Polyfluoroaromatic Derivatives of Metal Carbonyls. Part IX.[1] Reactions of Pentafluorophenylsilver(I) with some Transition-metal Halogeno-complexes; Oxidative-addition Reactions of the Complex Carbonyl(pentafluorophenyl)bis(triphenylphosphine)iridium(I)

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The complexes [M(C_6F_5)(CO)(PPh_3)$_2$] (M = Rh or Ir), [Rh(C_6F_5)(C_8H_{12})(PPh_3)] (C_8H_{12} = cyclo-octa-1,5-diene), [Fe(C_6F_5)$_2$(CO)$_4$], and [Pt(CF=CF_2)(C_6F_5)(PPh_3)$_2$] have been prepared by reactions between AgC_6F_5 and the appropriate halogeno-complexes; the platinum derivative was obtained from [Pt·CF_2CFCl(PPh_3)$_2$]. Oxidative-addition reactions of halogens, hydrogen halides, and hexafluorobut-2-yne to the iridium complex are described. Some of the products contain C_6F_5 groups in which all five fluorine atoms are inequivalent; the ^{19}F n.m.r. spectra are discussed.

MAJOR synthetic routes to transition-metal fluorocarbon complexes encompass the following general methods:[2] (*a*) decarbonylation of fluoroacylmetal complexes, obtained from fluoroacyl halides and metal carbonyl anions or some low-valent metal complexes; (*b*) reactions between fluoro-olefins or polyfluoroaromatic compounds and metal carbonyl anions;[3] (*c*) insertion of fluoro-olefins or -alkynes into M–H or M–C bonds; (*d*) oxidative-addition or -elimination reactions between low-valent transition-metal substrates and fluoro-olefins, fluoro-alkynes, perfluoroalkyl iodides, or fluorinated ketones and imines;[4] (*e*) reactions of metal halide derivatives with fluoroalkyl or fluoroaryl derivatives of lithium or magnesium. The limitations of these methods have been discussed recently,[5] in connection with the application of fluorocarbon derivatives of the coinage metals, particularly perfluoro-1-methylpropenylsilver(I), to the synthesis of new types of fluorocarbon-metal complexes. We have independently studied this type of reaction, using pentafluorophenylsilver(I).[6]

RESULTS AND DISCUSSION

The reaction between Vaska's complex, [IrCl(CO)(PPh_3)$_2$], and AgC_6F_5 afforded [Ir(C_6F_5)(CO)(PPh_3)$_2$], (I), as a bright yellow crystalline material, characterised by analytical and spectroscopic techniques. Thus the i.r. spectrum contained a single ν(CO) band at 1 965 cm^{-1} {*cf.* [IrCl(CO)(PPh_3)$_2$], 1 950 cm^{-1}} and the ^{19}F n.m.r. spectrum contained the expected resonances, confirming the presence of a C_6F_5 group (see below). The reaction between AgC_6F_5 and the rhodium analogue similarly gave [Rh(C_6F_5)(CO)(PPh_3)$_2$] as a yellow material. This complex has been reported previously as being formed from [RhCl(C_6F_5)$_2$(CO)(PPh_3)$_2$] and carbon monoxide,[7] but no further details have been given. Using [RhCl(PPh_3)(C_8H_{12})] (C_8H_{12} = cyclo-octa-1,5-diene), the yellow crystalline complex [Rh(C_6F_5)(PPh_3)(C_8H_{12})] was obtained as an unusual example of a stable olefin complex of rhodium also containing a metal–carbon σ-bond. In both cases spectroscopic evidence supported the assigned structures.

Pentafluorophenylsilver(I) when treated with the complex [Fe(CO)$_4$$I_2$] gave [Fe($C_6F_5$)$_2(CO)_4$], as a yellow solid. This result contrasts with the reaction using AgC(CF_3)=CF(CF_3), from which no identifiable products were obtained,[5] and with the action of LiC_6F_5, which affords only [C_6F_5Fe(CO)$_4$I].[8] The product from the three-membered ring complex [PtCFClCF_2(PPh_3)$_2$] and AgC_6F_5 corresponded to a simple replacement of Cl by C_6F_5. However, both the i.r. [ν(C=C), 1 716 cm^{-1}] and ^{19}F n.m.r. spectrum of this white complex showed that a σ-trifluorovinyl complex had been formed. This vinyl rearrangement reaction has been shown[9] to occur on heating under reflux in a polar solvent such as n-butanol, and is greatly facilitated by the addition of silver(I) ion (as acetate). The mechanism is thought to involve ionic intermediates, chloride ion being removed as AgCl in the present case, with formation of [Pt(CF=CF_2)(C_6F_5)(PPh_3)$_2$].

Oxidative-addition Reactions of the Complex [Ir(C_6F_5)(CO)(PPh_3)$_2$], (I).—It was to be expected that the complex (I) would be less reactive toward adduct formation than Vaska's complex. Although the inductive electron-withdrawing effect of the C_6F_5 group is less than that of, say, chlorine, more efficient π-overlap can occur when this group is σ-bonded to a metal, and hence the electron density on the metal atom is reduced. This is indicated by the ν(CO) band of complex (I), which lies 15 cm^{-1} above that of [IrCl(CO)(PPh_3)$_2$].

Chemically, complex (I) is less reactive than Vaska's

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[2] M. I. Bruce and F. G. A. Stone, *Prep. Inorg. React.*, 1968, **4**, 177.

[3] M. I. Bruce and F. G. A. Stone, *Angew. Chem.*, 1968, **80**, 835; *Angew. Chem. Internat. Edn.*, 1968, **7**, 747.

[4] F. G. A. Stone, *Pure Appl. Chem.*, 1972, **30**, 551.

[5] R. B. King and W. C. Zipperer, *Inorg. Chem.*, 1972, **11**, 2119.

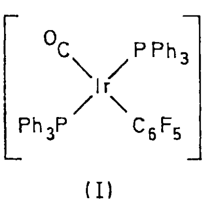
[6] K. K. Sun and W. T. Miller, *J. Amer. Chem. Soc.*, 1970, **92**, 6985.

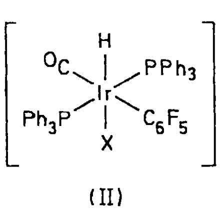
[7] R. S. Nyholm and P. Royo, *Chem. Comm.*, 1969, 421.

[8] P. M. Treichel, M. A. Chaudhari, and F. G. A. Stone, *J. Organometallic Chem.*, 1963, **1**, 98.

[9] M. Green, R. B. L. Osborn, A. J. Rest, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 2525.

complex, and under conditions where the latter readily reacts with MeI or MeCOCl, for example, no adducts were obtained with (I) and these reagents. In contrast, reactions with hydrogen halides (HCl or HBr) or halogens (Cl_2, Br_2, or I_2) occurred readily at room temperature, the yellow colour of the complex lightening, followed by separation of the white or pale yellow iridium(III) complexes. The product obtained with HCl was white $[Ir(H)Cl(C_6F_5)(CO)(PPh_3)_2]$. The i.r. spectrum showed ν(IrH) at 2 246 cm^{-1} and ν(CO) at 2 041 cm^{-1}, as expected for an iridium(III) complex. In the ^1H n.m.r. spectrum a triplet of doublets at τ 26·15, assigned to the metal-bonded proton, indicates mutually *trans* phosphine ligands, while coupling to only one fluorine atom suggests that the hydride ligand is *cis* to the C_6F_5 group. In the far i.r. spectrum ν(IrCl) at 273 cm^{-1} is characteristic of Cl *trans* to H {*cf.* ν(IrCl) at 270 cm^{-1} in $[Ir(H)_2Cl(CO)(PPh_3)_2]$}.[10] These data are consistent with structure (II; X = Cl) for the adduct. The corresponding HBr adduct (II; X = Br) exhibited similar spectral characteristics, and is assigned an analogous structure.


(I)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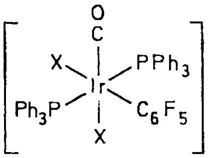
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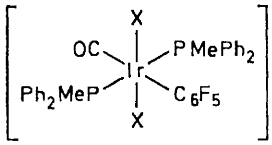
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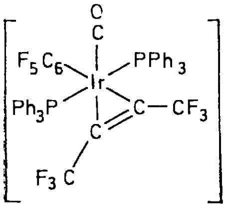
(V)

The halogen adducts $[IrX_2(C_6F_5)(CO)(PPh_3)_2]$ (X = Cl or Br) (III) have been characterised similarly. In particular, the far i.r. spectrum of (III; X = Cl) had two ν(IrCl) bands at 320 and 290 cm^{-1}, suggesting the two Cl atoms to be mutually *cis*. The band at 320 cm^{-1} can be assigned to a chlorine ligand *trans* to CO, and structure (III) accommodates all these data. The bromine and iodine adducts may be assigned similar structures. A second isomer of $[IrCl_2(C_6H_5)(CO)(PPh_3)_2]$, probably with mutually *trans* Cl atoms, was isolated from the reaction between complex (I) and C_3F_7COCl.

Further evidence for mutually *trans* phosphine ligands was provided by the ^1H n.m.r. spectra of analogous complexes containing $PMePh_2$ in place of PPh_3. The initial iridium(I) complex $[Ir(C_6F_5)(CO)(PMePh_2)_2]$, (Ia), and the HCl, Cl_2, Br_2, and I_2 adducts all showed an apparent triplet for the P*Me* signal. The presence of only one ν(IrCl) band, at 328 cm^{-1}, in the far i.r. spectrum of the dichlorine adduct, indicates a *trans*-ClIrCl arrangement, and allows structure (IV; X = Cl) to be written for this complex. The dibromine and di-iodine adducts exhibited similar spectral features, and probably have the same geometry. In the HCl adduct, the ν(IrCl) band was at 271 cm^{-1}, *i.e.* the chloride ligand is *trans* to the hydride.

It is not clear from our experiments whether the observed products are a result of thermodynamic or kinetic control in these reactions. The general lack of reactivity of complex (I) in oxidative-addition reactions of this type can probably be ascribed to (*i*) a reduction in electron density at the metal, caused by the presence of the electronegative C_6F_5 group, and (*ii*) to a steric crowding effect, resulting from the presence of the large phosphine and C_6F_5 ligands.

The adduct (V), obtained from hexafluorobut-2-yne, contained one molecule of the acetylene, and, unusually, gave a satisfactory mass spectrum. This showed parent ions at *m/e* 1 072 and 1 074 (for ^{191}Ir and ^{193}Ir, respectively). Other ions in the high-mass range included those formed by loss of CO, and of HF. The latter also occurred as a strong doubly charged ion. The alkyne was also lost to give intense ions at *m/e* 910, 912, although the usual loss of CO from these does not occur. At *m/e* 715, 717, another intense pair of ions is assigned to $[Ir(PPh_3)_2]^+$, which decomposes to give presumably metallated ions of the type $[Ir(C_6H_4)PPh_2]^+$ (*m/e* 452, 454) and $[IrPC_{12}H_8]^+$ (*m/e* 374, 376). In the mass spectra of some samples, weak ions were found at *m/e* ratios above that of the parent ion, corresponding to the 2 : 1 adduct $[Ir(C_6F_5)(CO)(PPh_3)_2(C_4F_6)_2]$; however, we were not able to obtain other evidence for this material, even from prolonged reactions, and it may have been formed in the spectrometer.

Reactions of complex (I) with $HSiCl_3$ and $NaBH_4$ afforded a 1 : 1 adduct and the dihydride $[IrH_2(C_6H_5)(CO)(PPh_3)_2]$ respectively. The ^1H n.m.r. spectra indicated these products to be mixtures of isomers whose stereochemistry was not determined.

Rhodium complexes are generally less reactive towards oxidative addition than those of iridium. The complex $[Rh(C_6F_5)(CO)(PPh_3)_2]$ proved to be relatively unreactive, and in addition cleavage of the C_6F_5–Rh bond occurred. Thus, with HBr, a yellow solid separated, and was characterised as $[Rh(H)Br_2(CO)(PPh_3)_2]$. The ν(RhH) and ν(CO) bands appeared at 2 107 and

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[10] J. M. Jenkins and B. L. Shaw, *J. Chem. Soc.*, 1965, 6789; D. M. Adams, J. Chatt, J. Gerratt, and A. D. Westland, *ibid.*, 1964, 734.

2 049 cm^{-1} respectively, and these and other properties of the complex, while apparently new, are similar to those of [$Rh(H)Cl_2(CO)(PPh_3)_2$].[11]

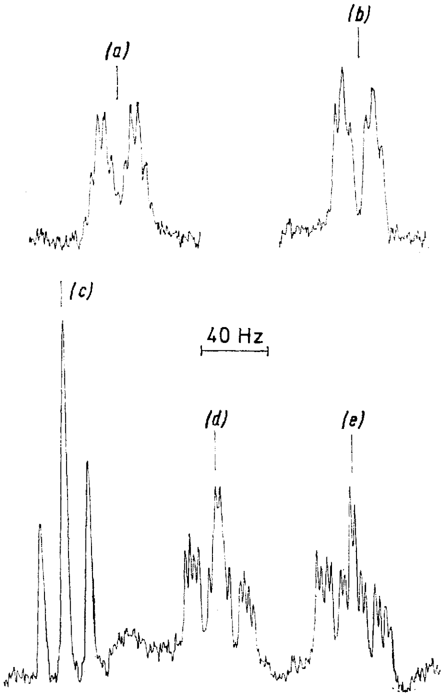
TABLE 1

^{19}F N.m.r. spectra

Complex	Chemical shifts/p.p.m. [a]					Coupling constants/Hz [b]
	F_2	F_6	F_3	F_5	F_4	
[$Ir(C_6F_5)(CO)(PPh_3)_2$]	114·8		165·1			
[$Rh(C_6F_5)(CO)(PPh_3)_2$]	107·5		164·0			
[$Rh(C_6F_5)(C_8H_{12})(PPh_3)$]	114·1		164·4			
[$Fe(C_6F_5)_2(CO)_4$]	109·8		162·0		157·5	
[$Pt(CF{=}CF_2)(C_6F_5)(PPh_3)_2$] [c]	117·3		164·5			
[$Ir(H)Cl(C_6F_5)(CO)(PPh_3)_2$]	100·1	112·2	164·5	166·0	163·2	J_{23}, 26·0, J_{25} 9·0, J_{34} 20·0, J_{35} 3·5, J_{36} 7·0, J_{45} 20·0, J_{56} 28·5
[$Ir(H)Br(C_6F_5)(CO)(PPh_3)_2$]	99·5	108·8	164·4	165·5	163·1	J_{23} 25·0, J_{34} 20·0, J_{45} 20·0, J_{56} 30·0
[$IrCl_2(C_6F_5)(CO)(PPh_3)_2$] [d]	103·3	108·6	163·5	164·5	162·0	J_{23} 24·0, J_{25} 5·0, J_{34} 20·0, J_{35} 3·0, J_{36} 7·0, J_{45} 20·0, J_{56} 26·0
[$IrBr_2(C_6F_5)(CO)(PPh_3)_2$]	101·8	104·0	163·2	164·1	161·4	J_{23} 27·0, J_{25} 6·0, J_{34} 20·0, J_{35} 3·0, J_{36} 8·0, J_{45} 20·0, J_{56} 25·0
[$IrI_2(C_6F_5)(CO)(PPh_3)_2$]	95·8	100·1	162·9	164·3	161·1	J_{23} 29·0, J_{25} 7·0, J_{34} 20·0, J_{35} 3·0, J_{36} 5·0, J_{45} 20·0, J_{56} 26·0
[$IrCl_2(C_6F_5)(CO)(PPh_3)_2$] [e]	100·1	112·1	164·8	165·9	163·1	J_{23} 28·0, J_{34} 19·0, J_{35} 3·0, J_{36} 7·0, J_{45} 19·0, J_{56} 27·0
[$IrH_2(C_6F_5)(CO)(PPh_3)_2$]	100·5		165·0		166·0	
	102·3		165·0		166·0	
[$IrH(SiCl_3)(C_6F_5)(CO)(PPh_3)_2$]	100·1	102·9	159·8	163·0	162·0	
[$Ir(C_6F_5)(C_4F_6)(CO)(PPh_3)_2$] [f]	94·9	101·6	162·3, 163·9			
[$IrCl_2(C_6F_5)(CO)(PMePh_2)_2$]	110·0		166·0		162·0	
[$IrI_2(C_6F_5)(CO)(PMePh_2)_2$]	96·3		165·2		161·5	

[a] Relative to internal $CFCl_3$ (0·0 p.p.m.). [b] J_{24} and J_{26} both 0. [c] $CF{=}CF_2$: 95·8, 124·9, and 152·0 p.p.m. J_{AB} 101, J_{AC} 30 J_{BC} 100, J_{PtFA} 55. [d] $C_2(CF_3)_2$: 51·1dq, 51·8q; J_{FF} 5·5; $J_{CF_3F\,2}$ 26·0. [e] From complex (I) and Cl_2. [f] From complex (I) and, C_3F_7COCl.

^{19}F *N.M.R. Spectra.*—^{19}F N.m.r. spectra (Table 1) of the products of the reactions between AgC_6F_5 and the various transition-metal halogeno-complexes described above exhibited the expected features, including marked deshielding of the *ortho*-fluorine atoms characteristic of a σ-bonded C_6F_5–M group. The rhodium and iridium complexes each showed only two resonances, those of the *meta*- and *para*-fluorine atoms overlapping. As a result, second-order effects precluded simple analyses of the spectra as AA'MXX' systems.



^{19}F N.m.r. spectrum of the complex [$Ir(H)Cl(C_6F_5)(CO)(PPh_3)_2$]. Chemical shifts: (*a*) 100·1 F(2); (*b*) 112·2 F(6); (*c*) 163·2 F(4); (*d*) 164·5 F(3); and (*e*) 166·0 p.p.m. F(5)

Of more interest were the spectra recorded for some of the iridium(III) adducts. Those of the hydrogen halide and dihalogen adducts of complex (I) were all of the same form, and consisted of five signals, all of equal intensity, instead of the more usual three-line pattern. The spectrum of the complex [$Ir(H)Cl(C_6F_5)(CO)(PPh_3)_2$] is typical (Figure). The assignments of the signals were confirmed by appropriate decoupling experiments. These showed that this adduct is pure and not a fortuitous equimolar mixture of isomers. Our explanation for these spectral patterns is restricted rotation of the C_6F_5 group, caused by its being positioned *cis* to two mutually *trans* triphenylphosphine ligands, as found for the $PMePh_2$ complex. The two *ortho*-fluorine atoms, while both being deshielded by the iridium, are in different environments and hence resonate at different frequencies. In addition, F_2 is closer to the hydrogen atom than is F_6, and showed a coupling J_{HF} of *ca.* 6 Hz. This would appear to be an example of through-space coupling, although an interaction H–Ir–C–C–F cannot be ruled out entirely.

The ^{19}F n.m.r. spectrum of complex (V) contained six resonances. Two multiplets, with relative intensities 1 : 1, occurred between 51 and 52 p.p.m., and were

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[11] M. C. Baird, J. T. Mayne, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1967, 1347.

assigned to the alkyne CF_3 groups. Decoupling experiments showed that the lower-field signal was split by one of the *ortho*-fluorine atoms of the C_6F_5 ring (at 94·9 p.p.m.). Both resonances were coupled to two phosphorus atoms; when this coupling was removed, the resonances appeared as a simple doublet of quartets, and a quartet, respectively. As with some of the other C_6F_5 complexes, the five fluorine atoms were non-equivalent, although two of the resonances overlapped (those at 162·3 p.p.m.); inter-ring coupling constants could not be determined, although decoupling experiments again confirmed that all the aromatic fluorine atoms were attached to the same ring.

TABLE 2

Analytical (%) and i.r. (cm^{-1}) data

Complex	M.p. (t/°C)	Found (calc.)				Other	I.r. bands	
		C	H	F	P		ν(CO)	ν(IrH)
$[Ir(C_6F_5)(CO)(PPh_3)_2]$	208—210	56·35 (56·7)	3·15 (3·3)	10·2 (10·4)	6·95 (6·85)		1 965s	
$[Rh(C_6F_5)(CO)(PPh_3)_2]$	202—203	62·65 (62·6)	3·9 (3·65)	11·35 (11·55)	6·75 (7·55)		1 955s	
$[Rh(C_6F_5)(C_8H_{12})(PPh_3)]$	208—209	60·3 (60·0)	4·2 (4·2)					
$[Fe(C_6F_5)_2(CO)_4]$	155—157	38·4 (38·2)					2 134m, 2 086vs, 2 048vs	
$[Pt(CF_2{=}CF)(C_6F_5)(PPh_3)_2]$	218—220	54·4 (54·5)	3·15 (3·1)					
$[Ir(H)Cl(C_6H_5)(CO)(PPh_3)_2]$	274—276	54·5 (54·5)	3·35 (3·3)	9·8 (10·05)	5·95 (6·55)	Cl 3·85 (3·75)	2 041s	2 246m
$[Ir(H)Br(C_6F_5)(CO)(PPh_3)_2]$		51·9 (52·05)	3·7 (3·15)	9·15 (9·6)			2 041s	2 225m
$[Ir(H)Cl(C_6F_5)(CO)(PMePh_2)_2]$	191—192	49·7 (48·1)	3·35 (3·3)		6·75 (7·5)		2 034s	2 226m
$[IrCl_2(C_6F_5)(CO)(PPh_3)_2]$		52·8 (52·55)	3·4 (3·1)		5·8 (6·3)		2 052s	
$[IrBr_2(C_6F_5)(CO)(PPh_3)_2]$	230—231	47·4 (47·2)	3·1 (2·8)	8·75 (8·85)	5·3 (5·8)	Br 14·7 (14·9)	2 053s	
$[IrI_2(C_6F_5)(CO)(PPh_3)_2]$	183—185	44·1 (44·3)	3·1 (2·6)	8·2 (8·15)	5·0 (5·3)	I 21·5 (21·8)	2 060s	
$[IrCl_2(C_6F_5)(CO)(PMePh_2)_2]$	236—237	45·9 (46·15)	3·1 (3·05)		7·0 (7·25)		2 073s	
$[IrI_2(C_6F_5)(CO)(PMePh_2)_2]$	196—197	38·45 (38·15)	2·6 (2·5)	9·05 (9·1)	5·85 (5·95)	I 23·35 (24·4)	2 057s	
$[IrH_2(C_6F_5)(CO)(PPh_3)_2]$	169—172	56·25 (56·55)	3·5 (3·5)		7·1 (6·8)		2 024s, 2 004s	2 164br
$[IrH(SiCl_3)(C_6F_5)(CO)(PPh_3)_2]$	>325	46·9 (49·4)	3·1 (3·0)	8·85 (9·1)	5·35 (5·9)		2 047s, 2 035s	2 244m, 2 212m
$[Ir(C_6F_5)(C_4F_6)(CO)(PPh_3)_2]$	186—188	52·55 (52·4)	2·8 (2·8)	19·2 (19·45)	5·6 (5·8)		2 035s	
$[IrCl_2(C_6F_5)(CO)(PPh_3)_2]$ [a]	268—269	51·3	3·15	9·05	5·7		2 045s	
$[Rh(H)Br_2(CO)(PPh_3)_2]$	160—163	53·9 (54·3)	3·8 (3·8)				2 049s	2 107w

[a] From reaction with C_3F_7COCl.

EXPERIMENTAL

General experimental details are similar to those reported in previous parts of this series. Analytical data are presented in Table 2. Literature methods were used to prepare the complexes $[RhCl(PPh_3)(C_8H_{12})]$,[12] $[\overline{\text{Pt}\cdot\text{CFClC}}\text{F}_2)(\text{PPh}_3)_2]$,[8] and AgC_6F_5.[6]

Reactions of Pentafluorophenylsilver(I).—(a) *With* $[IrCl(CO)(PPh_3)_2]$. A suspension of the complex $[IrCl(CO)(PPh_3)_2]$ (200 mg, 0·26 mmol) and AgC_6F_5 (107 mg, 0·39 mmol) in diethyl ether (200 cm^3) was stirred for 3 h at room temperature. Filtration and evaporation of the bright yellow filtrate afforded yellow *crystals* of $[Ir(C_6F_5)(CO)(PPh_3)_2]$, (I) (190 mg, 80%).

(b) *With* $[RhCl(CO)(PPh_3)_2]$. A similar experiment to (a) above, using the complex $[RhCl(CO)(PPh_3)_2]$ (100 mg, 0·14 mmol) and AgC_6F_5 (58 mg, 0·21 mmol) gave yellow *crystals* of $[Rh(C_6F_5)(CO)(PPh_3)_2]$ (63 mg, 55%).

(c) *With chloro*(*cyclo-octa*-1,5-*diene*)*triphenylphosphinerhodium*(I). Using the complex $[RhCl(C_8H_{12})(PPh_3)]$ (514 mg, 1·01 mmol) and AgC_6F_5 (414 mg; 1·51 mmol) in diethyl ether (60 cm^3) at room temperature overnight, followed by removal of silver(I) chloride and recrystallisation of the evaporated filtrate, gave yellow *crystals* of $[Rh(C_6F_5)(C_8H_{12})(PPh_3)]$ (246 mg, 38%).

(d) *With* $[FeI_2(CO)_4]$. Similarly, the complex $[FeI_2(CO)_4]$ (500 mg, 1·18 mmol) and AgC_6F_5 (486 mg, 1·77 mmol) after 18 h, afforded yellow crystals (from hexane–diethyl ether) of *tetracarbonylbis*(*pentafluorophenyl*)*iron* (141 mg, 24%).

(e) *With chlorotrifluoroethylenebis*(*triphenylphosphine*)-*platinum*(0). Stirring a suspension of the complex $[\overline{\text{Pt}\cdot\text{CFClC}}\text{F}_2(\text{PPh}_3)_2]$ (500 mg, 0·60 mmol) with AgC_6F_5 (250 mg, 0·90 mmol) in diethyl ether (50 cm^3) for 16 h at

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[12] J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 1957, 4735.

room temperature, and filtration, gave a colourless filtrate. Evaporation and recrystallisation (diethyl ether) afforded pure white *crystals* of [Pt(CF=CF$_2$)(C$_6$F$_5$)(PPh$_3$)$_2$] (260 mg, 45%).

Oxidative-addition Reactions of Pentafluorophenyliridium Complexes.—(a) *With hydrogen chloride.* Passage of gaseous HCl into a solution of the complex [Ir(C$_6$F$_5$)(CO)(PPh$_3$)$_2$] (150 mg, 0·165 mmol) in diethyl ether (60 cm^3) at room temperature caused immediate disappearance of the yellow colour. Addition of hexane (20 cm^3), followed by partial evaporation of the diethyl ether, caused separation of white *crystals* of [Ir(H)Cl(C$_6$F$_5$)(CO)(PPh$_3$)$_2$] (II; X = Cl) (124 mg, 79%). An analytical sample was recrystallised (diethyl ether).

(b) *With hexafluorobut-2-yne.* The alkyne (4·5 mmol) was condensed on to the complex [Ir(C$_6$F$_5$)(CO)(PPh$_3$)$_2$] (800 mg, 0·88 mmol) in diethyl ether (45 cm^3) in a Carius tube; after sealing, the mixture was kept at room temperature for 7 days. After this time a white precipitate had separated. The tube was opened, the solvent removed, and the residue recrystallised from diethyl ether or dichloromethane–light petroleum to give the pure *adduct* (351 mg, 37%).

(c) *Other reagents.* These reactions were carried out in a similar manner; details are collected in Table 3.

TABLE 3

Experimental details for oxidative-addition reactions

Reactant (mmol)	Additive (mmol)	Conditions	Product	Crystallised from	Colour	Yield/%
(I) (0·165)	HCl(g)	20 °C (instant.)	[Ir(H)Cl(C$_6$F$_5$)(CO)(PPh$_3$)$_2$]	Et$_2$O	White	79
(I) (0·165)	HBr(g)	20 °C (instant.)	[Ir(H)Br(C$_6$F$_5$)(CO)(PPh$_3$)$_2$]	Et$_2$O–hexane	White	61
(Ia) (0·63)	HCl(g)	20 °C (instant.)	[Ir(H)Cl(C$_6$F$_5$)(CO)(PMePh$_2$)$_2$]		White	46
(I) (0·11)	Cl$_2$(g)	20 °C (instant.)	[IrCl$_2$(C$_6$F$_5$)(CO)(PPh$_3$)$_2$]	Et$_2$O	White	93
(I) (0·10)	Br$_2$ in CCl$_4$ (0·10)	20 °C (instant.)	[IrBr$_2$(C$_6$F$_5$)(CO)(PPh$_3$)$_2$]	Et$_2$O	White	64
(I) (0·11)	I$_2$ in CCl$_4$ (0·11)	20 °C (instant.)	[IrI$_2$(C$_6$F$_5$)(CO)(PPh$_3$)$_2$]	Et$_2$O	Yellow	67
(Ia) (0·63)	Cl$_2$(g)	20 °C (instant.)	[IrCl$_2$(C$_6$F$_5$)(CO)(PMePh$_2$)$_2$]		White	53
(Ia) (0·63)	Br$_2$ in CCl$_4$ (0·63)	20 °C (instant.)	[IrBr$_2$(C$_6$F$_5$)(CO)(PMePh$_2$)$_2$]	Et$_2$O	White	20
(Ia) (0·63)	I$_2$ in CCl$_4$	20 °C (instant.)	[IrI$_2$(C$_6$F$_5$)(CO)(PMePh$_2$)$_2$]		Yellow	35
(I) (0·17)	SiHCl$_3$ (0·66)	20 °C (instant.)	[Ir(H)(SiCl$_3$)(C$_6$F$_5$)(CO)(PPh$_3$)$_2$] (isomeric mixture)	CH$_2$Cl$_2$–hexane	White	60
(I) (0·11)	C$_3$F$_7$COCl (1·0)	60 °C, 7 days	[IrCl$_2$(C$_6$F$_5$)(CO)(PPh$_3$)$_2$]	CH$_2$Cl$_2$–hexane	White	62
(I) (0·165)	NaBH$_4$ (0·66)	20 °C, 16 h	[IrH$_2$(C$_6$F$_5$)(CO)(PPh$_3$)$_2$] (isomeric mixture)	Et$_2$O	White	57

Reaction between [Rh(C$_6$F$_5$)(CO)(PPh$_3$)$_2$] *and* HBr.—This reaction was similar to that described in (a) above, using the complex [Rh(C$_6$F$_5$)(CO)(PPh$_3$)$_2$] (150 mg, 0·18 mmol) and hydrogen bromide. The yellow colour lightened, and yellow *crystals* separated. Filtration, followed by washing with diethyl ether, afforded pure [Rh(H)Br$_2$(CO)(PPh$_3$)$_2$].

We thank the S.R.C. for Research Studentships (to R. L. B. and R. C. F. G.) and Dr. R. J. Goodfellow for help in obtaining the ^{19}F n.m.r. spectra.

[3/1181 *Received, 7th June,* 1973]