Complexes of the Platinum Metals. Part V.[1] Perfluorocarboxylato-derivatives

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Perfluorocarboxylic acids, $\mathrm{R_FCO_2H}$ ($\mathrm{R_F = CF_3, C_2F_5}$, or $\mathrm{C_6F_5}$), react with hydrido(triphenylphoshine) or low-oxidation-state triphenylphosphine complexes of the platinum-group metals to yield a wide range of perfluorocarboxylato-derivatives. Products which have been prepared in this manner include $[\mathrm{RuCl(OCOCF_3)(CO)(PPh_3)_2}]$, $[\mathrm{Ru(OCOR_F)_2(CO)(PPh_3)_2}]$, $[\mathrm{Ru(OCOR_F)_2(CO)_2(PPh_3)_2}]$, $[\mathrm{RuH(OCOCF_3)(PPh_3)_3}]$, $[\mathrm{OsCl(OCOR_F)(CO)(PPh_3)_3}]$, $[\mathrm{OsH(OCOR_F)(CO)(PPh_3)_3}]$, $[\mathrm{Os(OCOR_F)_2(CO)(PPh_3)_2}]$, $[\mathrm{OsH(OCOR_F)(CO)_2(PPh_3)_2}]$, $[\mathrm{Os(OCOR_F)_2(CO)_2(PPh_3)_2}]$, $[\mathrm{OsH(OCOCF_3)(PPh_3)_3}]$, $[\mathrm{Rh(OCOR_F)(PPh_3)_3}]$, $[\mathrm{Rh(OCOR_F)(CO)(PPh_3)_2}]$, $[\mathrm{IrH(OCOR_F)_2(CO)(PPh_3)_2}]$, and $[\mathrm{Ir(H)_2(OCOR_F)(PPh_3)_3}]$. The new complexes have been characterised and, where possible, their stereochemistry has been determined by i.r. and n.m.r. spectroscopy. The occurrence of a rapid intramolecular exchange between uni- and bi-dentate perfluorocarboxylate ligands in the complexes $[\mathrm{M(OCOR_F)_2(CO)(PPh_3)_2}]$ (M = Ru or Os) has been established by observation of temperature-dependent ^{19}F n.m.r. spectra for the trifluoroacetate derivatives. Mechanisms involving oxidative addition of perfluorocarboxylic acids to the precursors, and subsequent reductive elimination of dihydrogen, are proposed for the reactions discussed. The tendency for unidentate perfluorocarboxylate ligands situated *trans* to strong σ-donor ligands to undergo alcoholysis is reported.

WE have recently described simple single-step syntheses for an extensive range of hydrido(triphenylphosphine) or low-oxidation-state triphenylphosphine complexes of the platinum-group metals,[2] and have shown that these pro-

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[1] Part IV, K. R. Laing, S. D. Robinson, and M. F. Uttley, *J.C.S. Dalton*, 1974, 1205.

[2] N. Ahmad, S. D. Robinson, and M. F. Uttley, *J.C.S. Dalton*, 1972, 843.

ducts undergo oxidative-addition reactions with carboxylic acids.[3,4] In Part II of the present series we reported the use of these latter reactions to synthesise an extensive range of aliphatic and aromatic carboxylato-complexes.[5] Preparation of the corresponding perfluorocarboxylato-complexes by a similar technique is discussed in the present paper.

TABLE 1

Analytical and spectroscopic data of some perfluorocarboxylato-complexes

Complex	R$_F$	M.p. (θ_c/°C)	Analyses [a]/% C	H	P	*M* [b]	I.r. bands [c]/cm^{-1} ν(MH)	ν(CO)	ν(OCO)$_{asym}$	N.m.r. spectra [d] τ(MH)	^2J(PH)/Hz
[RuCl(OCOR$_F$)CO(PPh$_3$)$_2$]	CF$_3$ [e]	198—203	55·85 (55·9)	3·55 (3·55)	7·5 (7·2)	1 200 (802)		1 980 1 974	1 648		
[Ru(OCOR$_F$)$_2$CO(PPh$_3$)$_2$]	CF$_3$ [e]	236—237	55·15 (55·5)	3·6 (3·6)	6·65 (6·85)	877 (879)		1 968	1 695 1 665		
	C$_2$F$_5$ [e]	207—208	52·15 (52·4)	3·25 (3·3)	5·9 (6·2)			1 968	1 692 1 664		
	C$_6$F$_5$	180 (decomp.)	56·8 (56·95)	2·85 (2·8)	5·8 (5·75)			1 981	1 663 1 648		
[Ru(OCOR$_F$)$_2$(CO)$_2$(PPh$_3$)$_2$]	CF$_3$	260—261	55·75 (55·45)	3·4 (3·3)	6·75 (6·85)	921 (911)		2 065 1 981	1 684 1 678		
	C$_2$F$_5$ [e]	258—260	51·45 (51·65)	2·95 (3·0)	5·95 (6·0)			2 052 1 993	1 697 1 682		
	C$_6$F$_5$ [e]	208—209	55·9 (55·8)	2·65 (2·75)	4·9 (5·5)			2 070 2 012	1 650		
[RuH(OCOR$_F$)(PPh$_3$)$_3$]	CF$_3$	236—237	67·05 (67·1)	4·85 (4·6)	9·15 (9·2)		2 032w		1 622	29·75	24·4(q)
[OsCl(OCOR$_F$)CO(PPh$_3$)$_3$]	CF$_3$ [e]	144—147	58·8 (59·0)	4·05 (3·95)	8·25 (7·9)	1 208 (1 203)		1 952	1 686		
	C$_2$F$_5$ [e]	157—159	57·25 (57·35)	4·2 (4·0)	7·60 (7·5)			1 940	1 674		
[Os(OCOR$_F$)$_2$CO(PPh$_3$)$_2$]	CF$_3$ [e]	234—236	50·7 (50·85)	3·2 (3·15)	6·35 (6·4)	967 (970)		1 948	1 700 1 655		
	C$_2$F$_5$	162—164	48·0 (48·3)	3·05 (2·8)	5·85 (5·8)			1 950	1 700 1 656		
	C$_6$F$_5$	173 (decomp.)	52·5 (52·6)	2·75 (2·6)				1 967	1 678 1 652		
[OsH(OCOR$_F$)CO(PPh$_3$)$_3$]	CF$_3$	251—253	61·15 (61·15)	4·15 (4·1)	8·05 (8·3)		2 115w	1 915	1 700 1 684	16·32	93·0(d) 25·0(t)
	C$_2$F$_5$ [e]	240—242	57·55 (57·25)	3·9 (3·9)	7·6 (7·55)		2 105w	1 912	1 701 1 694	16·32	93·0(d) 25·0(t)
[Os(OCOR$_F$)$_2$(CO)$_2$(PPh$_3$)$_2$]	CF$_3$	263—265	50·4 (50·6)	3·15 (3·0)	5·95 (6·2)			2 055 1 961	1 686		
	C$_2$F$_5$	223—224	48·7 (48·2)	2·95 (2·75)	5·4 (5·65)	1 084 (1 096)		2 064 1 983	1 686		
[OsH(OCOR$_F$)(CO)$_2$(PPh$_3$)$_2$]	CF$_3$	231—234	54·25 (54·3)	3·6 (3·55)	6·95 (7·0)	862 (884)	2 100w	2 070w 1 958	1 678	27·80	11·50(t)
	C$_2$F$_5$	204—206	53·05 (52·7)	3·55 (3·3)	6·45 (6·65)		2 120w	2 060w 1 950	1 680	28·05	12·50(t)
[OsH(OCOR$_F$)(PPh$_3$)$_3$]	CF$_3$	246—247	61·55 (61·65)	4·25 (4·2)	8·55 (8·55)		2 124w		1 612		
[Rh(OCOR$_F$)(PPh$_3$)$_3$]	CF$_3$	233—235	66·8 (67·1)	4·5 (4·5)	9·15 (9·3)	422 (1 002)			1 670		
	C$_2$F$_5$	236—237	64·7 (65·0)	4·35 (4·3)	8·75 (8·85)				1 685		
	C$_6$F$_5$ [e]	159—161	65·65 (65·75)	4·3 (4·25)	8·0 (8·2)				1 648		
[Rh(OCOR$_F$)CO(PPh$_3$)$_2$]	CF$_3$	204—206	60·95 (60·95)	4·0 (3·9)	8·3 (8·05)	810 (818)		1 981	1 689		
	C$_2$F$_5$	193—194	58·9 (58·65)	3·8 (3·65)	7·2 (7·6)			1 991	1 689		
	C$_6$F$_5$	167—168	60·85 (60·95)	3·7 (3·45)				1 978	1 649		
[IrH(OCOR$_F$)$_2$CO(PPh$_3$)$_2$]	CF$_3$	174—183	50·3 (50·6)	3·0 (3·2)			2 250w	2 040	1 700 1 678	27·49	11·0(t)
	C$_2$F$_5$						2 255w	2 045	1 702 1 678	27·54	11·0(t)
[Ir(H)$_2$(OCOR$_F$)(PPh$_3$)$_3$]	CF$_3$	261—263	61·05 (61·45)	4·35 (4·3)	8·65 (8·5)	1 089 (1 093)	2 224w 2 178w		1 682	33·55 21·14	8·0(d) 19·0(t) 136·5(d) 20·5(t)
	C$_2$F$_5$ [e]	250—251	59·2 (59·2)	4·3 (4·35)			2 220w 2 170w		1 698	35·00 20·56	8·0(d) 20·0(t) 137·0(d) 20·0(t)
	C$_6$F$_5$		57·85 (57·75)	3·95 (3·95)	7·4 (7·15)		2 236w 2 146w		1 650 1 639	34·78 20·59	10·5(d) 19·5(t) 141·5(d) 20·0(t)

[a] Calculated figures given in parentheses. [b] Calculated figures, given in parentheses, are for monomers. [c] Bands are strong unless otherwise indicated, w = weak. [d] Recorded in CDCl$_3$ solution; d = doublet, t = triplet, and q = quartet. [e] Spectroscopic and analytical data relate to solvated species; details of solvation are given in the Experimental section and have been confirmed by n.m.r. spectroscopy.

Several recent papers,[6-15] including some published while this work was in progress, describe reactions between perfluorocarboxylic acids and hydrido(triphenylphosphine) or low-oxidation-state triphenylphosphine complexes of the platinum-group metals. Products isolated include the trifluoroacetato-complexes [Ru(OCOCF$_3$)$_2$(CO)$_2$(PPh$_3$)$_2$],[6,7] [Rh(OCOCF$_3$)(PPh$_3$)$_2$],[8] [Rh(OCOCF$_3$)(CO)(PPh$_3$)$_2$],[9] [Ir(OCOCF$_3$)(CO)(PPh$_3$)$_2$],[9] [IrH(OCOCF$_3$)$_2$(CO)(PPh$_3$)$_2$],[9,10] [IrH(Cl)(OCOCF$_3$)(PPh$_3$)$_2$],[11] [IrH(Cl)(OCOCF$_3$)(CO)(PPh$_3$)$_2$],[12] and [PtH(OCOCF$_3$)(PPh$_3$)] [13] formed by oxidative-addition–reductive-elimination reactions, and the salts [Ir(H)$_2$(CO)(PPh$_3$)$_3$][(CF$_3$CO$_2$)$_2$H] [9,14] and [PtH(PPh$_3$)$_3$][(CF$_3$CO$_2$)$_2$H] [15] arising from protonation of the precursors [IrH(CO)(PPh$_3$)$_3$] and [Pt(PPh$_3$)$_3$] respectively. Metathetical reactions between halogeno-complexes and sodium or silver trifluoroacetates have been employed to prepare [RuH(OCOCF$_3$)(PPh$_3$)$_3$],[16] [IrH(OCOCF$_3$)$_2$(CO)(PPh$_3$)$_2$],[9] and [Pt(OCOCF$_3$)$_2$(PPh$_3$)$_2$].[17] In addition, other miscellaneous routes have been used to synthesise

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[3] S. D. Robinson and M. F. Uttley, *J.C.S. Chem. Comm.*, 1972, 1047.

[4] A. Dobson, K. R. Laing, S. D. Robinson, and M. F. Uttley, unpublished results.

[5] S. D. Robinson and M. F. Uttley, *J.C.S. Dalton*, 1973, 1912.

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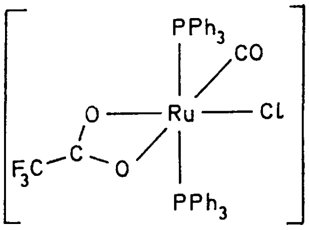
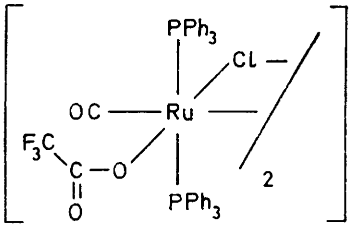
[16] D. Rose, J. D. Gilbert, R. P. Richardson, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1969, 2610.

[17] D. M. Barlex and R. D. W. Kemmitt, *J.C.S. Dalton*, 1972, 1436.

$[Pt(OCOCF_3)_2(PPh_3)_2]$,[18] $[Rh(OCOCF_3)(PPh_3)_3]$,[19] $[Rh(OCOCF_3)(CO)(PPh_3)_2]$,[19] $[Ir(H)_2(OCOC_2F_5)(CO)(PPh_3)_2]$,[8] and $[Ir(OCOCF_3)(CO)(PPh_3)_2]$.[10] However, no systematic attempt to develop a general synthesis for this class of perfluorocarboxylato(triphenylphosphine) complexes of the platinum-group metals has previously been reported. We now find that reactions of perfluorocarboxylic acids R_FCO_2H with hydrido(triphenylphosphine) or low-oxidation-state triphenylphosphine complexes of the platinum-group metals offer a convenient general route to a wide range of perfluorocarboxylato-complexes. In addition to providing improved syntheses for a number of known perfluorocarboxylato-complexes, the technique affords access to an important range of new ruthenium and osmium perfluorocarboxylato-derivatives.



(I)



(II)

RESULTS AND DISCUSSION

The structural and spectroscopic properties of the new complexes described in this work are discussed below; their extensive chemistry is currently being investigated and will be reported elsewhere. Unless otherwise indicated, the perfluorocarboxylato-complexes are air-stable crystalline solids and dissolve in common organic solvents to form air-stable solutions. With one apparent exception, $[RuCl(OCOCF_3)(CO)(PPh_3)_2]$, all are monomeric in chloroform solution, and some show evidence of appreciable dissociation. Many of the products retained solvent tenaciously and were therefore characterised and analysed as solvates. Stereochemical assignments for the new complexes have been made using i.r. and ^1H n.m.r. data (Table 1), augmented where necessary by chemical evidence. ^{31}P N.m.r. data have also been recorded (Table 2) for many of the complexes discussed; however, in the absence of metal–phosphorus couplings and adequate data for comparable complexes, they yield very little unambiguous stereochemical information. I.r. bands attributable to $\nu(OCO)_{sym}$, normally found in the range *ca.* 1 390—1 440 cm^{-1}, are either totally obscured or cannot be assigned with confidence in the majority of our carboxylato-complexes. Therefore, conclusions concerning the denticity of the carboxylate ligands are, of necessity, based on the values of $\nu(OCO)_{asym}$ [5] rather than on the more widely employed values of $[\nu(OCO)_{asym} - \nu(OCO)_{sym}]$.[20]

Ruthenium and Osmium Complexes.—$[RuCl(OCOCF_3)(CO)(PPh_3)_2]$ *and* $[OsCl(OCOR_F)(CO)(PPh_3)_3]$. Trifluoroacetic acid reacts with $[RuH(Cl)(CO)(PPh_3)_3]$ in boiling 2-methoxyethanol to yield a rather intractable material of apparent stoicheiometry $[RuCl(OCOCF_3)(CO)(PPh_3)_2],0{\cdot}5CF_3CO_2H$. This product has a molecular weight of 1 200, midway between the values expected for monomer and dimer formulations. Its i.r. spectrum shows a split carbonyl absorption [ν(CO) at 1 980 and 1 974 cm^{-1}] and its ^{31}P n.m.r. spectrum comprises a single peak. These data are consistent with, but do not establish, the presence of a labile equilibrium involving monomer and dimer species (I) and (II) respectively. This proposed equilibrium process bears a formal analogy to that observed to occur between uni- and bi-dentate trifluoroacetate ligands in the closely related complex $[Ru(OCOCF_3)_2(CO)(PPh_3)_2]$ (see below). Reactions of $[RuH(Cl)(CO)(PPh_3)_3]$ with other perfluorocarboxylic acids yielded intractable products which could not be obtained in an analytically pure state. Perfluorocarboxylic acids reacted with $[OsH(Cl)(CO)(PPh_3)_3]$ in benzene to yield air-stable complexes of stoicheiometry $[OsCl(OCOR_F)(CO)(PPh_3)_3]$. The i.r. spectra of these products confirmed the presence of carbonyl and unidentate perfluorocarboxylate ligands. Their ^{31}P n.m.r. spectra indicated a *mer*-configuration for the three triphenylphosphine ligands. These data are consistent with stereochemistry (IIIa), similar to

TABLE 2

^{31}P N.m.r. data * of some perfluorocarboxylato-complexes and their precursors

Complex	δ/p.p.m.	$^2J(PP')$/Hz
$[Ru(H)_2(CO)(PPh_3)_3]$	57·2(d) 44·8(t)	17·6
$[RuCl(OCOCF_3)(CO)(PPh_3)_2]$	38·55(s)	
$[Ru(OCOCF_3)_2(CO)(PPh_3)_2]$	42·75(s)	
$[Ru(OCOCF_3)_2(CO)_2(PPh_3)_2]$	30·3(s)	
$[Os(H)_2(CO)(PPh_3)_3]$	18·9(d) 14·4(t)	11·2
$[Os(OCOCF_3)_2(CO)(PPh_3)_2]$	−3·2(s)	
$[Os(OCOCF_3)_2(CO)_2(PPh_3)_2]$	8·35(s)	
$[OsH(OCOC_2F_5)(CO)(PPh_3)_3]$	13·9(d) 0·8(t)	11·9
$[OsH(OCOC_2F_5)(CO)_2(PPh_3)_2]$	12·6(s)	

* Recorded at 36·43 MHz in $CDCl_3$ solution and referenced to external H_3PO_4; all ^1H nuclei decoupled, $CDCl_3$ used to provide ^2D field-frequency lock, couplings ±0·2 Hz.

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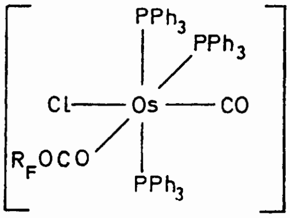
[18] C. J. Nyman, C. E. Wymore, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 561.

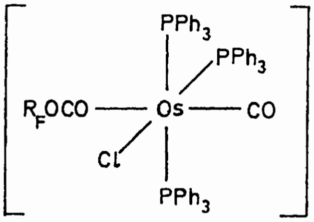
[19] R. W. Mitchell, J. D. Ruddick, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1971, 3224.

[20] K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds,' Wiley, New York, 1963 and refs. therein.

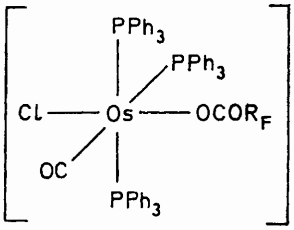
that previously proposed for the related ruthenium complexes [RuCl(OCOR)(CO)(PMe$_2$Ph)$_3$],[21] but do not exclude alternative structures (IIIb) and (IIIc). Stereochemistry (IIIb), containing perfluorocarboxylate ligands *trans* to carbonyl ligands of low σ-donor capacity, is a very feasible alternative.



(IIIa)

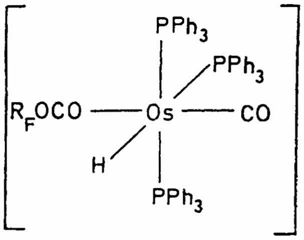


(IIIb)



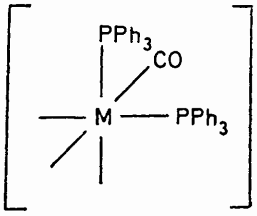
(IIIc)

[OsH(OCOR$_F$)(CO)(PPh$_3$)$_3$]. These white air-stable crystalline products, obtained by treating [Os(H)$_2$(CO)(PPh$_3$)$_3$] with perfluorocarboxylic acids in cold benzene, are assigned stereochemistry (IV) on the basis of their high-field ^{1}H n.m.r. spectra [τ 16·32 (OsH), doublet of triplets ^2J(PH)(*trans*) *ca.* 93·0, ^2J(PH)(*cis*) *ca.* 25·0 Hz]. This assignment was supported by the ^{31}P n.m.r. spectra (Table 2). Perfluorobenzoic acid failed to react with [Os(H)$_2$(CO)(PPh$_3$)$_3$] in cold benzene. Attempts to form analogous ruthenium complexes, [RuH(OCOR$_F$)(CO)(PPh$_3$)$_3$], with perfluorocarboxylic acids under similar conditions gave analytically impure products which appeared to contain appreciable amounts of the corresponding bis(perfluorocarboxylato) derivatives (see below).

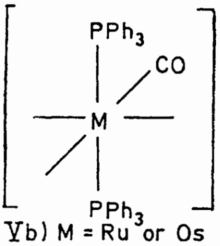


(IV)

[Ru(OCOR$_F$)$_2$(CO)(PPh$_3$)$_2$] *and* [Os(OCOR$_F$)$_2$(CO)(PPh$_3$)$_2$]. These air-stable crystalline products, obtained by treating the dihydrides [M(H)$_2$(CO)(PPh$_3$)$_3$] (M = Ru or Os) with perfluorocarboxylic acids in boiling benzene or toluene, each contain one uni- and one bi-dentate perfluorocarboxylate ligand. Their ^{31}P n.m.r. spectra (298 K) each show the presence of two equivalent ^{31}P nuclei, and are therefore consistent with the *fac*- and *mer*-structures (Va) and (Vb) respectively. In order to distinguish between these two possible structures it is necessary to employ chemical evidence concerning the solvolytic tendencies of perfluorocarboxylate ligands. Barlex and Kemmitt have recently reported[17] that, whereas the complex [Pt(OCOCF$_3$)$_2$(PPh$_3$)$_2$] of unspecified stereochemistry readily undergoes alcoholysis, the related species *trans*-[Pt(OCOCF$_3$)$_2$(PMe$_2$Ph)$_2$] is resistant to attack by alcohols even under vigorous conditions. We have now established that the complex [Pt(OCOCF$_3$)$_2$(PPh$_3$)$_2$] has *cis*-stereochemistry [^1J(PtP) 3 935 Hz], and conclude that the solvolytic susceptibilities of the perfluorocarboxylate ligands, in these and related bis(perfluorocarboxylato) complexes, are governed primarily by the nature of the *trans*-group rather than the basicity of the phosphine ligands present.[17] In particular, unidentate perfluorocarboxylate ligands are susceptible to alcoholysis when *trans* to good σ-donors such as triphenylphosphine, but inert to alcohols when *trans* to poor σ-donors such as carbonyl or perfluorocarboxylate ligands. Thus the susceptibility to alcoholysis shown by the complexes [M(OCOR$_F$)$_2$(CO)(PPh$_3$)$_2$] is indicative of the *fac*-stereochemistry (Va) with the perfluorocarboxylate ligands *trans* to PPh$_3$. In contrast, the reluctance of the complexes [M(OCOR$_F$)$_2$(CO)$_2$(PPh$_3$)$_2$] to undergo a similar process is consistent with the presence of perfluorocarboxylate ligands *trans* to poor σ-donor groups (Vb).



(Va) M = Ru or Os



(Vb) M = Ru or Os

(Remaining three co-ordination sites shared by two R$_F$CO$_2^-$ ligands)

The variable-temperature ^{19}F n.m.r. spectra of the trifluoroacetato-derivatives [M(OCOCF$_3$)$_2$(CO)(PPh$_3$)$_2$] are indicative of rapid exchange between uni- and bi-dentate carboxylate ligands, similar to those previously noted for the corresponding acetates [M(OCOMe)$_2$(CO)(PPh$_3$)$_2$].[3] This process occurs sufficiently slowly at room temperature to permit resolution of two discrete CF$_3$ resonances for each trifluoroacetato-complex and, in the case of the osmium derivative, to cause appreciable broadening of the singlet ^{31}P resonance. The low-temperature (213 K) ^{31}P n.m.r. spectra of the complexes [M(OCOCF$_3$)$_2$(CO)(PPh$_3$)$_2$] each comprise an AB type pattern [^2J(PP)(*cis*) 29·3 (Ru), 11·7 Hz (Os)]. These spectra are indicative of species containing two non-equivalent mutually *cis*-phosphine ligands and thus confirm the *fac*-stereochemistry proposed for the complexes [M(OCOR$_F$)$_2$(CO)(PPh$_3$)$_2$] on the basis of solvolytic behaviour. A kinetic and mechanistic study of

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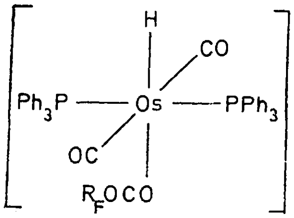
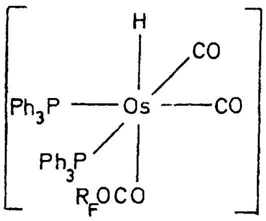
[21] M. S. Lupin and B. L. Shaw, *J. Chem. Soc.* (*A*), 1968, 741.

these and related fluxional systems is in progress and will be reported elsewhere.

$[\mathrm{OsH(OCOR_F)(CO)_2(PPh_3)_2}]$. These white air-stable complexes, obtained by treating the dihydride $[\mathrm{Os(H)_2(CO)_2(PPh_3)_2}]$ with perfluorocarboxylic acids under mild conditions, each contain a hydride ligand *cis* to two equivalent $^{31}\mathrm{P}$ nuclei and *trans* to the carboxylate group [τ *ca.* 27·9 (OsH), triplet, ^2J(PH)(*cis*) *ca.* 12·0 Hz]. Their i.r. spectra contain a band at *ca.* 2 110 $\mathrm{cm^{-1}}$ attributable to ν(OsH) and two bands at *ca.* 2 065 and 1 954 $\mathrm{cm^{-1}}$ assigned to ν(CO). The high-frequency ν(CO) band is very weak relative to that at low frequency and we therefore tentatively formulate the complexes as *trans*-dicarbonyl [stereochemistry (VIa)] rather than *cis*-dicarbonyl [stereochemistry (VIb)] derivatives. Confirmation that these complexes are dicarbonyl rather than monocarbonyl derivatives is provided by the reaction of $[\mathrm{OsH(OCOCF_3)(CO)_2(PPh_3)_2}]$ with cold neat $\mathrm{CF_3CO_2H}$ to yield $[\mathrm{Os(OCOCF_3)_2(CO)_2(PPh_3)_2}]$, identical with an authentic sample.



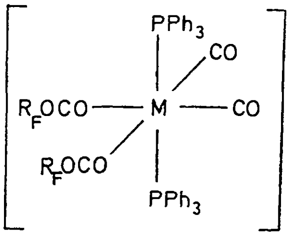
(VIa)



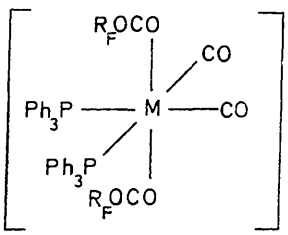
(VIb)

The *cis–trans*-dicarbonyl rearrangement, which accompanied the conversion of $[\mathrm{Os(H)_2(CO)_2(PPh_3)_2}]$ to $[\mathrm{OsH(OCOR_F)(CO)_2(PPh_3)_2}]$, is unexpected in view of the known tendency for strongly π-bonding carbonyl ligands to adopt a mutually *cis*-geometry, and presumably indicates that the reaction product is kinetically determined. Perfluorobenzoic acid failed to react with $[\mathrm{Os(H)_2(CO)_2(PPh_3)_2}]$.

$[\mathrm{Ru(OCOR_F)_2(CO)_2(PPh_3)_2}]$ *and* $[\mathrm{Os(OCOR_F)_2(CO)_2(PPh_3)_2}]$. These ruthenium and osmium complexes were obtained as white air-stable crystals by treating $[\mathrm{Ru(CO)_3(PPh_3)_2}]$ and $[\mathrm{Os(H)_2(CO)_2(PPh_3)_2}]$ respectively with perfluorocarboxylic acids under vigorous conditions (neat acid in the case of osmium). Their spectroscopic properties indicate the presence of unidentate carboxylate ligands [$\nu(\mathrm{OCO})_{\mathrm{asym}}$ at *ca.* 1 680 $\mathrm{cm^{-1}}$], a pair of mutually *cis*-carbonyl ligands [ν(CO) *ca.* at 2 060s and 1 980s $\mathrm{cm^{-1}}$], and a pair of equivalent triphenylphosphine ligands [$^{31}\mathrm{P}$ n.m.r. singlet]. These data are consistent with two possible stereochemical assignments, (VIIa) and (VIIb). However, the values of ν(CO) are similar to those reported for the corresponding chlorides $[\mathrm{MCl_2(CO)_2(PPh_3)_2}]$ both of which are now thought to possess stereochemistry (VIIa) (Cl replacing $\mathrm{R_FOCO}$). We therefore conclude that the perfluorocarboxylates $[\mathrm{M(OCOR_F)_2(CO)_2(PPh_3)_2}]$ also adopt stereochemistry (VIIa).[22] This assignment is in accord with that previously reported for the osmium formate $[\mathrm{Os(OCOH)_2(CO)_2(PPh_3)_2}]$.[23] However, the alternative stereochemistry (VIIb), advanced for the ruthenium complexes $[\mathrm{Ru(OCOR)_2(CO)_2(PPh_3)_2}]$ (R = alkyl [5,7] or $\mathrm{CF_3}$ [6]) on the basis of an earlier erroneous assignment for the dihalides $[\mathrm{RuX_2(CO)_2(PPh_3)_2}]$,[6] now requires revision in the light of the results discussed above.



(VIIa) M = Ru or Os



(VIIb) M = Ru or Os

Assuming that our stereochemical assignments are correct, the conversion of $[\mathrm{Os(H)_2(CO)_2(PPh_3)_2}]$ to $[\mathrm{OsH(OCOR_F)(CO)_2(PPh_3)_2}]$ and thence, under more vigorous conditions, to $[\mathrm{Os(OCOR_F)_2(CO)_2(PPh_3)_2}]$ involves a *cis–trans–cis*-rearrangement of the carbonyl ligands. It appears highly probable that these rearrangements involve stereochemically non-rigid seven-co-ordinate osmium(IV) intermediates[24] formed by protonation of the osmium(II) precursors in the presence of the highly acidic perfluorocarboxylic acids [scheme (1)]. Similar reaction schemes can be advanced for

$$\begin{aligned}&[\mathrm{Os(H)_2(CO)_2(PPh_3)_2}] \xrightarrow{\mathrm{R_FCO_2H}}\\&[\mathrm{Os(H)_3(CO)_2(PPh_3)_2}][\mathrm{OCOR_F}] \xrightarrow{-\mathrm{H_2}}\\&[\mathrm{OsH(OCOR_F)(CO)_2(PPh_3)_2}] \xrightarrow{\mathrm{R_FCO_2H}}\\&[\mathrm{Os(H)_2(OCOR_F)(CO)_2(PPh_3)_2}][\mathrm{OCOR_F}] \longrightarrow\\&\qquad[\mathrm{Os(OCOR_F)_2(CO)_2(PPh_3)_2}] + \mathrm{H_2} \quad (1)\end{aligned}$$

the other syntheses described in this work, and have been established for the reaction of $[\mathrm{IrH(CO)(PPh_3)_3}]$ [9,14] and $[\mathrm{Pt(PPh_3)_3}]$ [15] with perfluorocarboxylic acids. Attempts to isolate the proposed ionic intermediates $[\mathrm{Os(H)_3(CO)_2(PPh_3)_2}][\mathrm{OCOR_F}]$ by reacting $[\mathrm{Os(H)_2(CO)_2(PPh_3)_2}]$ with perfluorocarboxylic acids in cold toluene solution and precipitating the products with cold diethyl ether were unsuccessful; only the uncharged species $[\mathrm{OsH(OCOR_F)(CO)_2(PPh_3)_2}]$ were obtained.

$[\mathrm{RuH(OCOCF_3)(PPh_3)_3}]$ *and* $[\mathrm{OsH(OCOCF_3)(PPh_3)_3}]$. These complexes were obtained by treating $[\mathrm{Ru(H)_2(PPh_3)_4}]$ and $[\mathrm{Os(H)_4(PPh_3)_3}]$ respectively with trifluoroacetic acid in boiling alcoholic media, and were immediately deposited from the reaction mixture thus obviating the need to work up highly air-sensitive solutions. Attempts to prepare the corresponding pentafluoro-propionate and -benzoate derivatives led to carbonylation side reactions; in particular the treatment of $[\mathrm{Os(H)_4(PPh_3)_3}]$ with pentafluoropropionic acid in boiling 2-methoxyethanol gave $[\mathrm{OsH(OCOC_2F_5)(CO)}$-

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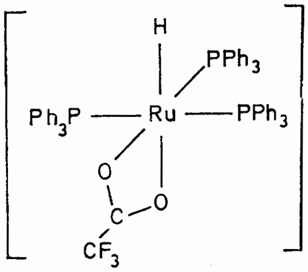
[22] J. P. Collman and W. R. Roper, *J. Amer. Chem. Soc.*, 1966, **88**, 3504.

[23] K. R. Laing and W. R. Roper, *J. Chem. Soc.* (*A*), 1969, 1889.

[24] B. Bell, J. Chatt, and G. J. Leigh, *J.C.S. Dalton*, 1973, 997 and refs. therein.

$(PPh_3)_3]$, identical with an authentic specimen (see above). The complexes $[MH(OCOCF_3)(PPh_3)_3]$ are stable in the solid state for several days but are rapidly attacked by dioxygen in solution. The ruthenium complex is identical with an authentic specimen prepared according to Wilkinson's method.[16] The osmium analogue, $[OsH(OCOCF_3)(PPh_3)_3]$, shows an i.r. vibration ν(OsH) at 2 124 cm^{-1}; however its rapid decomposition in solution prevented us from obtaining meaningful n.m.r. data. A distorted octahedral structure with a chelate carboxylate ligand has been established for the acetate $[RuH(OCOMe)(PPh_3)_3]$;[25] similar structures (VIII) seem probable for the ruthenium and osmium trifluoroacetates $[MH(OCOCF_3)(PPh_3)_3]$, and are consistent with the available spectroscopic data.

Rhodium Complexes.—$[Rh(OCOR_F)(PPh_3)_3]$. These air-sensitive orange complexes have previously been obtained by reacting the binuclear cations 'Rh_2^{4+}' with triphenylphosphine and the lithium salts of the appropriate perfluorocarboxylic acids, and have been formulated as square-planar derivatives of rhodium(I) containing unidentate carboxylate ligands.[19] The synthesis employed in the present work involved reaction of $[RhH(PPh_3)_4]$ with perfluorocarboxylic acids in boiling ethanol. Use of this solvent led to direct precipitation of the products and thus obviated the need to work up air-sensitive solutions. Molecular weights recorded using chloroform solutions confirmed a previous finding that, in the presence of dioxygen, these complexes are heavily dissociated.[19]

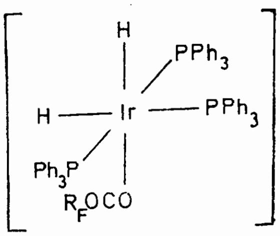


(VIII)

trans-$[Rh(OCOR_F)(CO)(PPh_3)_2]$. These complexes were originally obtained by carbonylation of the above-mentioned derivatives, $[Rh(OCOR_F)(PPh_3)_3]$, using carbon monoxide or aldehydes.[19] A recently reported alternative synthesis of $[Rh(OCOCF_3)(CO)(PPh_3)_2]$ involves reaction of $[RhH(CO)(PPh_3)_3]$ with trifluoroacetic acid in cold toluene.[9] The method employed in the present work to prepare the complexes $[Rh(OCOR_F)(CO)(PPh_3)_2]$ is similar to the latter synthesis but employed boiling ethanol as solvent. The trifluoroacetate complex prepared in this manner shows the extraneous i.r. band at 832 cm^{-1} first reported by Wilkinson and his co-workers;[9] the corresponding pentafluoro-propionate and -benzoate complexes show similar i.r. bands at *ca.* 812 cm^{-1}.

Iridium Complexes.—Our results[3] on the reactions of perfluorocarboxylic acids with the iridium complex $[IrH(CO)(PPh_3)_3]$ are confirmed by the recent work of Roundhill[14] and Wilkinson and his co-workers,[9] and are therefore not discussed further.

$[Ir(H)_2(OCOR_F)(PPh_3)_3]$. Perfluorocarboxylic acids react with *mer*-$[Ir(H)_3(PPh_3)_3]$ in boiling ethanol to yield a series of complexes $[Ir(H)_2(OCOR_F)(PPh_3)_3]$ analogous to the previously reported non-fluorinated derivatives, $[Ir(H)_2(OCOR)(PPh_3)_3]$.[5,26] High-field ^1H n.m.r. spectra permit unambiguous assignment of stereochemistry (IX) for these products. Attempts to induce further reaction between these complexes and excess of perfluorocarboxylic acid were unsuccessful.



(IX)

EXPERIMENTAL

Triphenylphosphine complexes of the platinum metals were prepared as previously described.[2] Perfluorocarboxylic acids were used as purchased (Fluorochem and B.D.H.). All reflux reactions were carried out under nitrogen.

N.m.r. spectra were recorded on Varian HA 100 and Bruker HFX 90 spectrometers, and i.r. spectra on Perkin-Elmer 457 and 621 grating spectrometers for samples mulled in Nujol. M.p.s were measured for samples sealed under nitrogen.

Ruthenium Complexes.—*Carbonylchloro(trifluoroacetato)bis(triphenylphosphine)ruthenium*(II)-*trifluoroacetic acid* (2/1), $[RuCl(OCOCF_3)CO(PPh_3)_2],0{\cdot}5CF_3CO_2H$. Trifluoroacetic acid (0·5 cm^3) was added to a suspension of carbonylchlorohydridotris(triphenylphosphine)ruthenium (0·3 g) in 2-methoxyethanol (5·0 cm^3). This mixture was heated under reflux for 10 min, during which time a clear yellow solution formed. The 2-methoxyethanol was evaporated under reduced pressure and the residual yellow oil crystallised from dichloromethane–hexane as tacky yellow *crystals*. These were filtered off, washed with water and hexane, and dried *in vacuo* (86%). *Carbonylchloro(pentafluoropropionato)bis(triphenylphosphine)ruthenium*(II) and *carbonylchloro(pentafluorobenzoato)bis(triphenylphosphine)ruthenium*(II) were similarly prepared but contained impurities which could not be eliminated.

Carbonylbis(trifluoroacetato)bis(triphenylphosphine)ruthenium(II)-*methanol* (4/3). $[Ru(OCOCF_3)_2CO(PPh_3)_2],0{\cdot}75MeOH$. Trifluoroacetic acid (1·0 cm^3) was added to a solution of carbonyldihydridotris(triphenylphosphine)ruthenium (0·46 g) in benzene (10·0 cm^3). The mixture was heated under reflux for 60 min and then evaporated under reduced pressure. The residual yellow oil was crystallised from dichloromethane–methanol and the product filtered off, washed successively in methanol, water, and methanol, then dried *in vacuo* as yellow *crystals* (77%). The following were similarly prepared as yellow

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[25] A. C. Skapski and F. A. Stephens, *Chem. Comm.*, 1969, 1008.

[26] M. Angoletta and A. Araneo, *Gazzetta*, 1963, **93**, 1343.

crystals using the appropriate acid: *carbonylbis(pentafluoropropionato)bis(triphenylphosphine)ruthenium*(II)*–methanol* (3/2) (89%) and *carbonylbis(pentafluorobenzoato)bis(triphenylphosphine)ruthenium*(II) (58%).

Dicarbonylbis(trifluoroacetato)bis(triphenylphosphine)ruthenium(II), [Ru(OCOCF$_3$)$_2$(CO)$_2$(PPh$_3$)$_2$]. Trifluoroacetic acid (0·5 cm^3) was added to a suspension of tricarbonylbis(triphenylphosphine)ruthenium (0·2 g) in 2-methoxyethanol (5·0 cm^3). The suspension was heated under reflux for 30 min, the solvent was removed under reduced pressure, and the residual oil was crystallised from dichloromethane–methanol. The resulting white *crystals* were filtered off, washed successively in methanol, water, and methanol, and dried *in vacuo* (78%). The following were similarly prepared as white *crystals* using the appropriate acid: *dicarbonylbis(pentafluoropropionato)bis(triphenylphosphine)ruthenium*(II)*–dichloromethane* (4/1) (88%) and *dicarbonylbis(pentafluorobenzoato)bis(triphenylphosphine)ruthenium*(II)*–dichloromethane* (4/1) (85%).

Hydrido(trifluoroacetato)tris(triphenylphosphine)ruthenium(II), [RuH(OCOCF$_3$)(PPh$_3$)$_3$]. Trifluoroacetic acid (1·0 cm^3) was added to a suspension of dihydridotetrakis(triphenylphosphine)ruthenium (0·38 g) in ethanol (10·0 cm^3) and the mixture was heated under reflux for 10 min. After cooling the precipitate was filtered off, washed successively with methanol, water, and methanol, and dried *in vacuo* as orange *crystals* (88%). *Hydrido(pentafluoropropionato)tris(triphenylphosphine)ruthenium*(II) was similarly prepared but found to contain an impurity [i.r. band at 1 920w cm^{-1}] and could not be obtained analytically pure.

Osmium Complexes.—*Carbonylchloro(trifluoroacetato)tris(triphenylphosphine)osmium*(II)*–methanol* (4/3), [OsCl(OCOCF$_3$)CO(PPh$_3$)$_3$],0·75MeOH. Trifluoroacetic acid (0·5 cm^3) was added to carbonylchlorohydridotris(triphenylphosphine)osmium (0·2 g) in benzene (5·0 cm^3) and the mixture was heated under reflux for 10 min. Evaporation under reduced pressure gave an oil which was crystallised from the minimum volume of methanol as white *crystals*. These were filtered off, washed with a minimum of methanol, water, and methanol, and then dried *in vacuo* (65%). Similarly prepared as white *crystals* using pentafluoropropionic acid was *carbonylchloro(pentafluoropropionato)tris(triphenylphosphine)osmium–methanol* (1/1) (89%).

Carbonylbis(trifluoroacetato)bis(triphenylphosphine)osmium(II)*–methanol* (3/1), [Os(OCOCF$_3$)$_2$CO(PPh$_3$)$_2$],0·33MeOH. Trifluoroacetic acid (1·0 cm^3) was added to a solution of carbonyldihydridotris(triphenylphosphine)osmium (0·4 g) in toluene (10·0 cm^3) and the mixture was heated under reflux for 30 min. The solution was evaporated under reduced pressure and the resultant dark oil crystallised from a minimum volume of methanol to yield cream *crystals*. These were filtered off, washed successively in methanol, water, and methanol, and dried *in vacuo* (96%). The following were similarly prepared as cream *crystals* using the appropriate acid: *carbonylbis(pentafluoropropionato)bis(triphenylphosphine)osmium*(II) (80%) and *carbonylbis(pentafluorobenzoato)bis(triphenylphosphine)osmium*(II) (35%).

Carbonylhydrido(trifluoroacetato)tris(triphenylphosphine)osmium(II), [OsH(OCOCF$_3$)CO(PPh$_3$)$_3$]. Trifluoroacetic acid (1·0 cm^3) was added to carbonyldihydridotris(triphenylphosphine)osmium (0·4 g) in benzene (10·0 cm^3) and the mixture shaken in the cold for 20 min. The solution was then filtered and evaporated under reduced pressure, and the residue was crystallised from hot methanol as white *crystals*. These were filtered off, washed successively in methanol, water, and methanol, and dried *in vacuo* (78%). Similarly prepared as white *crystals* using pentafluoropropionic acid was *carbonylhydrido(pentafluoropropionato)tris(triphenylphosphine)osmium*(II)*–dichloromethane* (4/3) (60%).

Dicarbonylbis(trifluoroacetato)bis(triphenylphosphine)osmium(II), [Os(OCOCF$_3$)$_2$(CO)$_2$(PPh$_3$)$_2$]. Trifluoroacetic acid (1·0 cm^3) was added to dicarbonyldihydridobis(triphenylphosphine)osmium (0·2 g). The mixture was warmed gently until effervescence ceased and then allowed to stand for 30 min. Methanol (10·0 cm^3) was added to precipitate white *crystals*, which were filtered off, washed successively in methanol, water, and methanol, recrystallised from dichloromethane–methanol, and dried *in vacuo* (91%). Similarly prepared as white *crystals* using pentafluoropropionic acid was *dicarbonylbis(pentafluoropropionato)bis(triphenylphosphine)osmium*(II) (65%).

Dicarbonylhydrido(trifluoroacetato)bis(triphenylphosphine)osmium(II),[OsH(OCOCF$_3$)(CO)$_2$(PPh$_3$)$_2$]. Trifluoroacetic acid (0·5 cm^3) was added to dicarbonyldihydridobis(triphenylphosphine)osmium (0·2 g) in benzene (5·0 cm^3) and the mixture heated under reflux for 30 min. The filtered solution was evaporated under reduced pressure and the residual oil was crystallised from methanol. The white *crystals* were filtered off, washed successively in methanol, water, and methanol, and dried *in vacuo* (72%). The following was similarly prepared as white *crystals* using pentafluoropropionic acid: *dicarbonylhydrido(pentafluoropropionato)bis(triphenylphosphine)osmium*(II) (80%).

Hydrido(trifluoroacetato)tris(triphenylphosphine)osmium(II), [OsH(OCOCF$_3$)(PPh$_3$)$_3$]. Trifluoroacetic acid (0·5 cm^3) was added to a suspension of tetrahydridotris(triphenylphosphine)osmium (0·33 g) in 2-methoxyethanol (5·0 cm^3) and the mixture heated under reflux for 10 min. During this time the suspension cleared and the product precipitated as orange *crystals*. After cooling these were filtered off, washed successively in methanol, water, and methanol, and dried *in vacuo* (66%). A similar procedure using pentafluoropropionic acid resulted in formation of a product identified by i.r. spectroscopy as *carbonylhydrido(pentafluoropropionato)tris(triphenylphosphine)osmium*(II).

Rhodium Complexes.—*(Trifluoroacetato)tris(triphenylphosphine)rhodium*(I), [Rh(OCOCF$_3$)(PPh$_3$)$_3$]. Trifluoroacetic acid (0·5 cm^3) was added to a suspension of hydridotetrakis(triphenylphosphine)rhodium (0·29 g) in ethanol (10·0 cm^3). The mixture was heated under reflux for 15 min, during which time the suspension cleared and orange *crystals* were precipitated. The mixture was cooled, the crystals filtered off, washed successively with methanol, water, and methanol, and dried *in vacuo* (96%). The following were similarly prepared as orange *crystals* using the appropriate acid: *(pentafluoropropionato)tris(triphenylphosphine)rhodium*(I) (94%) and *(pentafluorobenzoato)tris(triphenylphosphine)rhodium*(I)*–ethanol* (2/1) (67%).

Carbonyl(trifluoroacetato)bis(triphenylphosphine)rhodium(I), [Rh(OCOCF$_3$)CO(PPh$_3$)$_2$]. Trifluoroacetic acid (0·5 cm^3) was added to a suspension of carbonylhydridotris(triphenylphosphine)rhodium (0·3 g) in ethanol (10·0 cm^3). The mixture was heated under reflux for 15 min, during which time the suspension cleared to give a yellow solution which on cooling gave the product as yellow *crystals*. These were filtered off, washed successively with methanol, water, and methanol, and then dried *in vacuo* (92%). The following were similarly prepared as yellow *crystals* using the appropriate acid: *carbonyl(pentafluoropropionato)bis(triphenylphosphine)rhodium*(I) (90%) and *carbonyl(pentafluorobenzoato)bis(triphenylphosphine)rhodium*(I) (88%).

Iridium Complexes.—*Carbonylhydridobis(trifluoroacetato)bis(triphenylphosphine)iridium*(III), $[IrH(OCOCF_3)_2CO(PPh_3)_2]$. Trifluoroacetic acid (0·5 cm^3) was added to carbonylhydridotris(triphenylphosphine)iridium (0·2 g) in 2-methoxyethanol (5·0 cm^3), and the mixture was heated under reflux for 20 min. The solution was then cooled and methanol (10·0 cm^3) added to precipitate the product, which was filtered off, washed successively in methanol, water, and methanol, and dried *in vacuo* as pale yellow *crystals* (47%). Similarly prepared from pentafluoropropionic acid was *carbonylhydridobis(pentafluoropropionato)bis(triphenylphosphine)iridium*(III) as pale yellow *crystals*. This complex was identified by n.m.r. and i.r. spectroscopy only.

Dihydrido(trifluoroacetato)tris(triphenylphosphine)iridium(III), $[Ir(H)_2(OCOCF_3)(PPh_3)_3]$. Trifluoroacetic acid (0·5 cm^3) was added to a suspension of *mer*-trihydridotris(triphenylphosphine)iridium (0·2 g) in ethanol (10·0 cm^3) and the mixture was heated under reflux for 30 min. The resulting solution was evaporated to small volume under reduced pressure and left to crystallise. The product was filtered off, washed successively in methanol, water, and methanol, recrystallised from dichloromethane–methanol, and dried *in vacuo* as white *crystals* (88%). The following were similarly prepared as white *crystals* using the appropriate acid: *dihydrido(pentafluoropropionato)tris(triphenylphosphine)iridium*(III)*–methanol* (1/1) and *dihydrido(pentafluorobenzoato)tris(triphenylphosphine)iridium*(III)*–methanol* (2/1)*–dichloromethane* (1/1). The amount of solvation was found to vary, the above being supported by analytical and n.m.r. data; the nature and amount of solvation depended on the conditions of crystallisation.

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