Reactions of Co-ordinated Ligands. Part VII.[1] Tetrafluoroethylene with π-Allyliridium(I) Complexes †

By **Michael Green** * and **Susan H. Taylor**, Department of Inorganic Chemistry, University of Bristol, Bristol BS8 1TS

Reaction of tetrafluoroethylene with $[Ir(\pi\text{-allyl})(CO)L_2]$ ($L = PPh_3$ or $AsPh_3$; allyl $= C_3H_5$, $1\text{-}MeC_3H_4$, or $2\text{-}MeC_3H_4$) affords the iridium(III) species $[\overline{IrCF_2C}F_2(\pi\text{-allyl})(CO)L]$. The corresponding reaction of $[Ir(\pi\text{-}2\text{-}MeC_3H_4)(CO)(diphos)]$ gives $[\overline{IrCF_2C}F_2(\sigma\text{-}2\text{-}MeC_3H_4)(CO)(diphos)]$. These iridium(III) complexes do not undergo insertion reactions on treatment with carbon monoxide or phosphine. However, reaction with C_2F_4 at 80 °C affords the insertion products $[\overline{CF_2CF_2I}\overline{rCF_2\cdot CF_2\cdot CH_2\cdot CMe}{=}CH_2(CO)(L)]$ ($L = PPh_3$ or $AsPh_3$) and $[\overline{CF_2CF_2I}\overline{rCF_2\cdot CF_2\cdot CH_2\cdot CH}{=}CHMe(CO)(PPh_3)]$, the latter complex existing in solution as isomers which interconvert by olefin rotation. Carbon monoxide or triphenylphosphine readily displace C_2F_4 from these systems to give $[\overline{IrCF_2CF_2\cdot CH_2\cdot CMe}{=}CH_2(CO)_2(PPh_3)]$ and $[\overline{IrCF_2CF_2\cdot CH_2\cdot CMe}{=}CH_2(CO)(PPh_3)_2]$. In contrast, reaction of $[\overline{IrCF_2C}F_2(\pi\text{-}C_3H_5)(CO)(PPh_3)]$ with an excess of C_2F_4 affords an unusual iridabicyclo[3.3.0]octane, the metal being sited at the ring junction. The n.m.r. spectra and mechanism of formation of these complexes are discussed.

IN previous papers [1-3] we have discussed the observation that on u.v. irradiation diene Fe^0 complexes undergo a formal oxidative $[Fe^0 \longrightarrow Fe^{II}]$ insertion reaction with fluoro-olefins. In contrast, tricarbonyl(π-allyl)cobalt reacts [4] with C_2F_4 at room temperature without irradiation to give the insertion product $[\overline{CoCF_2CF_2CH_2CH}{=}CH_2(CO)_3]$, a reaction which clearly resembles those observed with the iron systems but which does not involve a change in the formal oxidation state of the cobalt. It was important to understand the relationship between these two reactions of a co-ordinated hydrocarbon ligand, and in this paper we describe a study of the reaction of fluoro-olefins with π-allylic iridium(I) complexes.

RESULTS

(π-Allyl)carbonylbis(triphenylphosphine)iridium [5] reacts at room temperature with tetrafluoroethylene with replacement of triphenylphosphine to yield the colourless crystalline adduct (I). Examination of the i.r. and mass spectrum together with the n.m.r. data showed, however, that the product was not an iridium analogue of the cobalt insertion product, but a species, in which the C_2F_4 is directly co-ordinated onto the iridium, the π-allyl ligand remaining intact as shown in the illustrated structure. This was also indicated by the observation that treatment of (I) with carbon monoxide led to the displacement of C_2F_4 and the formation of $[Ir(\pi\text{-}C_3H_5)(CO)_2(PPh_3)]$. Whereas, the complex $[Ir(\pi\text{-}C_3H_5)(CO)(PPh_3)_2]$ shows a terminal carbonyl band in the i.r. region at 1930 cm^{-1}, the complex (I) shows a band at 2045 cm^{-1}, a change consistent with the replacement of the PPh_3 by the partial oxidising ligand C_2F_4.

The ^{19}F n.m.r. spectrum of (I) exhibits four resonances, typical of two AB spin systems for F^1 and F^2, F^3 and F^4; the latter three resonances have very similar chemical shifts at 110·0, 112·8, and 115·2 p.p.m., whereas F^1 resonates at higher field (138·1 p.p.m.) possibly due to a shielding effect caused by proximity to the allyl group. The observed ^{19}F–^{19}F coupling constants (Table 2) are closely analogous to those observed [6,7] for structures containing the ring system $\overline{M\cdot CF_2C}F_2$ (M = Ru, Rh, or Pt). Heteronuclear phosphorus-decoupling experiments showed that an additional large doublet splitting on F^1 and F^2 of 45 and 47 Hz respectively is due to ^{31}P–^{19}F coupling. These coupling constants are similar to that calculated (59 Hz) for *J*(*trans* PF) for the complex $[\overline{RuCF_2C}F_2(CO)_2\{P(OMe)_3\}_2]$.[7] The values found for $J(F^3P)$ and $J(F^4P)$ (7·0 and 8·0 Hz respectively) are also of the same magnitude as the calculated (12·2 Hz) value of *J*(*cis* PF) for the ruthenium species. Hence, as illustrated the CF^1F^2 group is assigned to a position *trans* to the co-ordinated PPh_3, and CF^4F^3 must be *cis* to the phosphine.

The ^1H n.m.r. spectrum shows five inequivalent resonances, typical (Table 1) of an AGKPX system of an asymmetric π-allyl group. Double irradiation of the H^5 resonance removed couplings of 11·0 and 9·0 Hz from H^2 and H^3 respectively, establishing these as the *anti*-protons. Similarly, removal of couplings of 6·0 and 5·0 Hz from H^1 and H^4 is compatible with a *syn*-proton assignment. Further decoupling established small couplings (1·0 Hz) between H^1 and H^2, and H^3 and H^4, as is usually observed for geminal coupling constants between terminal protons of an asymmetric π-allyl group. Hence H^1 and H^2 must form one terminal CH_2 group, and H^3 and H^4 the other. The value of $J_{1,4}$ (3 Hz) also compares well with typical *syn–syn*-proton couplings.

It is notable that although both *anti*-protons resonate at higher field than both *syn*-protons, the H^1,H^2 pair resonate at lower field than the H^3,H^4 pair. This has been represented in structure (I) by indication of a higher bond order for the C^1–C^2 bond relative to the C^2–C^3 bond. Asymmetric bonding of this type is generally attributed to the relative *trans*-influence of the *trans*-ligands, however, differences in

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† No reprints available.

[1] Part VI, M. Green, B. Lewis, J. J. Daly, and F. Sanz, *J.C.S. Dalton*, 1975, preceding paper.

[2] A. Bond and M. Green, *J.C.S. Dalton*, 1972, 763.

[3] A. Bond, B. Lewis, and M. Green, *J.C.S. Dalton*, 1975, 1109.

[4] A. Greco, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1971, 3476.

[5] C. K. Brown, W. Howat, G. Yagupsky, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1971, 850.

[6] R. Cramer, J. B. Kline, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1969, **91**, 2519.

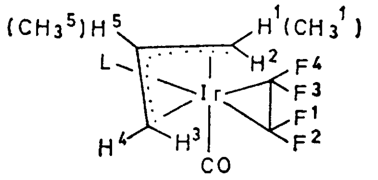
[7] R. Burt, M. Cooke, and M. Green, *J. Chem. Soc.* (*A*), 1970, 2975.

shielding caused by the different environments of the two ends of the allyl system may be responsible for the observed chemical shifts.

A further interesting aspect of the ^{1}H spectrum of (I) is that both *anti*-protons, H^2 and H^3, exhibit a very large coupling to phosphorus ($J_{2,P}$ = 12 Hz, $J_{3,P}$ = 16 Hz), whereas, for the *syn*-protons this coupling is only small ($J_{1,P}$ = 2 Hz, $J_{4,P}$ = 1 Hz). Although, usually both the *syn*- and *anti*-protons of a terminal CH_2 group *trans* to phosphorus are coupled more strongly than either the *syn*- or *anti*-protons *cis* to phosphorus, $^{1}H\{^{31}P\}$ decoupling experiments firmly established this point. However, in (I) the co-ordination site *trans* to phosphorus has been assigned to the CF^1F^2 group, so that both ends of the allyl ligand must be *cis* to phosphorus. Examination of molecular models indicates that for co-ordination of the allyl group as shown in structure (I), there is a vicinal dihedral angle between phosphorus and either *anti*-proton close to 180°, which may explain the large magnitude of the $J(PH_{anti})$ coupling constants. No such relationship exists for the *syn*-protons, which exhibit only very small phosphorus coupling.

TABLE 1

^{1}H N.m.r. data ($CDCl_3$) for the complexes $[\overline{IrCF_2C}F_2(\pi\text{-allyl})(CO)L]$



Complex	Allyl	L	Chemical shift τ						Coupling constants (in Hz)												
			Ph	H^1	H^2	H^3	H^4	H^5	$J_{1,2}$	$J_{1,4}$	$J_{1,5}$	$J_{2,5}$	$J_{3,4}$	$J_{3,5}$	$J_{4,5}$	$J_{1,P}$	$J_{2,P}$	$J_{3,P}$	$J_{4,P}$	$J_{5,P}$	$J_{H^2F^1}$
(I)	C_3H_5	Ph_3P	2·57 m	6·37 m	8·44 td	9·21 dd	7·68 m	4·71 m	>1	3	6	11	1	9	5	2	12	16	1	>1	4
(II)	1-C_4H_7	Ph_3P	2·60 m	8·24 d	7·64 non	9·39 dd	7·89 br, d	4·76 m	5	0	0	12	2	8	6	0	12	17	>1	>1	5
(III)	2-C_4H_7	Ph_3P	2·61 m	6·43 t	8·42 d	9·02 br, d	7·57 br, s	7·36 d	0	2	0	0	2	0	0	2	16	18	1	3	1
(IV)	2-C_4H_7	Ph_3As	2·60 m	6·44 d	8·16 br, s	8·64 d	7·58 t	7·40 s	>1	3	0	0	2	0	0						0
(V)	2-C_4H_7	$Bu^t{}_2MeP$ *		6·60 t	7·91 d	†	7·67 br, s	7·31 d	0	3	0	0	†	0	0	3	15	†	>1	3	0

* Other resonances occur at 8·79(9), d, *Bu*^{t}Bu^{t}MeP, $J_{H,P}$ = 13·5 Hz; 8·72(9),d, Bu^t*Bu*^{t}MeP, $J_{H,P}$ = 13·0 Hz; 9·09(3), d, Bu$^t{}_2$*Me*P, $J_{H,P}$ = 7·0 Hz. † The H^3 signal occurs at *ca.* τ 8·7, but is obscured by the Bu^t resonances.

TABLE 2

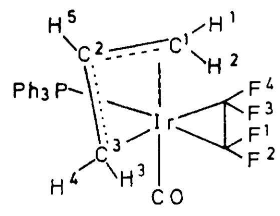
^{19}F N.m.r. data (CH_2Cl_2) for the complexes $[\overline{IrCF_2C}F_2(\pi\text{-allyl})(CO)L]$

Complex	Allyl	L	Chemical shift (p.p.m.)				Coupling constants (in Hz)										
			F^1	F^2	F^3	F^4											
			AB		AB		$J_{1,2}$	$J_{1,3}$	$J_{1,4}$	$J_{2,3}$	$J_{2,4}$	$J_{3,4}$	$J_{1,P}$	$J_{2,P}$	$J_{3,P}$	$J_{4,P}$	$J_{F^1H^2}$
(I)	C_3H_5	Ph_3P	138·1 dddd	110·0 ddd	112·8 ddd	115·2 ddd	153	33	1	2	30	169	45	47	7	8	4
(II)	1-C_4H_7	Ph_3P	138·9 dddd	109·3 ddd	111·1 ddd	115·2 ddd	157	35	0	0	33	169	44	47	7	7	5
(III)	2-C_4H_7	Ph_3P	140·0 dddd	112·1 dddd	113·3 dddd	115·1 dddd	154	31	5	6	29	170	41	53	9	11	1
(IV)	2-C_4H_7	Ph_3As	137·3 ddd	109·4 ddd	110·0 ddd	113·2 ddd	149	56	3	3	31 32	171 170					0
(V)	2-C_4H_7	$Bu^t{}_2MeP$	139·0 dddd	116·0 dddd	107·8 ddd	117·0 ddd	158	34 *	5 *	4 *			39	51	8	8	0

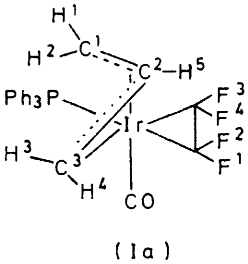
* Value uncertain due to complexity arising from 2nd-order effects.

An alternative structure (Ia), in which the π-allyl ligand is co-ordinated to the metal by its opposite face, was also considered in an attempt to explain the magnitude of $J(PH_{anti})$. In such a structure a close approach to protons H^2 and H^3 to phosphorus could lead to a 'through-space' coupling. However, this structure (Ia) is discounted because of the existence of coupling between H^2 and F^1 and further evidence provided by complex (III). The coupling $J(H^2F^1)$ = 4 Hz was established both by heteronuclear decoupling of F^1 from the ^{1}H spectrum, when the small doublet coupling on H^2 is removed, and by decoupling H^2 from the ^{19}F spectrum, when the F^1 resonance is considerably sharpened. A long range 'W' coupling through the metal could be visualised between H^2 and F^1; however, on the basis of structure (Ia), the chemical shift difference between F^1 and F^2, F^3 and F^4 is inexplicable. Whereas, examination of molecular models of structure (I) illustrates a close approach between H^2 and F^1, and such ^{1}H–^{19}F 'through-space' couplings are now well established.

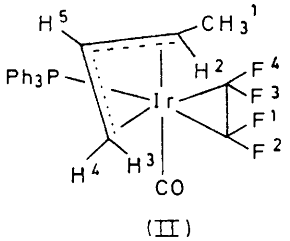
To establish the effect, if any, of variation of the allyl ligand on the course of the reaction both $[Ir(\pi\text{-1-MeC}_3H_4)(CO)(PPh_3)_2]$ and $[Ir(\pi\text{-2-MeC}_3H_4)(CO)(PPh_3)_2]$ were allowed to react similarly with tetrafluoroethylene to give the adducts (II) and (III), respectively. Adduct (II) showed closely similar mass spectrum and i.r. and ^{19}F n.m.r. data (Table 2) to those observed for (I), and examination of the ^{1}H n.m.r. spectrum (Table 1) indicates a *syn*-methylallyl isomer as illustrated. Protons H^3 and H^4 show only a small variation in chemical shift from those observed for (I), whereas the H^1 resonance is replaced by the CH_3 doublet, and the H^2 resonance is removed downfield by the presence of the methyl group. Although the observed resonances for (II) are generally at higher field, they fall in a similar order to those observed [8] for the *syn*-isomer of $[Co(\pi\text{-}1\text{-}MeC_3H_4)(CO)_3]$ and are not analogous to those of the *anti*-isomer. The *anti*-assignment is further confirmed by the complex nature of the H^2 resonance, which approximates to a nonet, caused by overlapping couplings with the methyl group (quartet, $J_{1,2}$ 5·0 Hz), H^5 (doublet, $J_{2,5}$ 10·0 Hz), phosphorus (doublet, $J_{2,P}$ 12·0 Hz), and F^1 (doublet, J_{2,F^1} 5·0 Hz), all of which were confirmed by decoupling experiments.



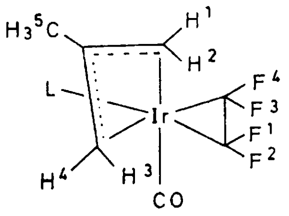
(I)



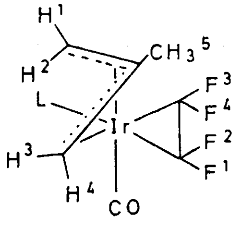
(Ia)



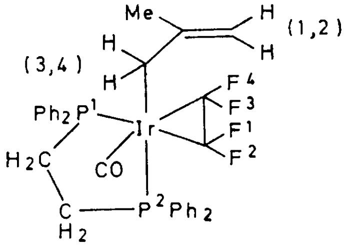
(II)



(III) L : PPh3
(IV) L : AsPh3
(V) L : PMeBu$^t_2$



(IIIa) L : PPh3
(IVa) L : AsPh3
(Va) L : PMeBu$^t_2$



(VI)

Although the adduct (III) shows very similar mass and ^{19}F n.m.r. spectra to complexes (I) and (II), there were two additional spectroscopic features, which were useful in structure assignment. Examination of the ^1H n.m.r. spectrum of (III) showed the existence of a ^{31}P–methyl-proton coupling of 3·0 Hz. Such a coupling is rarely observed, and examination of a molecular model of (III) demonstrated a close approach between the methyl protons and the phosphorus, allowing the possibility of a ' through-space ' coupling. However, it is more difficult to find an explanation for this coupling based on structure (IIIa) and, furthermore, significant changes in chemical shift might be expected for F^2 and F^3 of structures (Ia), (IIa), and (IIIa) caused by shielding effects of the methyl substituents, and such an effect is not observed.

The solution i.r. spectrum of (III) shows two narrowly separated terminal carbonyl bands [ν_{CO} (hexane) 2041s and 2032ms cm^{-1}] when a dicarbonyl structure can be discounted. A possible explanation for this observation is that reversible isomerisation of (III) to (IIIa) occurs similar to that proposed [9,10] to account for the variable-temperature ^1H n.m.r. spectrum of $[Mo(\pi\text{-}2\text{-}RC_3H_4)(CO)(\pi\text{-}C_5H_5)]$; however, no change in the ^1H spectrum of (III) is observed on cooling to −90 °C. An alternative tentative rationale is that there is some hindered rotation of the π-allyl group with respect to the triphenylphosphine ligand, and that this is emphasised by the presence in (III) of a 2-methyl substituent.

To assess the effect of variation of the ligand L in $[Ir(\pi\text{-}2\text{-}MeC_3H_4)(CO)L_2]$ on the course of the reaction with tetrafluoroethylene, the triphenylarsine derivative was prepared. The adduct isolated, (IV), showed, however, very similar characteristics to (III), in fact the ^1H and ^{19}F n.m.r. spectra of (IV) were closely analogous to the phosphorus-decoupled spectra of (III), indicating no effect on the course of the reaction.

Studies by Shaw and Stainbank [11] on the relative reactivities of *trans*-$[IrCl(CO)L_2]$ (L = tertiary phosphine) towards addition of benzoic acid and hydrogen chloride have indicated that when L is a bulky phosphine of the type Bu^t_2RP, although an increase in basicity compared to complexes with L = Me_2PhP or Ph_3P might be expected, the oxidative-addition reaction is hindered by over-riding steric factors. Hence, it seemed possible that addition of C_2F_4 to the complex $[Ir(\pi\text{-}2\text{-}MeC_3H_4)(CO)(Bu^t_2MeP)_2]$ might lead to a different kind of reaction. However, attempts to synthesise the required complex by reaction of 2-methylallylmagnesium chloride with *trans*-$[IrCl(CO)(Bu^t_2MeP)_2]$ afforded a highly reactive species, which from the presence in the i.r. spectrum of a band at 1945 cm^{-1} and its reaction with C_2F_4 to give (V) was assumed to be $[Ir(\pi\text{-}2\text{-}MeC_3H_4)(CO)(Bu^t_2MeP)]$. Since the steric effect of a single bulky phosphine ligand in a four co-ordinate complex would be smaller it is not surprising that the reaction with C_2F_4 led to a product isostructural with (I), (II), (III), and (IV).

In each of the reactions so far described, except for the

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[8] J. A. Bertrand, H. B. Jonassen, and D. W. Moore, *Inorg. Chem.*, 1963, **2**, 601.

[9] Chin-Chun Chen, J. W. Faller, A. Jakubowski, and M. J. Mattina, *J. Organometallic Chem.*, 1973, **52**, 361.

[10] J. W. Faller and M. J. Incorvia, *Inorg. Chem.*, 1968, **7**, 840.

[11] B. L. Shaw and R. E. Stainbank, *J. Chem. Soc.* (*A*), 1971, 3716.

latter, replacement of a ligand L from [Ir(π-allyl)(CO)L_2] by tetrafluoroethylene was observed. The complex [Ir(π-2-MeC_3H_4)(CO)(diphos)] was therefore synthesised from [Ir(π-2-MeC_3H_4)(CO)(Ph_3P)$_2$] by ligand exchange, in the hope that an insertion reaction would be observed with tetrafluoroethylene. However, the reaction with C_2F_4 gave instead (VI), a σ-allyl oxidative-addition adduct.

The ^{19}F n.m.r. spectrum of (VI) showed four inequivalent resonances of equal intensity characteristic of two AB spin systems, indicating that the two CF_2 groups must be *trans* to dissimilar ligands. The values of the ^{19}F–^{19}F and ^{19}F–^{31}P coupling constants showed marked similarities to those observed for complexes (I)—(V), although additional ^{19}F–^{31}P coupling was evident, due to the presence of a second phosphorus ligand P^2. Hence CF^1F^2 was assigned a position *trans* to P^1 and CF^3F^4 *cis* to P^1. As in complexes (I)—(V) the chemical shift of F^1 (103·2 p.p.m.) was different from those of F^2, F^3, and F^4 (128·1, 121·1, and 133·5 p.p.m., respectively), but to lower rather than higher field. Hence, the fluorine F^1 is assigned the illustrated position, since this is the only site which would be isolated from the anisotropic effects of the aromatic phenyl groups of the diphos ligand. This assignment seems consistent with the large values of $J(F^1P^2)$ = 39 Hz and $J(F^4P^2)$ = 31 Hz, since from examination of a molecular model the dihedral angle between P^2 and F is close to 180°. Values of $J(F^2P^2)$ = 5·0 Hz and $J(F^3P^2)$ = 4·0 Hz are smaller, the dihedral angles being close to zero.

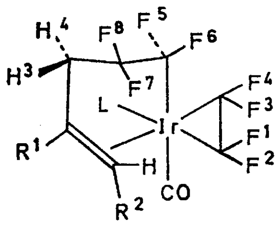
The ^1H n.m.r. spectrum of (VI) is characteristic of an asymmetric σ-allyl complex, showing A_3GKXY spin system superimposed on the CH_2 resonance of the diphos ligand. The inequivalence of the ^{31}P nuclei and the unavailability of a broad-band decoupler made heteronuclear ^{31}P decoupling difficult. However, by trial and error, the central position of the ^{31}P AB resonance was found, which on irradiation gave the simplest proton spectrum. This allowed assignments to be made, although the results cannot be regarded as unambiguous due to the unsophisticated nature of the technique used. The H^3 and H^4 resonances can be distinguished by their large geminal coupling constant (10 Hz), characteristic of protons attached to a saturated carbon atom, and are non-equivalent since there is no plane of symmetry through the iridium–carbon bond, as has been previously observed[12] in the complexes *cis*-[$IrCl_2$(σ-2-ClC_3H_4)(CO)L_2] (L = Me_2PhP or Me_2PhAs). The value of $J(H^4P)$ = 8·0 Hz suggests a co-ordination site *trans* to phosphorus, and hence the σ-allyl ligand is assigned a position *trans* to P^2 as illustrated. As required by a σ-allyl complex H^1 and H^2 show only a small geminal coupling.

Thus when L_2 is the bidentate ligand diphos, reaction of C_2F_4 with [Ir(π-2-MeC_3H_4)(CO)L_2] occurs with the partial displacement of π-allyl ligand in preference to L. When the complex (VI) was refluxed in benzene for 18 h there was no evidence for the insertion of the co-ordinated C_2F_4 into the iridium–allyl bond, and the adduct was recovered unchanged.

In contrast, further treatment of the adduct (III) with tetrafluoroethylene at 80° for 4 days afforded a new crystalline complex (VII) for which the illustrated structure is proposed. The ^{19}F n.m.r. spectrum of (VII) showed eight inequivalent resonances characteristic of four AB pairs. Examination of chemical-shift and coupling-constant data of four of these resonances, F^1, F^2, F^3, and F^4 (Table 3), showed a close similarity to those observed for the complexes (I)—(V) (Table 2), and therefore these resonances are assigned to the fluorine nuclei of co-ordinated C_2F_4. The remaining four resonances show obvious differences from those characteristic of the arrangement $IrCF_2CF_2$. For example, the values of the geminal coupling constants $J(F^5F^6)$ = 265 Hz and $J(F^7F^8)$ = 243 Hz are closer to those observed[13] for fluorine nuclei attached to sp^3 hybridised carbon atoms. Moreover, the resonances of F^5 and F^6 are at low field (74·7 and 90·8 p.p.m. respectively) as is characteristic of an α-CF_2 group of a σ-bonded fluoroalkyl metal complex, as shown in the illustrated structure. Of these four resonances, only F^5 showed ^{31}P coupling [$J(F^5P)$ 67 Hz], as established by a heteronuclear decoupling experiment. This can be understood by the stereochemical arrangement

TABLE 3

^{19}F N.m.r. data (CH_2Cl_2) for the complexes [$IrCF_2CF_2(CF_2CF_2CH_2CR^1{=}CHR^2)$(CO)L]



(VII) L = Ph_3P, R^1 = Me, R^2 = H
(VIII) L = Ph_3As, R^1 = Me, R^2 = H
(IX) L = Ph_3P, R^1 = H, R^2 = Me
(measured at −20°C)

Complex	Chemical shift (p.p.m.)								Assignable coupling constants (in Hz)														
	F^1	F^2	F^3	F^4	F^5	F^6	F^7	F^8															
	AB		AB		AB		AB		$J_{1,2}$	$J_{1,3}$	$J_{1,4}$	$J_{2,3}$	$J_{2,4}$	$J_{3,4}$	$J_{1,P}$	$J_{2,P}$	$J_{3,P}$	$J_{4,P}$	$J_{5,6}$	$J_{7,8}$	$J_{6,1}$	$J_{6,4}$	$J_{5,P}$
(VII)	138·1	115·2	101·9	126·7	74·7	90·8	98·7	108·4	156	39	1	2	39	168	37	33	12	5	265	243	53	51	67
	ddt	dd	dddd	dddd	dd	dt	ddd	d															
(VIII)	135·6	111·3	100·0	125·1	70·3	92·0	99·8	108·9	150	38	1	3	39	168					263	243	56	51	
	ddd	ddd	ddd	ddd	d	dt	ddd	d															
(IXa)	133·4	105·1	103·1	126·9	75·8	91·3	100·0	112·2	151	38	?	?	36	166	39	36	12	?	264	239	57	49	61
	ddt	dt	ddd	ddd	dd	dt	ddd	d															
(IXb)	129·9	114·3	106·9	123·1	65·5	108·7	106·8	113·7	151	38	?	?	38	167	41	37	?	?	266	239	41	45	105
	dq	dt	dd	ddd	dd	dt	ddt	d															

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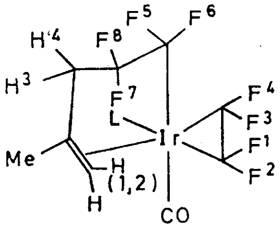
[12] A. J. Deeming and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 1562.

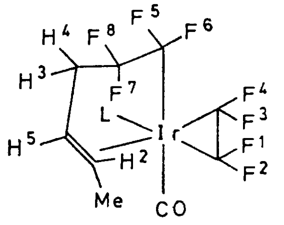
[13] E. Pitcher, A. D. Buckingham, and F. G. A. Stone, *J. Chem. Phys.*, 1962, **36**, 124.

shown, in which F^5 is directed towards the Ph$_3$P ligand. Moreover, a close spacial relationship between F^6 and F^1 and F^4 may explain the ^{19}F–^{19}F couplings J(F^{6}F^1) = 53 Hz and J(F^{6}F^4) = 51 Hz. Variation of the value of $^4J_{FF}$ with internuclear separation between two fluorine nuclei has been studied [14] for 1,3-difluoropropane, for which a coupling constant of 50 Hz implies an internuclear distance of *ca.* 1·9 Å. Examination of a molecular model suggests such a separation between F^6 and both F^1 and F^4 to be realistic.

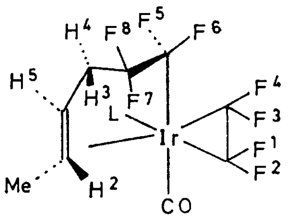
The ^{1}H n.m.r. spectrum of (VII) is not compatible with a σ- or π-allyl system, but is consistent with the illustrated structure in which C$_2$F$_4$ has formally inserted into an allyl–iridium bond. The similarity of the chemical shifts made assignment difficult, however, decoupling the phosphorus led to considerable simplification of the spectrum, and allowed the assignments listed in the Experimental section. Although the value of the geminal coupling constant between H^1 and H^2 (5 Hz) is larger than is usually observed between olefinic protons, it is much smaller than that between saturated carbon methylene protons, and hence H^1 and H^2 are assigned as shown. The H^3 signal (less obscured in C$_6$D$_6$ solutions) is very complex, even after ^{31}P decoupling, and the spectrum is clearly complicated by second-order effects arising from ^{1}H–^{19}F coupling. The complexity of the F^6, F^7, and F^8 resonances substantiated this.



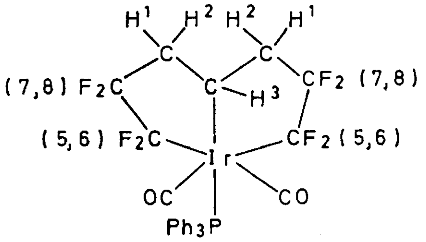
(VII) L : PPh$_3$
(VIII) L : AsPh$_3$



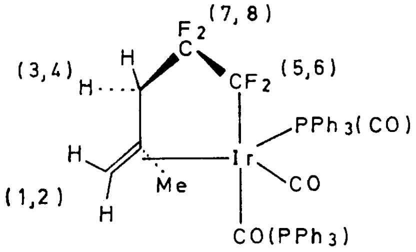
(IXa) L : PPh$_3$



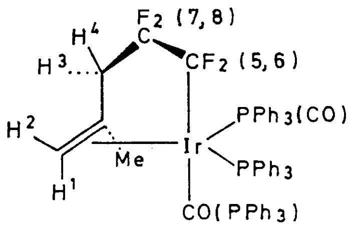
(IXb) L : PPh$_3$



(X)



(XI)



(XII)

There are two possible conformations for (VII), one in which the co-ordinated olefin originating from the allyl group is in the same plane as the $\overline{\mathrm{IrCF_2CF_2}}$ system as shown, and one where the olefin lies in a plane perpendicular to the $\overline{\mathrm{IrCF_2CF_2}}$ plane. Since there is a large ^{31}P coupling to both H^4 (11·0 Hz) and the methyl group (5·0 Hz) structure (VII) seems more plausible; in such a structure ' through-space ' couplings can be envisaged. When (IV) was heated in the presence of C$_2$F$_4$ an analogous product (VIII) was obtained. The i.r. and mass spectra are similar to those observed for (VII), and the ^{1}H and ^{19}F n.m.r. spectra closely resemble those of (VII) after ^{31}P decoupling. Although (II) also reacted with C$_2$F$_4$ in a similar way, the product, (IX), showed temperature-dependent ^{1}H and ^{19}F n.m.r. spectra compatible with the presence of interconvertible isomers (IXa) and (IXb). At −20 °C the rate of interconversion of the two isomers was very slow and the ^{19}F spectrum showed 16 inequivalent resonances, which could be separated into 8 AB pairs. Comparison with the spectra of (VII) and (VIII) allowed assignments to be made. In agreement with the illustrated structures the F^1 resonance of only (IXb) [the isomeric form not observed with (VII) and (VIII)] showed ' through-space ' coupling of 41·0 Hz to F^7.

The low temperature (−20 °C) ^{1}H spectrum of (IX) showed resonances corresponding to the presence of both isomers (IXa) and (IXb); in particular H^2 and H^5 (for which assignments were proved by ^{1}H{^{1}H} decoupling) resonate at considerably different chemical shifts for the two isomers. Proton–phosphorus coupling was observed for all the resonances except that due to the methyl group of (IXa). The coupling exhibited by the methyl group of (IXb) is explicable in terms of a proximity effect.

At 60 °C the ^{1}H spectrum in C$_6$H$_5$Cl showed a broad doublet methyl resonance, the other signals being indistinguishable. However, at 90 °C the averaged resonances of H^2, H^3, H^4, and H^5 appeared in the expected positions as broad signals.

It is suggested then, that in (IX) there is a ready interconversion involving a rotation about an axis perpendicular to the plane of the olefin and passing through the iridium atom. The absence of such an effect with (VII) and (VIII) is attributed to an interaction between the methyl group and the triphenylphosphine or triphenylarsine ligand. A conformational change of this type is not common. However, such a rotation about a metal–olefin bond has been proposed [15] to account for the presence of six rather than the expected four terminal carbonyl bands in the i.r. spectrum

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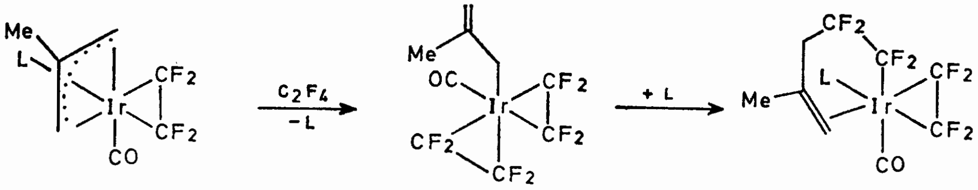
[14] K. Hirao, H. Nakatsuji, and H. Kato, *J. Amer. Chem. Soc.*, 1973, **95**, 31.

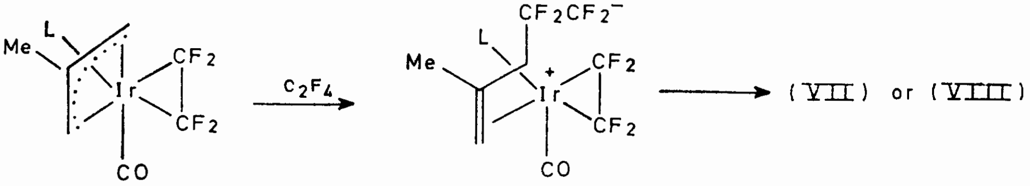
[15] M. A. Bennett and I. B. Tomkins, *J. Organometallic Chem.*, 1973, **51**, 289; P. E. Garrou and G. E. Hartwell, *ibid.*, **55**, 331.

of tetracarbonyl(*o*-styryldiphenylphosphine)tungsten. Examination of molecular models of adduct (IX) indicates that conversion between isomers (a) and (b) can readily occur, there being no steric constraint imposed by a terminal methyl group.

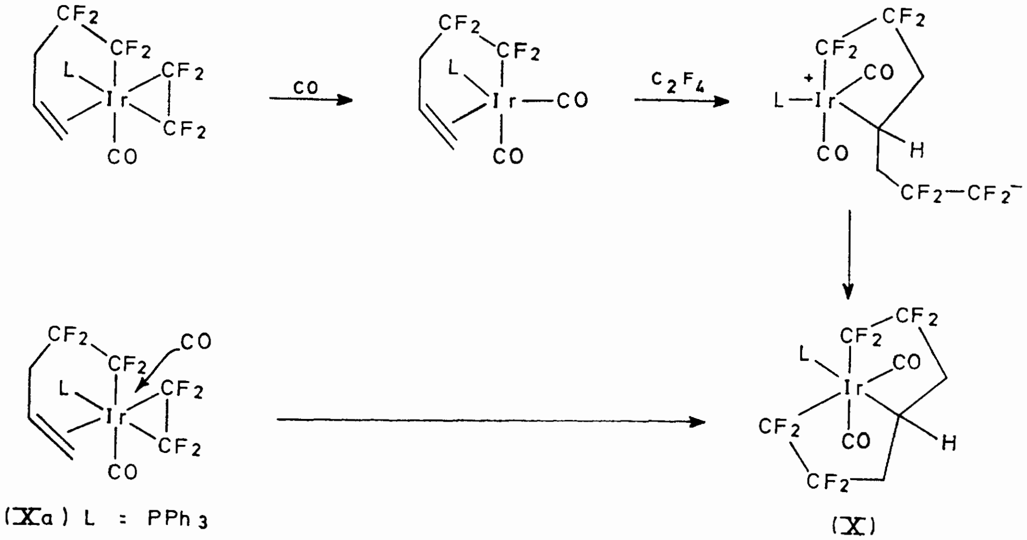
When adduct (I) was heated (80 °C) in the presence of C_2F_4 in an attempt to prepare the unsubstituted analogues of (VII), (VIII), and (IX), a deep red colour developed after only 18 h. Chromatography of the reaction mixture gave a crystalline adduct (X), for which the illustrated structure is suggested.



SCHEME 1 L = PPh_3 or $AsPh_3$



SCHEME 2 L = PPh_3 or $AsPh_3$



SCHEME 3

The i.r. spectrum showed two strong terminal carbonyl bands at 2109 and 2067 cm^{-1}, characteristic of *cis*-dicarbonyliridium(III) species. There were no bands in the i.r. typical of an $\overline{\text{IrCF}_2\text{CF}_2}$ system, also, unlike the previous complexes described, there was no evidence in the mass spectrum for peaks corresponding to the loss of C_2F_4.

The ^{19}F n.m.r. spectrum of (X) showed only four resonances characteristic of two AB spin systems, suggesting that the molecule has a plane of symmetry such that the two C_2F_4 groups are equivalent. The chemical shifts of F^5 (70·3 p.p.m.) and F^6 (92·5 p.p.m.) are at low field, and are typical of an α-CF_2 group of a σ-bonded fluoroalkyl complex. The observed geminal coupling constants and chemical shifts are also very similar to those observed for F^5, F^6, F^7, and F^8 of the adducts (VII), (VIII), and (IX). Thus, the illustrated symmetrical structure is proposed. In agreement the ^1H n.m.r. spectrum showed only three resonances; however, second-order effects precluded a detailed analysis.

The complex (VII) reacted at room temperature with carbon monoxide to give a species (ν_{CO} 2118 and 2066 cm^{-1}) possibly analogous to (III), however, insufficient product could be obtained for characterisation. At 60 °C carbon monoxide displaced C_2F_4 from (VII) to give a crystalline dicarbonyl species (XI). A similar reaction between (VII) and triphenylphosphine in refluxing benzene also led to the displacement of co-ordinated C_2F_4, and afforded a crystalline iridium(I) species (XII). The low temperature (−30 °C) n.m.r. spectra of (VII) were consistent with the illustrated structure; however, at higher temperatures there was evidence of a change in stereochemistry, which is difficult to fully explain on the basis of the present evidence.

DISCUSSION

The apparent change in the mode of reaction of the π-allylic iridium(I) species compared with the insertion products formed from C_2F_4 and $[Co(\pi\text{-}C_3H_5)(CO)_3]$ is interesting, particularly because cobalt species analogous to (I) are possible intermediates in the insertion reaction. However, attempts to convert (I) into an insertion product by reaction with carbon monoxide or triphenylphosphine led instead to the displacement of tetrafluoroethylene. It was also found that the adduct (VI) showed no evidence of undergoing an insertion reaction on refluxing in benzene for an extended period, and was recovered unchanged. Thus it would appear that in the reaction of allylic iridium(I) complexes with C_2F_4 preferential attack occurs at the metal centre to form stable adducts, in which the iridium achieves a formal oxidation state of (3+).

The further reaction of the adducts (II), (III), and (IV) with C_2F_4 to afford (IX), (VII), and (VIII) respectively is an unusual reaction, and one possible reaction path leading to the formation of these complexes would involve initial co-ordination of a second molecule of C_2F_4 prior to insertion into a σ-allyl bond (Scheme 1).[1,2,16]

However, it is unlikely that an intermediate of the type depicted could be formed, as this would involve the iridium achieving a rather high (5+) oxidation state.

A more plausible mechanism would involve either *exo*- or *endo*-attack by the second molecule of C_2F_4 to form a dipolar intermediate, which could collapse either after C–C bond rotation or directly to give the product. In such a sequence (Scheme 2) there would be no change in the formal oxidation state of the metal.

That attack at the metal occurs with the complexes $[Ir(\pi\text{-allyl})(CO)L_2]$ to afford the adducts (I)—(VI) may then be explained by the greater susceptibility of the iridium over the allyl ligand to electrophilic attack. However, in the adducts (II), (III), and (IV) attack at the metal centre is blocked, and therefore reaction at carbon can then proceed, but, of course, at higher temperatures.

The ready displacement of C_2F_4 from (VII) by carbon monoxide or triphenylphosphine to give respectively (XI) and (XII), compounds which are isostructural to the cobalt-insertion product, suggests that the cobalt complexes could also be formed *via* a similar sequence of reactions. If this is the case the preferred stereochemistry for the insertion product $[\overline{CoCF(CF_2)CF_2{\cdot}C_2H{\cdot}CH}{=}CH_2(CO)_3]$ could then be explained. However, there remains the possibility that in the cobalt system preferential attack by C_2F_4 occurs on the allyl group of $[Co(\pi\text{-allyl})(CO)_3]$, rather than at the metal.

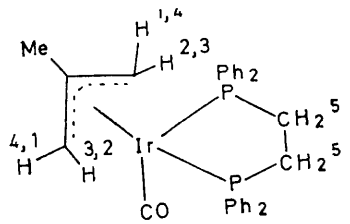
As discussed earlier, in attempting to convert (I) into an analogue of the complexes (VII), (VIII), and (IX), the formation of the unusual complex (X) was observed. This complex can be viewed as an iridabicyclo[3.3.0]octane. This reaction involves a formal 1,3-di-insertion into two metal–allyl bonds, and is not unrelated to the 1,3-addition of tetracyanoethylene to the σ-allyl group of $[Fe(\sigma\text{-}CH_2{\cdot}CMe{=}CH_2)(CO)_2(\eta^5\text{-}C_5H_5)]$.[17]

Examination of the i.r. spectrum of the reaction mixture during the formation of (X) from (I) showed the appearance and disappearance of a band at 2084 cm^{-1} (hexane), which can be assigned to (Xa). It is suggested that (Xa) is the precursor of (X). Since decompositon occurs in this reaction free carbon monoxide is probably liberated. This may either promote linking of the co-ordinated olefin and C_2F_4 moieties or displace C_2F_4 from (Xa) allowing subsequent attack by C_2F_4 on the resultant iridium(I)–olefin complex (Scheme 3).

EXPERIMENTAL

The spectroscopic data were obtained by the methods outlined in Part (V) of this series. The $^1H\{^{31}P\}$ and $^{19}F\{^{31}P\}$ decoupling experiments were carried out by the INDOR technique.[18] All reactions were conducted in an oxygen-free nitrogen atmosphere or in Carius tubes *in vacuo*. The starting materials were prepared by the published methods.

Preparation of 1,2-*Bis*(*diphenylphosphino*)*ethanecarbonyl*(π-2-*methylallyl*)*iridium*.—1,2-Bis(diphenylphosphino)ethane (1·0 g, 2·5 mmol) was added to a stirred solution of carbonyl(π-2-methylallyl)bis(triphenylphosphine)iridium (2·0 g, 2·5 mmol) in benzene (20 ml). After ½ h at room temperature the volume of the orange-yellow solution was reduced *in vacuo*. Filtration of the solution into stirred ethanol (70 ml) precipitated the product as yellow air-stable *crystals* (1·27 g, 75%), m.p. 151—153 °C (decomp.) (Found: C, 55·4; H, 4·7. $C_{31}H_{31}IrOP_2$ requires C, 55·3; H, 4·6%), ν_{CO} (Nujol) 1928vs and 1913s. The ^1H n.m.r. spectrum (CH_2Cl_2, −90 °C) showed resonances at τ 2·60 (m, 20H, C_6H_5), 7·50 (br,m, 8H, Me, H^1 and H^5), 8·64 (s, 1H, H^4), 9·65 [d, 1H, H^2, $J(H^2P)$ 17·0 Hz], and 10·38 [d, 1H, H^3, $J(H^3P)$ 22·0 Hz]. The ambient temperature spectrum exhibits two doublet resonances at τ 7·50 (*J* 3·5 Hz) and 7·58 (*J* 7·5 Hz).



The same general method was used for the preparation of the air-stable tetrafluoroethylene adducts (I)—(VI), and details are given only for the synthesis of (I). Unless included with the preparation, ^1H and ^{19}F n.m.r. data are listed in Tables 1 and 2.

Reactions of Tetrafluoroethylene.—(*a*) *With* π-*Allylcarbonylbis*(*triphenylphosphine*)*iridium*. An excess of C_2F_4 (5 mmol) was condensed (−196 °C) into a Carius tube (100 ml) containing π-allylcarbonylbis(triphenylphosphine)iridium (0·500 g, 0·64 mmol) dissolved in benzene (20 ml). The tube was sealed and allowed to stand at room temperature for 5 days when a slow decolourisation of the yellow solution occurred. The solvent was removed *in vacuo* and the residue chromatographed on an alumina-packed column. Elution with methylene chloride–hexane (1 : 9) afforded first triphenylphosphine followed by a material which was recrystallised from methylene chloride–hexane to give colourless *crystals* of (I) (0·330 g, 84%), m.p. 149—151 °C (decomp.)

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[16] P. K. Maples, M. Green, and F. G. A. Stone, *J.C.S. Dalton*, 1973, 388.

[17] S. R. Su and A. Wojcicki, *J. Organometallic Chem.*, 1973, **31**, C34.

[18] P. L. Coggin, R. J. Goodfellow, J. R. Knight, M. G. Norton, and B. F. Taylor, *J.C.S. Dalton*, 1973, 2220.

(Found: C, 46·0; H, 3·2; F, 12·0. $C_{24}H_{20}F_4IrOP$ requires C, 46·2; H, 3·2; F, 12·2%), ν_{CO} (hexane) 2044s; ν (Nujol) 3058w, 2045s, 1583w, 1570w, 1480m, 1435s, 1414s, 1315w, 1185m, 1165w, 1123s, 1093s, 1051s, 1001w, 961w, 919w, 792s, 757m, 748s, 706s, and 698s. The mass spectrum showed peaks at *m/e* 524 ($P - C_2F_4$), 496 ($P - C_2F_4 - CO$), and 482 ($P - C_3H_5$).

(b) *With carbonyl(π-1-methylallyl)bis(triphenylphosphine)iridium.* Reaction of carbonyl(π-1-methylallyl)bis(triphenylphosphine)iridium (0·50 g, 0·63 mmol) with tetrafluoroethylene (5 mmol) gave on elution with benzene–hexane (2 : 3) colourless *crystals* of (II) (0·25 g, 63%), m.p. 152—153 °C (Found: C, 47·0; H, 3·4; F, 11·8; Ir, 29·8; P, 5·0. $C_{25}H_{22}F_4IrOP$ requires C, 47·1; H, 3·5; F, 11·9; Ir, 30·1; P, 4·9%), ν_{CO} (hexane) 2036s; ν (Nujol) 3055w, 2026vs, 1586w, 1572w, 1482m, 1433s, 1408s, 1378s, 1182w, 1165w, 1116w, 1107s, 1089s, 1073s, 1041s, 999w, 975w, 801s, 755m, 753m, 750sh, and 743s cm^{-1}. The mass spectrum showed peaks at *m/e* 538 ($P - C_2F_4$), 508 ($P - C_2F_4 - C_2H_6$), and 482 ($P - C_2F_4 - C_4H_8$).

(c) *With carbonyl(π-2-methylallyl)bis(triphenylphosphine)iridium.* A similar reaction of carbonyl(π-2-methylallyl)bis(triphenylphosphine)iridium (0·60 g, 0·75 mmol) gave on elution with methylene chloride–hexane (1 : 9) colourless *crystals* of (III) (0·35 g, 73%), m.p. 138—140 °C (Found: C, 47·0; H, 3·5; F, 11·9; P, 5·0. $C_{25}H_{22}F_4IrOP$ requires C, 47·1; H, 3·5; F, 11·9; P, 4·9%), ν_{CO} (hexane) 2041s and 2032ms; ν (Nujol) 3050w, 2030s, 1585w, 1480m, 1433s, 1400m, 1182w, 1100s, 1090s, 1038s, 998w, 960w, 819s, 813s, 796s, 751m, 746m, 703m, and 695s cm^{-1}. The mass spectrum showed peaks at *m/e* 638 (P), 610 ($P - C_2F_4$), and 510 ($P - C_2F_4 - CO$).

(d) *With carbonyl(π-2-methylallyl)bis(triphenylarsine)iridium.* Similar reaction of carbonyl(π-2-methylallyl)bis(triphenylarsine)iridium (0·70 g, 0·79 mmol) gave on elution with benzene–hexane (3 : 7) colourless *crystals* of (IV) (0·46 g, 85%), m.p. 150—153 °C (Found: C, 44·2; H, 3·3; F, 11·1. $C_{25}H_{22}AsF_4IrO$ requires C, 44·1; H, 3·2; F, 11·2%), ν_{CO} (hexane) 2041s; ν (Nujol) 3066w, 3048w, 2048vs, 2037s, 2017m, 1577w, 1482m, 1433s, 1403m, 1381m, 1309w, 1187w, 1156w, 1110s, 1092m, 1083m, 1078m, 1041s, 1025m, 1000w, 965w, 852w, 825m, 801s, 750m, 742s, and 699s cm^{-1}. The mass spectrum showed peaks at *m/e* 682 (P), 654 ($P - CO$), 582 ($P - C_2F_4$), 554 ($P - C_2F_4 - CO$), 376 ($P - AsPh_3$), 348 ($P - CO - AsPh_3$), and 276 ($P - AsPh_3 - C_2F_4$).

(e) *With carbonyl(π-2-methylallyl)(methyldi-t-butylphosphine)iridium.* The highly reactive solution (ν_{CO} 1945s cm^{-1}) prepared from 2-methylallylmagnesium chloride and $[IrCl(CO)(Bu^t_2MeP)_2]$ was treated with an excess of tetrafluoroethylene to give on elution with benzene–hexane (1 : 4) colourless *crystals* of (V), m.p. 96—97 °C (Found: C, 36·2; H, 5·3; F, 14·4; P, 5·8. $C_{16}H_{28}F_4IrOP$ requires C, 35·9; H, 5·2; F, 14·2; P, 5·8%), ν_{CO} (hexane) 2028s; ν (Nujol) 3069w, 2017vs, 1489m, 1392s, 1381s, 1374s, 1295m, 1180m, 1101s, 1090s, 1080sh, 1034s, 1023sh, 959w, 931w, 919w, 878m, 872m, 850m, 818s, 801s, 785s, and 711m cm^{-1}. The mass spectrum showed peaks at *m/e* 508 ($P - CO$), 436 ($P - C_2F_4$), and 408 ($P - C_2F_4 - CO$).

(f) *With 1,2-bis(diphenylphosphino)ethanecarbonyl(π-2-methylallyl)iridium.* Reaction of an excess of C_2F_4 (5·0 mmol) with 1,2-bis(diphenylphosphino)ethanecarbonyl(π-2-methylallyl)iridium (0·80 g, 1·2 mmol) and elution with methylene chloride–hexane (2 : 3) gave colourless *crystals* of (VI) (0·20 g, 35%), m.p. 208—210 °C (Found: C, 51·2; H, 4·1; F, 9·9; P, 8·0. $C_{33}H_{31}F_4IrOP$ requires C, 51·2; H, 4·0; F, 9·8; P, 8·0%), ν_{CO} ($CHCl_3$) 2018s; ν (Nujol) 2012vs, 2003s, 1620w, 1586w, 1571w, 1482m, 1436s, 1419m, 1409m, 1350s, 1308w, 1277w, 1186w, 1162m, 1154m, 1147m, 1103m, 1068s, 1042s, 996w, 968w, 868m, 860w, 838w, 830w, 807s, 744s, 737m, 708m, 701s, 692s, 688m, 672m, and 650w cm^{-1}. The mass spectrum showed peaks at *m/e* 774 (P), 746 ($P - CO$), 719 ($P - C_4H_7$), 691 ($P - C_4H_7 - CO$), 646 ($P - CO - C_2F_4$), and 619 ($P - C_4H_7 - C_2F_4$). The ^{1}H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 2·0—3·1 (m, 24H, C_6H_5), 6·15 (br,s, 1H, H^1), 6·65 (br,s, 1H, H^2), 7·37 (m, 4H, Ph_2PCH_2), 7·68 (m, 1H, H^3), 8·15 (t, 1H, H^4), and 8·37 (s, 3H, Me). A $^1H\{^{31}P\}$ spin-decoupling experiment, irradiating an average position between the two non-equivalent ^{31}P resonances, allowed the following coupling constants to be assigned: $J_{1,2} = 1·5$, $J_{3,4} = 10·0$, and $J(H^4P) = 8·0$ Hz. The ^{19}F n.m.r. spectrum (CH_2Cl_2–CAT) showed AB resonances at 103·2 p.p.m. (dddd, 1F, F^1) and 128·1 (br, ddd, 1F, F^2), 121·1 (dtd, 1F, F^4), and 135·5 (dddd, 1F, F^3) where $J_{1,2} = 168$, $J_{1,3} = 31$, $J_{1,4} = 0$, $J_{2,3} = 0$, $J_{2,4} = 31$, $J_{3,4} = 186$, $J(H^1P^1) = 46$, $J(H^2P^1) = 46$, $J(H^3P^1) = 11$, $J(H^4P^1) = 13$, $J(H^1P^2) = 39$, $J(H^2P^2) = 5$, $J(H^3P^2) = 4$, and $J(H^4P^2) = 31$ Hz.

Further Reaction of Complex (III) with Tetrafluoroethylene.—A solution of complex (III) (0·25 g, 0·4 mmol) and tetrafluoroethylene (5 mmol) in benzene was heated (80 °C) in a Carius tube for 4 days. The solvent was removed *in vacuo*, and the residue chromatographed on an alumina-packed column. Elution with benzene–hexane (2 : 3) gave a material, which was crystallised from methylene chloride–hexane to give colourless *prisms* of (VII) (0·20 g, 69%), m.p. 160—164 °C (Found: C, 44·2; H, 3·0; F, 20·4. $C_{27}H_{22}F_8IrOP$ requires C, 44·0; H, 3·0; F, 20·6%), ν_{CO} (hexane) 2081s; ν (Nujol) 3060w, 2074vs, 1482m, 1439s, 1422s, 1351m, 1271m, 1215w, 1147s, 1128s, 1096m, 1089m, 1080m, 1065s, 1051s, 1020s, 998w, 957m, 907s, 887s, 837w, 790vs, 759w, 745s, and 698s cm^{-1}. The mass spectrum showed peaks at *m/e* 710 ($P - CO$), 691 ($P - CO - F$), 638 ($P - C_2F_4$), and 610 ($P - C_2F_4 - CO$). The ^{1}H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 2·5 (br,m, 15H, C_6H_5), 6·94 (br,td, 1H, H^3), 7·02 (br,d, 1H, H^1), 7·21 (t, 1H, H^2), 7·43 (d, 1H, H^4), 7·70 (d, 3H, Me) where $J_{1,2} = 5$, $J(H^1P) = 1$, $J(H^2P) = 5$, $J(H^3P) = 2$, $J(H^4P) = 11$, and $J(CH_3P) = 5$ Hz. The above coupling constants were assigned on the basis of a $^1H\{^{31}P\}$ spin-decoupling experiment. The ^{3}H resonance was observed in the $CDCl_3$ spectrum, but was clearer in C_6D_6, showing the unassignable couplings of value 16·5, 16·5, and 9·5 Hz. The spectrum was unchanged on cooling to −60 °C. The ^{19}F n.m.r. parameters are given in Table 3; the phosphorus–fluorine coupling constants were established by a $^{19}F\{^{31}P\}$ spin-decoupling experiment.

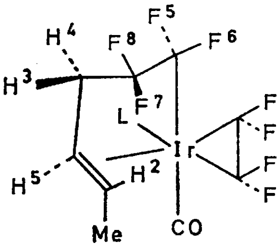
Reaction of Complex (IV) with Tetrafluoroethylene.—A solution of complex (IV) (0·20 g, 0·3 mmol) and C_2F_4 (4·0 mmol) in benzene was heated (80 °C) similarly for 3 days. Removal of the solvent *in vacuo* followed by chromatography on alumina gave, on elution with benzene–hexane (7 : 3), a fraction which was recrystallised from methylene chloride–hexane to give colourless *needles* of (VIII) (0·15 g, 65%), m.p. 158—160 °C (Found: C, 41·3; H, 2·9; F, 19·0 $C_{27}H_{22}AsF_8IrO$ requires C, 41·5; H, 2·8; F, 19·4%), ν_{CO} (hexane) 2078s; ν (Nujol) 2080vs, 1482m, 1439s, 1423s, 1350m, 1273m, 1215w, 1187w, 1149s, 1139m, 1130s, 1079m, 1067s, 1051s, 1038m, 1020s, 956m, 910s, 888m, 840w, 790s, 755m, 743s, 739s, and 696s cm^{-1}. The mass spectrum showed peaks at *m/e* 754 ($P - CO$), 735 ($P - CO - F$), 682

($P - C_2F_4$), 654 ($P - C_2F_4 - CO$), and 476 ($P - AsPh_3$). The ^1H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 2·5 (m, 15H, C_6H_5), 6·92 (d, 1H, H^1), 6·96 (td, 1H, H^3), 7·02 (s, 1H, H^4), 7·23 (d, 1H, H^2), and 7·57 (s, 3H, Me) where $J_{1,2}$ = 5 Hz. The H^3 resonance was more clearly observable in C_6D_6 solution showing unassignable couplings of 17, 17, and 9·0 Hz. The ^{19}F n.m.r. parameters are given in Table 3.

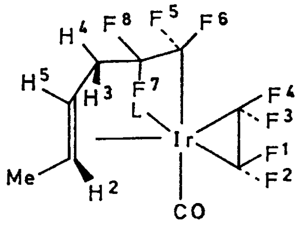
Reaction of Complex (II) with Tetrafluoroethylene.—A similar reaction (80 °C/4 days) of complex (II) (0·20 g, 0·25 mmol) with C_2F_4 (4 mmol) in benzene (20 ml) gave, after removal of solvent and chromatography, a material which eluted with benzene–hexane (1 : 1), and which on recrystallisation from methylene chloride–hexane afforded colourless crystals of (IX) (0·10 g, 45%), m.p. 147—150 °C (Found: C, 44·3; H, 3·1; F, 20·4. $C_{27}H_{22}F_8IrOP$ requires C, 44·0; H, 3·0; F, 20·6%), ν_{CO} (hexane) 2080s; ν (Nujol) 3060w, 2098s, 2089s, 1482m, 1440s, 1436s, 1419s, 1354m, 1302m, 1282w, 1211m, 1187w, 1157s, 1149s, 1119s, 1098m, 1076s, 1060s, 1045s, 1022m, 994s, 932s, 919w, 908m, 863w, 792s, 759m, 746s, 708m, and 696s cm^{-1}. The mass spectrum showed peaks at *m/e* 638 ($P - C_2F_4$) and 610 ($P - C_2F_4 - CO$). The ^1H n.m.r. spectrum showed temperature dependence, the low-temperature spectrum exhibiting resonances corresponding to two isomers (IXa) and (IXb), the latter predominating. Assigned coupling constants were determined by $^1H\{^1H\}$ and $^1H\{^{31}P\}$ spin-decoupling experiments.

^1H N.m.r. spectrum of (IXa) and (IXb), chemical shifts in τ values, coupling constants in Hz

Solvent		Ph	H^2	H^3	H^4	H^5	Me	$J_{2,5}$	$J(H^2Me)$	J(MeP)	$J_{3,4}$
$CDCl_3$, −20 °C	(IXa)	2·5m	5·95m	6·9—7·7m		4·87m	8·03d	12	5·5	0	
	(IXb)	2·5m	4·25m	6·9—7·7m		6·27m	7·80t	12	5·5	4	
C_6H_5Cl, 90 °C		2·5m	4·98m	7·30d	7·58d	5·62m	7·99d		5·5	2	15



(IXa) L = PPh3



(IXb) L = PPh3

The ^{19}F n.m.r. parameters are listed in Table 3.

Reaction of Complex (I) with Tetrafluoroethylene.—A solution of complex (I) (0·25 g, 0·32 mmol) and C_2F_4 (4 mmol) in benzene was heated (80 °C) for 18 h, the reaction mixture changing colour to deep red. The solvent was removed *in vacuo* and the residue chromatographed. Elution with benzene–hexane (2 : 3) gave a material which on crystallisation from methylene chloride–hexane yielded colourless *crystals* of (X) (0·10 g, 70%), m.p. 197—199 °C (Found: C, 43·5; H, 2·7; F, 19·8; P, 4·2. $C_{27}H_{20}F_8IrOP$ requires C, 43·2; H, 2·7; F, 20·2; P, 4·1%), ν_{CO} (hexane) 2109s and 2067s; ν (Nujol) 2121s, 2018s, 2086s, 2070s, 1482m, 1437s, 1361m, 1339m, 1318m, 1288m, 1272m, 1229m, 1208m, 1170s, 1159s, 1132s, 1109s, 1091s, 1071s, 1048s, 1029s, 1012m, 992s, 964m, 920s, 908s, 893m, 854m, 753m, 748s, 703s, and 691s cm^{-1}. The mass spectrum showed peaks at *m/e* 724 ($P - CO$), 696 ($P - 2CO$), 677 ($P - 2CO - F$), and 524 ($P - 2C_2F_4CH_2$). The ^1H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 2·5 (m, 15H, C_6H_5), 6·89 (m, 1H, H^3), and 7·1—8·0 (complex m, 4H, H^1 and H^2). The ^{19}F n.m.r. spectrum (CH_2Cl_2) showed resonances at 70·3 p.p.m. (m, 2F, F^5), 92·5 (m, 2F, F^6), 110·5 (m, 2F, F^7), and 115·5 (m, 2F, F^8); F^5 and F^6 form an AB system where $J_{5,6}$ = 255 Hz, and F^7 and F^8 form an AB system where $J_{7,8}$ = 234 Hz.

Reaction of Complex (VII) with Carbon Monoxide.—Carbon monoxide was bubbled through a solution of (VII) (0·45 g, 0·74 mmol) in benzene (50 ml) at 60 °C for 26 h. Removal of the solvent *in vacuo* and chromatography gave on elution with benzene–hexane (3 : 7) a product, which, on recrystallisation from methylene chloride–hexane, gave colourless *crystals* of (XI) (0·09 g, 22%), m.p. 139—140 °C (Found: C, 46·8; H, 3·4; F, 11·6; P, 4·6. $C_{26}H_{22}F_4IrOP$ requires C, 46·9; H, 3·3; F, 11·4; P, 4·7%), ν_{CO} (hexane) 2063s and 2015s; ν (Nujol) 2072vs, 2015vs, 1482m, 1440s, 1435s, 1378m, 1345m, 1316m, 1278w, 1205m, 1184w, 1149s, 1091m, 1067s, 1055s, 1040m, 1021s, 1000m, 990m, 979m, 959m, 911s, 885m, 874w, 798w, 789w, 750s, 703s, and 694s cm^{-1}. The mass spectrum showed peaks at *m/e* 666 (P), 638 ($P - CO$), 610 ($P - 2CO$), and 376 ($P - CO - PPh_3$). The ^1H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 2·60 (m, 15H, C_6H_5), 6·8—7·8 (complex m, 1H, H^3), 7·59 (d, 1H, H^4), 7·81 (d, 3H, Me), 7·90 (dd, 1H, H^1), and 8·12 (dd, 1H, H^2) where $J_{1,2}$ = 2, $J(H^1P)$ = 6, $J(H^2P)$ = 8·5, $J(H^4P)$ = 5, J(MeP) = 9·5 Hz; these assignments were confirmed by $^1H\{^{31}P\}$ spin decoupling. The spectrum was temperature invariant between −60 and 90 °C. The ^{19}F n.m.r. spectrum (CH_2Cl_2) showed resonances at 81·6 p.p.m. (dm, 1F, F^5), 93·2 (ddd, 1F, F^6), 108·9 (dtd, 1F, F^7), and 114·2 (dm, 1F, F^8) where $J_{5,6}$ = 255 and $J_{7,8}$ = 233 Hz; $^{19}F\{^{31}P\}$ spin decoupling showed that $J(F^5P) = J(F^6P)$ = 33·0 Hz. Couplings for F^6 (9 Hz) and for F^7 (23, 23, and 11 Hz) could not be assigned unambiguously.

Reaction of Complex (VII) with Triphenylphosphine.—A solution of complex (VII) (0·25 g, 0·34 mmol) and triphenylphosphine (0·10 g, 0·38 mmol) in benzene (10 ml) was heated under reflux for 1 h. The solvent was removed and the residue recrystallised (twice) from methylene chloride–hexane to give pink *crystals* of (XII) (0·225 g, 74%), m.p. 146—149 °C (Found: C, 57·5; H, 4·3; F, 8·4; P, 7·1. $C_{43}H_{37}F_4IrOP$ requires C, 57·4; H, 4·1; F, 8·5; P, 6·9%), ν_{CO} ($CHCl_3$) 2007s; ν (Nujol) 3060w, 2019w, 1989s, 1588w, 1572w, 1482m, 1439s, 1433s, 1349w, 1307w, 1270w, 1201m, 1185w, 1160w, 1140s, 1089m, 1068s, 1053s, 1032m, 1000m, 967s, 954m, 907s, 878m, 852w, 829w, 751s, 743s, and 698s cm^{-1}. The mass spectrum showed peaks at *m/e* 872 ($P - CO$), 638 ($P - PPh_3$), 610 ($P - PPh_3 - CO$), and 376 ($P - 2PPh_3$).

^1H N.m.r. spectrum of (XII), chemical shifts in τ values, coupling constants in Hz

Solvent	Ph	Assignment H^1 H^2 H^3 H^4	Me	Coupling constant J_{MeP}
CH_2Cl_2, −30 °C	2·60m	7·40—8·5br, m	8·29d	9
C_6H_5Cl, 90 °C	2·60m	7·30—7·7	7·89s	0

The ^{19}F n.m.r. spectrum (CH_2Cl_2, −30 °C) showed resonances at 64·9 p.p.m. (dd, 1F, F^5), 77·1 (dd, 1F, F^6), 98·5 (ddd, 1F, F^7), and 107·6 (dd, 1F, F^8) where $J_{5,6} = 265$, $J_{7,8} = 234$, $J_{5,P} = 82$ and $J_{6,P} = 54$ Hz.

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