3^1$  collapsed  $\text{CF}_3^2$  to a quartet and similarly irradiation of  $\text{CF}_3^4$  collapsed to a quartet.

(d) *With [1,2-bis(diphenylphosphino)ethane]carbonyl( $\pi$ -2-methylallyl)iridium.* A solution of [1,2-bis(diphenylphosphino)ethane]carbonyl( $\pi$ -2-methylallyl)iridium<sup>8</sup> (0.50 g, 0.74 mmol) and hexafluorobut-2-yne (2 mmol) in toluene (20 ml) was allowed to react ( $-30^\circ\text{C}$ ) for 7 days. No polymerisation of the acetylene occurred. Removal of the solvent *in vacuo* and extraction of the remaining solid with benzene-hexane (2:3) left relatively insoluble crystals of (X) (0.20 g, 32%), m.p. 256–257  $^\circ\text{C}$  (decomp.) (Found: C, 50.3; H, 4.0; F, 14.0; P, 7.3.  $\text{C}_{35}\text{H}_{31}\text{F}_6\text{IrOP}_2$  requires C, 50.3; H, 3.7; F, 13.7; P, 7.4%),  $\nu$  (Nujol) 3060w, 3038w, 1968vs (CO), 1602m (C=C), 1587w, 1572w, 1483m, 1435s, 1315m, 1277s, 1244s, 1218m, 1180w, 1157s, 1147s, 1110s, 1065m, 1047m, 1027w, 999w, 958m, 929m, 904w,

881m, 813w, 809m, 743m, 729m, 713m, 701s, 695s, 675m, and 647m  $\text{cm}^{-1}$ . The mass spectrum showed peaks at  $m/e$  836 (*P*), 808 (*P* - CO), 739 (*P* - CO -  $\text{CF}_3$ ), and 610 (*P* - CO -  $\text{C}_4\text{H}_7\text{C}_4\text{F}_5$ ). The  $^1\text{H}$  n.m.r. spectrum ( $\text{CDCl}_2$ , COT) showed resonances at  $\tau$  2.60 (m, 20H,  $\text{C}_6\text{H}_5\text{P}$ ), 6.60–7.94 (complex m, 7H,  $\text{H}^1$ ,  $\text{H}^2$ ,  $\text{H}^4$ , diphos  $\text{CH}_2$ ), 8.32 [d, 3H, Me,  $J(\text{HP})$  10 Hz], and 9.54 (br, d, 1H,  $\text{H}^3$ ,  $J_{3,4}$  19.0 Hz). The  $^{19}\text{F}$  n.m.r. spectrum ( $\text{CH}_2\text{Cl}_2$ , CAT) showed resonances at 50.5 p.p.m. [qd, 3F,  $\text{CF}_3^1$ ,  $J(\text{CF}_3^1\text{-CF}_3^2)$  15.0 Hz,  $J(\text{CF}_3^1\text{-P})$  10 Hz] and 57.7 [qd, 3F,  $\text{CF}_3^2$ ,  $J(\text{CF}_3^1\text{-CF}_3^2)$  15.0 Hz,  $J(\text{CF}_3^2\text{-P})$  5.0 Hz].

The solvent was removed from the above-mentioned benzene-hexane extract, and the residue chromatographed on an alumina-packed column. Elution with benzene-hexane (1:4) afforded a fraction, which after two recrystallisations (0  $^\circ\text{C}$ ) from methylene chloride-hexane yielded pale yellow crystals of (XI) (0.19 g, 26%), m.p. 236–237  $^\circ\text{C}$  (decomp.) (Found: C, 46.4; H, 3.2; F, 22.5; P, 6.4.  $\text{C}_{39}\text{H}_{31}\text{F}_{12}\text{IrOP}_2$  requires C, 46.9; H, 3.1; F, 22.8; P, 6.2%),  $\nu_{\text{CO}}$  (hexane) 2020s;  $\nu$  (Nujol) 2027vs, 1756m (C=C), 1650w, 1639w, 1483w, 1440m, 1435m, 1416w, 1311m, 1278w, 1254sh, 1240s, 1229s, 1196m, 1151m, 1121s, 1104s, 1059m, 1028w, 999w, 923w, 899m, 829w, 819m, 749m, 741m, 714m, 702m, 689m, 623m, and 602m  $\text{cm}^{-1}$ . The mass spectrum showed peaks at  $m/e$  998 (*P*), 970 (*P* - CO), 836 (*P* -  $\text{C}_4\text{F}_6$ ), 808 (*P* -  $\text{C}_4\text{F}_6$  - CO), and 619 (*P* -  $\text{C}_4\text{F}_6$  - CO -  $\text{C}_4\text{H}_7\text{C}_4\text{F}_5$ ). The  $^1\text{H}$  n.m.r. spectrum ( $\text{CDCl}_3$ ) showed resonances at  $\tau$  1.90–3.30 (m, 20H,  $\text{C}_6\text{H}_5\text{P}$ ), 5.43 (s, 1H,  $\text{H}^1$ ), 5.76 (s, 1H,  $\text{H}^2$ ), 7.06 (s, 2H,  $\text{H}^3$ ,  $\text{H}^4$ ), 6.8–7.8 (m, 4H, diphos  $\text{CH}_2$ ), and 8.56 (s, 3H, Me). The  $^{19}\text{F}$  n.m.r. spectrum ( $\text{CH}_2\text{Cl}_2$ ) showed resonances at 42.6 p.p.m. [dm, 3F,  $\text{CF}_3^1$ ,  $J(\text{CF}_3^1\text{-CF}_3^2)$  5 Hz,  $J(\text{CF}_3^1\text{-P})$  19 Hz], 52.7 [q, 3F,  $\text{CF}_3^3$ ,  $J(\text{CF}_3^3\text{-CF}_3^4)$  5.0 Hz], and 54.2 [m, 6F,  $\text{CF}_3^2$ ,  $\text{CF}_3^4$ ,  $J(\text{CF}_3^1\text{-CF}_3^2)$  5.0 Hz,  $J(\text{CF}_3^3\text{-CF}_3^4)$  5.0 Hz].

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