Oxidative Addition of Carboxylic Acids to *trans*-Carbonylhalogenobis(tertiary phosphine)iridium(I) Complexes

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Complexes of the type *trans*-$[\mathrm{IrX(CO)L_2}]$ ($\mathrm{L = PEt_3, PMe_2Ph}$, or $\mathrm{PPh_3}$; X = Cl, Br, or I) undergo rapid oxidative addition with carboxylic acids $\mathrm{RCO_2H}$ (R = H, Me, $\mathrm{CF_3}$, Ph, or 1-naphthyl) to give iridium(III) complexes $[\mathrm{IrXH(O_2CR)(CO)L_2}]$ corresponding to both (formal) *cis* and *trans* addition of the carboxylic acid to the iridium(I) species. In solution these complexes undergo rapid anion exchange such that, at equilibrium, two additional hydrido-species, $[\mathrm{IrX_2H(CO)L_2}]$ and $[\mathrm{IrH(O_2CR)_2(CO)L_2}]$, are present. In all these octahedral complexes the tertiary phosphine groups are mutually *trans*, the hydride and carbonyl groups mutually *cis*, and the carboxylic unit is unidentate. The ease of formation of the different complexes depends on the nature of the carboxylic acid. The *cis* adduct containing chloride and having hydride and carbonyl mutually *trans* can be prepared by the action of carbon monoxide on complexes $[\mathrm{IrCl(H)(O_2CR)L_2}]$ which contain a bidentate carboxylate ligand. With weak acids, *e.g.* acetic, conversion of the iridium(I) into the iridium(III) species is incomplete; the exchange between free and co-ordinated acid is, however, slow on the n.m.r. time scale over the range −60 to 30 °C. The adducts formed between *trans*-$[\mathrm{IrX(CO)L_2}]$ (X = Cl, Br, or I) and formic acid are smoothly converted on heating in solution into dihydrido-complexes $[\mathrm{IrXH_2(CO)L_2}]$ with expulsion of carbon dioxide; with $\mathrm{L = PPh_3}$ or $\mathrm{PEt_3}$, trihydrido-complexes $[\mathrm{IrH_3(CO)L_2}]$ are also formed.

ALTHOUGH there have been several reports [1-5] dealing with the addition of carboxylic acids to iridium(I) species of type *trans*-$[\mathrm{IrCl(CO)L_2}]$ (1; L = tertiary phosphine) the exact nature of the complexes formed remains unclear. Deeming and Shaw [3] have demonstrated a correlation between the $\mathrm{p}K_\mathrm{a}$ of the carboxylic acid and the extent of conversion of the iridium(I) complex into an iridium(III) species and suggested the formation of a complex of type $[\mathrm{IrCl(H)(O_2CR)(CO)L_2}]$. However, no direct spectroscopic evidence (n.m.r. or i.r.) of these complexes could be obtained and no discussion of stereochemistry was included. Singer and Wilkinson [2] reported that trifluoroacetic acid and pentafluoropropionic acid react immediately with yellow *trans*-$[\mathrm{IrCl(CO)(PPh_3)_2}]$ in deuteriochloroform to give colourless solutions, the n.m.r. spectra of which indicate the presence of four different hydrido-species. However, once again the exact nature of these species was unclear. In view of this somewhat confused picture and the importance of carboxylic acid complexes of transition metals [6] in homogeneous catalysis we decided to examine the reaction between simple carboxylic acids and iridium(I) species.

RESULTS AND DISCUSSION

(*a*) *Formic Acid.*—The complete sequence of reactions discussed is shown in Scheme 1. Addition of a two-fold excess of formic acid to a solution of *trans*-$[\mathrm{IrCl(CO)(PMe_2Ph)_2}]$ in benzene resulted in an instantaneous bleaching of the yellow solution. The n.m.r. spectrum (see Figure and Table 1) of the resulting mixture contained four high-field signals,‡ indicating the presence of four different hydrido-species. Two of these hydride signals were independently coupled (5 Hz) to two low-field (δ 8.40 and 8.31 p.p.m.) signals. A further complex absorption, not due to free formic acid, was centred at δ 7.91 p.p.m. The methyl groups of the dimethylphenylphosphine ligands gave rise to overlapping, virtually coupled, triplets, indicating that in all the complexes formed the tertiary phosphine ligands are mutually *trans*. We initially considered that the reaction with formic acid had yielded two complexes containing a formyl group and two complexes containing a formate group, the H–H coupling of 5 Hz then being due to a hydride–formyl H coupling. This was not the case for the following reasons.

(*i*) The $^{13}\mathrm{C}$ n.m.r. spectrum (with complete $^1\mathrm{H}$ decoupling) of the complexes resulting from the reaction between $\mathrm{H^{13}CO_2H}$ and *trans*-$[\mathrm{IrCl(CO)(PMe_2Ph)_2}]$ in benzene consisted of four singlets at $\delta(\mathrm{SiMe_4})$ 168.4, 166.9, 162.6, and 162.3 p.p.m., indicating the presence of four closely similar formic acid-derived units in the product complexes. These values, when compared with those obtained for tetramethylammonium formate (δ *ca.* 161 p.p.m. in water),[7] formic acid [$\delta(\mathrm{SiMe_4})$ 165.4 p.p.m. in benzene], the formyl carbon atom in $\mathrm{Na[Fe(OCH)(CO)_4]}$ [$\delta(\mathrm{SiMe_4})$ 275.8 p.p.m. in tetrahydrofuran],[8] and the acetyl carbon atom in $[\mathrm{Fe(\eta\text{-}C_5H_5)(OCMe)(CO)_2}]$[$\delta(\mathrm{SiMe_4})$ 254.4 p.p.m. in benzene] [9] indicate that no formyl-containing species are present. (*ii*) When the solution was left for *ca.* 48 h at ambient temperature (20 °C) all the four complexes were smoothly converted into the dihydride species [10] (2; $\mathrm{L = PMe_2Ph}$) (n.m.r. data in Table 2), with exclusive evolution of carbon dioxide. Carbon monoxide or formaldehyde, which would be expected if a hydride–formyl species

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‡ The two weak signals at δ −18.8 and −7.6 p.p.m. are assigned to the dihydrido-complex $[\mathrm{IrClH_2(CO)(PMe_2Ph)_2}]$ (see below).

[1] J. P. Collman and W. R. Roper, *Adv. Organometallic Chem.*, 1968, **7**, 53.

[2] H. Singer and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 2516.

[3] A. J. Deeming and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 1802.

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

[5] E. M. Miller and B. L. Shaw, *J.C.S. Dalton*, 1974, 480.

[6] G. N. Schrauzer, 'Transition Metals in Homogeneous Catalysis,' Marcel Dekker, New York, 1971.

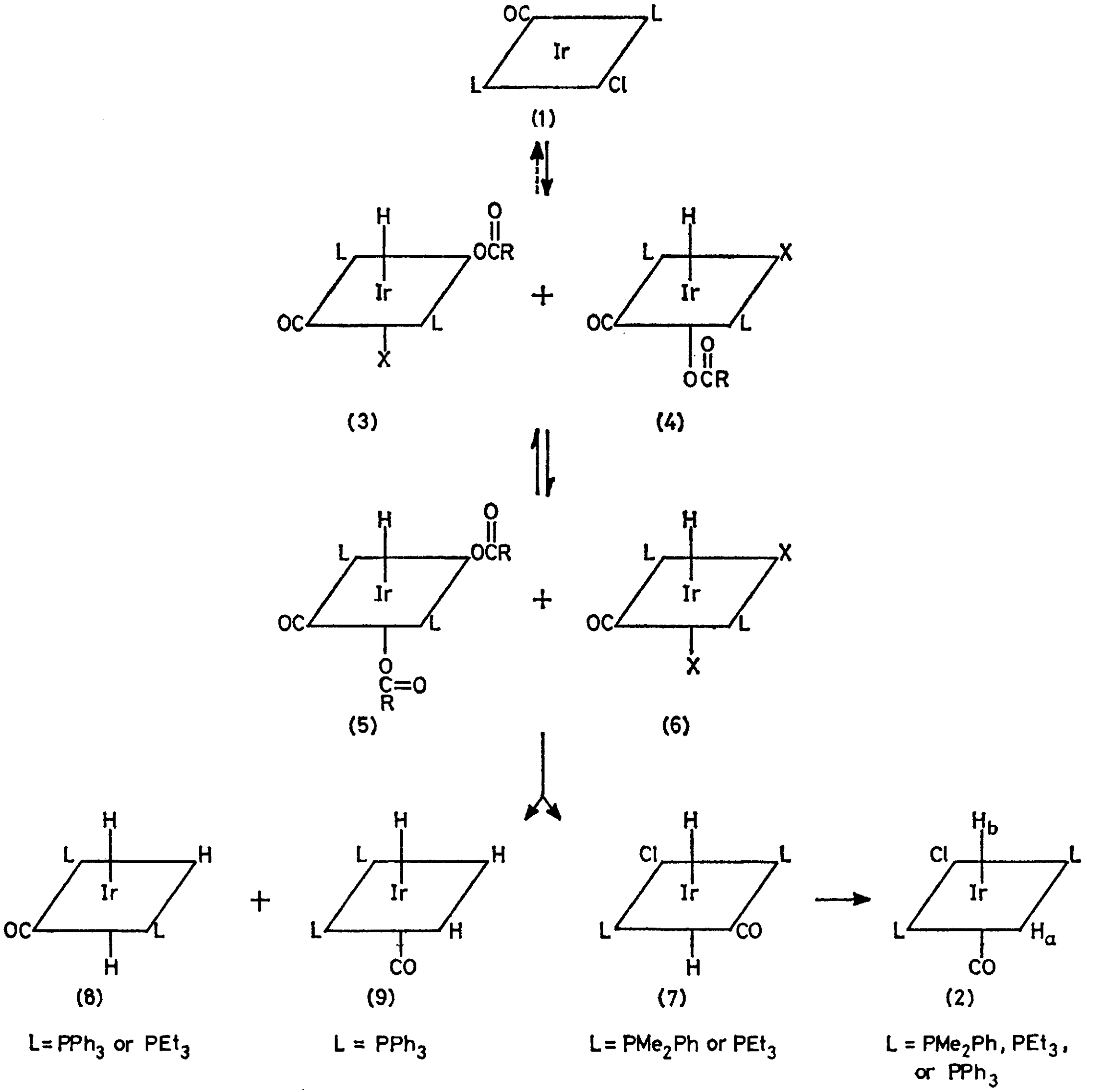
[7] R. Hagen and J. D. Roberts, *J. Amer. Chem. Soc.*, 1969, **91**, 4504.

[8] J. P. Collman and S. R. Winter, *J. Amer. Chem. Soc.*, 1973, **95**, 4089.

[9] L. F. Farnell, E. W. Randall, and E. Rosenberg, *Chem. Comm.*, 1971, 1078.

[10] A. J. Deeming and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 1128.

were present in solution, could not be detected (mass spectroscopy, g.l.c., and i.r.). Using DCO_2H in place of HCO_2H showed that addition occurs exclusively at the O–H bond since no iridium deuteride species were formed.



SCHEME 1

Thus we must seek an alternative explanation. As can be seen from the data in Table 1, the relative amounts of the four complexes formed depend on the type of solvent, on the nature of the tertiary phosphine ligand, and on the nature of the halogen atom. The ratios given in Table 1 were those observed after *ca.* 15 min at ambient temperature. On mixing *trans*-$[IrCl(CO)L_2]$ and HCO_2H in $C_6D_5CD_3$ at −60 °C and immediately recording the ^1H n.m.r. spectrum (at −60 °C) only the complex giving rise to the hydride resonance at δ −19.8 p.p.m. was observed. When the solution was allowed to warm to *ca.* 0 °C the triplet resonance at δ −14.4 p.p.m. appeared and after *ca.* 10 min at 28 °C all the four hydride signals were present in the ratio given in Table 1. Subsequent cooling of the solution to −60 °C had no effect on this ratio.

As previously indicated, the complexes formed from the reaction between *trans*-$[IrCl(CO)(PMe_2Ph)_2]$ and formic acid are thermally unstable. However, careful removal of the solvent and excess of formic acid by freeze drying resulted in the isolation of a white solid whose n.m.r. spectrum in benzene was essentially the same as that of the complexes formed *in situ*. This white solid was non-conducting in nitrobenzene at 22 °C {equivalent conductivity 2.1×10^{-2}, *cf.* 5.6×10^{-2} for *trans*-$[IrCl(CO)(PMe_2Ph)_2]$ and 17.5 S cm^{-1} mol^{-1} for $[IrCl(CO)(PMe_2Ph)_3][BPh_4]$[11]}. Its i.r. spectrum (see Table 3) contained two absorptions characteristic of iridium(III) hydride species and two absorptions characteristic of a carbonyl ligand bound to an iridium(III) centre. The absorptions assigned to ν_{asym}-

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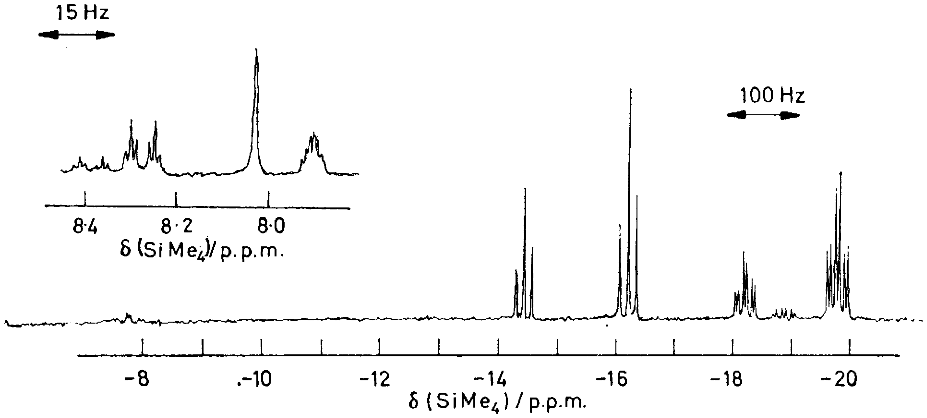
[11] A. J. Deeming and B. L. Shaw, *J. Chem. Soc. (A)*, 1970, 3356.

TABLE 1

90-MHz ^1H n.m.r. data for the complexes formed on addition of formic acid to *trans*-$[IrX(CO)L_2]$

		Hydride resonances [a]								Formate resonances								Methyl (of PMe_2Ph) resonances δ/p.p.m. (±0.2) [c]				Ratio [d]
		δ/p.p.m. (±0.2)				$J(^{31}P-H)$ ±0.5 Hz				δ/p.p.m. (±0.02)				$J(^{31}P-H)$ ±0.2 Hz								
L	X	(3)	(6)	(5)	(4)	(3)	*cis*-(5) [b]	*trans*-(5) [b]	(4)	(3)	*cis*-(5) [b]	*trans*-(5) [b]	(4)	(3)	*cis*-(5) [b]	*trans*-(5) [b]	(4)	(3)	(6)	(5)	(4)	(3) : (6) : (5) : (4)
PMe_2Ph	Cl	−14.4	−16.2	−18.2	−19.8	12.5	12.5	12	13	7.93	7.92	8.40	8.31	1.7 [e]	1.7 [e]			1.66(9) 1.55(9)	1.84(8) 1.76(8)	1.47(8) 1.42(8)	1.63(8) 1.58(8)	1 : 1.2 : 1 : 2.3 [f]
PMe_2Ph	Br	−13.4	−15.5	−18.0	−19.6	12	12	12	12	8.00	7.92	8.51	8.40	1.5 [e]	1.5 [g]			[h]	2.01(8) 1.93(8)	[h]	[h]	
PMe_2Ph	I	−11.8	−14.2	−18.2	−20.7	12	11	12	12	[i]	[i]	8.39	[j]	[i]	[i]	1	[j]	1.86(8) 1.68(8)	2.23(8) 2.16(8)	1.47(8) 1.42(8)	[j]	1.8 : 1 : 1.4 : 0.1
PEt_3	Cl	−14.3	−16.0	−17.8	−19.3	11	11	12.5	12	8.10 [k]	8.10 [k]	8.45	8.33	*ca.* 1	*ca.* 1	1	1					3.1 : 1.5 : 1 : 10
PPh_3	Cl	−13.0	−14.9	−16.8	−18.4	11	11	12	12	[l]	[l]	[l]	[l]	[l]	[l]	[l]	[l]					1 : 1.2 : 1 : 2.3
PMe_2Ph [m]	Cl	−14.2 [n]	−16.0	−18.1 [o]	−19.7	12	12	14	14	[p]	[q]	[q]	[q]	[r]	[r]	[r]						

[a] $J(H_f-H)$, where H_f refers to the hydrogen in the formate group, is <0.5 Hz for (3) and *cis*-(5) [b] and 5 Hz for (4) and *trans*-(5).
[b] *cis*-(5) refers to the formate group of (5) which is mutually *cis* to the hydride ligand and *trans*-(5) to that which is mutually *trans*.
[c] Figures in parentheses are $|^2J(P-H) + {}^4J(P-H)|$.
[d] As obtained after *ca.* 15 min at 28 °C (see text).
[e] A further coupling of *ca.* 0.8 Hz was observed on this signal (see text).
[f] With CD_3NO_2 as solvent the ratio was 1.7 : 3.3 : 1 : 4.6 and with $CDCl_3$ 3 : 2 : 1 : 5.
[g] A further coupling of *ca.* 0.5 Hz was observed on this signal; source as for *e* (see text).
[h] We were unable to assign absorption due to extensive signal overlap.
[i] Masked by absorptions due to free formic acid.
[j] Not observed due to complex being present in low concentration.
[k] Two signals not clearly resolved; composite signal centred at δ 8.10 p.p.m. $[J(^{13}P-H_f) = 1\ Hz]$.
[l] Masked by absorptions due to PPh_3 ligand.
[m] Using $H^{13}CO_2H$; solvent C_6D_6.
[n] No $J(^{13}C-H)$ detected.
[o] $J(^{13}C-H) = 1$ Hz for formate *trans* to hydride.
[p] Only half the expected signal observed at δ 9.12 p.p.m., the other half being masked by resonance due to the phenyl groups of the PMe_2Ph ligands; assuming no ^{13}C isotope effect on the ^1H chemical shift, $J(^{13}C-H_f)$ 227 Hz.
[q] Only half the expected signal observed at δ 9.61 and 9.48 p.p.m. for 5 and 4, the other half being masked by the absorptions due to the phenyl groups of the PMe_2Ph, $J(^{13}C-H_f)$ 227 and 218 Hz for 5 and 4, respectively.
[r] Not resolved.



Hydrogen-1 n.m.r. spectrum, excluding absorptions due to tertiary phosphine ligands, of the adducts formed during the reaction of HCO_2H with *trans*-[IrCl(CO)(PMe$_2$Ph)$_2$] in C_6D_6 at 28 °C

(OCO) and ν_{sym}(OCO) are indicative of a unidentate, rather than a chelate, formate moiety.[12-14] The absorptions assigned to ν(C≡O) and ν(Ir–H) appear at >2 000 cm^{-1}, suggesting that in none of the complexes formed are the hydrido- and carbonyl units mutually *trans*.[10,11,15] Furthermore, in the i.r. spectrum of the deuterido-complex (prepared using DCO_2D) we observed no significant change in the ν(CO) frequency (see Table 3), indicating the absence of *trans* H–CO vibrational interaction.[16] Comparison of the i.r. spectra of the deuterido- and hydrido-complexes allows the bands at 2 225 and 2 194 cm^{-1} to be unambiguously assigned to ν(Ir–H).

TABLE 2

90-MHz ^{1}H n.m.r. data for complexes [IrXH$_2$(CO)L$_2$] of configuration (2) formed by thermal decomposition of the formic acid–*trans*-[IrX(CO)L$_2$] adducts

		Hydride resonances			
L	X	δ(H$_a$) [a]/ p.p.m. (±0.2)	δ(H$_b$)/ p.p.m. (±0.2)	*J*(^{31}P–H$_a$)/ Hz (±1)	*J*(^{31}P–H$_b$)/ Hz (±1)
PMe$_2$Ph [b]	Cl	−18.5	−7.6 [c]	14	20
PMe$_2$Ph	Br	−17.9	−8.3 [c]	14	20
PMe$_2$Ph	I	−16.3	−9.5 [c]	14	20
PEt$_3$ [d]	Cl	−19.6	−8.3	13	18
PPh$_3$ [e]	Cl	−17.5	−6.7	14	18

[a] *J*(H$_a$–H$_b$) 5 Hz. [b] Spectral data previously reported, measured at 60 MHz (ref. 10). Hydride signal at δ −5.4 p.p.m. [*J*(^{31}P–H) 15 Hz] also observed, assigned to [IrClH$_2$(CO)L$_2$], configuration (7) (see text). [c] Slightly broadened. [d] Hydride signal at δ −6 p.p.m. [*J*(^{31}P–H) 15 Hz] also observed, assigned to [IrClH$_2$(CO)L$_2$], configuration (7) (see text). [e] Spectral data previously reported at 56.5 MHz in CH_2Cl_2 (R. C. Taylor, J. F. Young, and G. Wilkinson, *Inorg. Chem.*, 1966, **5**, 20); *J*(H–H) not previously reported.

It is well established[1] that in oxidative-addition reactions involving *trans*-[IrX(CO)L$_2$] (X = Cl, Br, or I; L = tertiary phosphine) the addendum, in this case a carboxylic acid RCO_2H, can add formally either *cis*, configuration (3), or *trans*, configuration (4). When the carboxylic acid is formic these two isomers would account for two of the hydride signals observed in the n.m.r. spectrum of the [IrX(CO)L$_2$]–HCO_2H mixture, *viz.* one triplet (*cis* adduct) and one double triplet (*trans* adduct). This, however, leaves two hydride signals unexplained.

TABLE 3

Infrared data (cm^{-1}) for the complexes isolated from the reaction between RCO_2H and *trans*-[IrCl(CO)(PMe$_2$Ph)$_2$] [a]

R	ν(Ir–H)	ν(C≡O)	ν_{asym}(OCO)	ν_{sym}(OCO)
H	2 225m 2 194m	2 040s 2 033s	1 609s	1 302s
D [b]	1 570m [c]	2 043s 2 033s	1 600s	1 283s
CF$_3$	2 238m 2 218m	2 038s 2 055s	1 682s	1 412 [d]

[a] Recorded as Nujol mulls. [b] Complex prepared using DCO_2D, ν(C–D) at 2 107—2 122 cm^{-1}. [c] ν(Ir–D). [d] Coincident with one of the other ligand vibrations.

Careful examination of the n.m.r. data (Table 1) shows that the hydride chemical shift of one of the species formed is independent of the nature of the halogen (*viz.* the double triplet at δ −18.2 ± 0.2 p.p.m.). Since substitution of the chloride for iodine would be expected to affect the hydride chemical shift, this observation suggests that in all the three cases this is the same species and further that it does not contain a halogen. The spectroscopic data are consistent with a diformate of configuration (5).

The observation (see below) that the remaining triplet hydride resonance at δ −16.1 ± 0.2 p.p.m. (in C_6D_6) is essentially independent of the carboxylic acid used suggests that this complex does not contain a carboxylate unit. The spectroscopic data are consistent with those previously reported[17] for the HCl adduct of configuration (6; X = Cl).* With *trans*-[IrX(CO-)

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* The presence of this species was confirmed by adding independently synthesized [IrCl$_2$H(CO)(PMe$_2$Ph)$_2$], configuration (6), to the *trans*-[IrCl(CO)(PMe$_2$Ph)$_2$]–HCO_2H reaction mixture and recording the ^{1}H n.m.r. spectra at both 90 and 270 MHz. A perfect peak match was obtained in both the tertiary phosphine and hydride regions of the spectrum.

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

[13] B. F. G. Johnson, R. D. Johnston, J. Lewis, and I. G. Williams, *J. Chem. Soc.* (*A*), 1971, 689.

[14] J. D. Donaldson, J. F. Knofton, and S. D. Ross, *Spectrochim. Acta*, 1965, **21**, 1043.

[15] L. Vaska and J. W. Diluzio, *J. Amer. Chem. Soc.*, 1966, **88**, 679.

[16] L. Vaska, *J. Amer. Chem. Soc.*, 1966, **88**, 4100.

[17] A. J. Deeming and B. L. Shaw, *J. Chem. Soc.* (*A*), 1968, 1887.

$(\mathrm{PMe_2Ph})_2]$ (X = Br or I) the corresponding HBr and HI adducts were obtained, in addition to the two simple oxidative-addition products and the dicarboxylato-species.

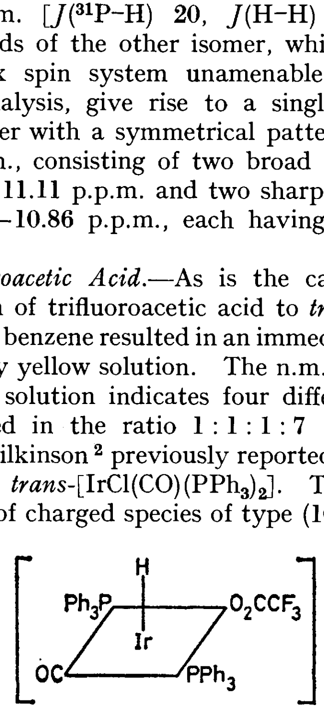
Thus the four species initially formed (within *ca.* 15 min at 25 °C) when $\mathrm{HCO_2H}$ is added to *trans*-[IrX(CO)$\mathrm{L_2}$] are the *cis* and *trans* adducts (3) and (4) (R = H), together with the dihalogeno- and diformato-anion-exchange products (6) and (5). The two complexes containing H and $\mathrm{O_2CH}$ groups mutually *trans*, *i.e.* (4) and (5), give rise to the two double triplets in both the hydride and formate regions, and the two species containing mutually *trans* H and halogen, *i.e.* (3) and (6), give rise to the two triplets in the hydride region of the ^{1}H n.m.r. spectrum. When the formate and hydride ligands are mutually *cis* no hydride(H)–formate(H) coupling is observed. However, in addition to a $J(^{31}\mathrm{P}\text{–}\mathrm{H})$ coupling of 1.7 Hz, a small coupling of *ca.* 0.8 Hz is present on the formate hydrogen resonance. We tentatively suggest that this arises *via* coupling to one of the hydrogens, possibly an *ortho*-hydrogen of the phenyl ring, in the tertiary phosphine ligand. A complete assignment of the n.m.r. data is given in Table 1. As evidenced by the low-temperature experiment (see above), the *trans* adduct (4) is first formed. The next species observed is the *cis* adduct, probably formed by partial isomerization of the *trans* adduct (no attempt was made to follow this process). Once formed these two species undergo a disproportionation reaction giving the dichloro- and diformato-complexes (6) and (5). Once formed in solution all the four species are in dynamic equilibrium since after *ca.* 48 h at 20 °C the only hydrido-species remaining in solution is the dihydrido-complex (2). [In the absence of the other hydrido-species the HCl adduct (6; X = Cl) is indefinitely stable (several months) in solution.]

It appears that, at elevated temperature (70 °C), the establishment of the disproportionation equilibrium is relatively slow compared to the decarboxylation reaction which after 30 min at 70 °C affords a *ca.* 5 : 1 mixture of dihydride and HCl adduct.

With L = $\mathrm{PEt_3}$ or $\mathrm{PMe_2Ph}$ (in $\mathrm{C_6D_6}$) and $\mathrm{PMe_2Ph}$ (in $\mathrm{CD_3NO_2}$) warming the mixture gave rise not only to the formation of the *cis*-dihydrido-complex (2) but also to the transient appearance in solution of a species having, in its n.m.r. spectrum, a hydride signal at relatively low field {δ −6.0 p.p.m. for L = $\mathrm{PEt_3}$ in $\mathrm{C_6D_6}$ and $\mathrm{PMe_2Ph}$ in $\mathrm{CD_3NO_2}$, and 5.4 p.p.m. for $\mathrm{PMe_2Ph}$ in $\mathrm{C_6D_6}$ [$J(^{31}\mathrm{P}\text{–}\mathrm{H})$ 15 Hz]}. We suggest that this is the *trans*-hydrido-complex (7), formed directly from the *trans* adduct (4). In solution it rapidly undergoes isomerization to the *cis*-dihydrido-complex (2). With the L = $\mathrm{PEt_3}$ system a small amount, *ca.* 10% relative to the dihydrido-species, of the *mer*-trihydrido-complex (8) [δ(H *trans* to CO) −11.9 p.p.m., $J(^{31}\mathrm{P}\text{–}\mathrm{H})$ 20 Hz; δ(H *trans* to H) −11.3 p.p.m., $J(^{31}\mathrm{P}\text{–}\mathrm{H})$ 16 Hz; $J(\mathrm{H}\text{–}\mathrm{H})$ 5 Hz] was also detected on heating the *trans*-[IrCl(CO)$(\mathrm{PEt_3})_2$]–$\mathrm{HCO_2H}$–$\mathrm{C_6D_6}$ mixture for 30 min at 70 °C.

With L = $\mathrm{PPh_3}$ the situation is somewhat more complex since in addition to the dihydrido-complex (2) the trihydrido-species (8) and (9) are also formed in the ratio *ca.* 6 : 3 : 1, when the *trans*-[IrCl(CO)$(\mathrm{PPh_3})_2$]–$\mathrm{HCO_2H}$–$\mathrm{C_6D_6}$ mixture is allowed to stand for *ca.* 100 h at 25 °C. Although it seems likely that these trihydrido-species are directly formed from the diformatohydrido-species *via* decarboxylation, the occurrence of disproportionation reactions, analogous to those which give the HCl adduct (6) and the diformato-complex (5), cannot be excluded. In the ^{1}H n.m.r. spectrum the hydride ligands of the *mer* isomer, (8), give rise to a triplet of doublets (H *trans* to H) at δ − 9.2 p.p.m. [$J(^{31}\mathrm{P}\text{–}\mathrm{H})$ 16, $J(\mathrm{H}\text{–}\mathrm{H})$ 5 Hz] and double triplet (H *trans* to CO) at δ − 9.9 p.p.m. [$J(^{31}\mathrm{P}\text{–}\mathrm{H})$ 20, $J(\mathrm{H}\text{–}\mathrm{H})$ 5 Hz]. The hydride ligands of the other isomer, which forms part of a complex spin system unamenable to a simple first-order analysis, give rise to a singlet at δ − 9.4 p.p.m. together with a symmetrical pattern, centred at −10.29 p.p.m., consisting of two broad absorptions at −9.47 and −11.11 p.p.m. and two sharp ' doublets ' at −9.72 and −10.86 p.p.m., each having a separation of 2 Hz.

(*b*) *Trifluoroacetic Acid*.—As is the case for formic acid, addition of trifluoroacetic acid to *trans*-[IrCl(CO)$(\mathrm{PMe_2Ph})_2$] in benzene resulted in an immediate bleaching of the initially yellow solution. The n.m.r. spectrum of the resulting solution indicates four different hydrido-species formed in the ratio 1 : 1 : 1 : 7 (see Table 4). Singer and Wilkinson [2] previously reported an analogous reaction with *trans*-[IrCl(CO)$(\mathrm{PPh_3})_2$]. They suggested the presence of charged species of type (10). However,



(10)

by analogy with our observation with the formic acid systems, coupled with the fact that after isolation the complexes are non-conducting in nitrobenzene (equivalent conductivity 12×10^{-2} S cm^2 mol^{-1}), we suggest that the four complexes are similar to those formed in the formic acid addition *viz.* the *cis* and *trans* adducts, (3) and (4), together with the HCl adduct (6) and the dicarboxylate (5) (L = $\mathrm{PMe_2Ph}$, X = Cl, R = $\mathrm{CF_3}$). In the i.r. spectrum of the isolated material in Nujol we observed two broad (width at half-height *ca.* 40 cm^{-1}) carbonyl-stretching absorptions at 2 038 and 2 055 cm^{-1} (see Table 3). By analogy with the formic acid system we assign the absorption at 2 038 cm^{-1} to a carbonyl *trans* to a chlorine, as present in both (4) and (6) {ν(CO) in pure [$\mathrm{IrCl_2H(CO)(PMe_2Ph)_2}$], configuration (6), occurs [17] at 2 025 cm^{-1}} and the absorption at 2 055 cm^{-1} to the carbonyl ligand *trans* to a trifluoroacetate group, as found in both the *cis* adduct (3) and the dicarboxylate (5). As in the case of the formic acid adduct, the values of ν_{asym}(OCO) and ν_{sym}(OCO) suggest that the trifluoroacetate group is acting as a unidentate ligand.[12] A molecular-weight determination, in benzene solution, confirmed that the isolated material is monomeric (Found: 651. Calc.: 645).

(*c*) *Other Carboxylic Acids* (*Benzoic*, 1-*Naphthoic, and Acetic*).—The reaction between RCO_2H (R = Me, Ph, or 1-naphthyl) and *trans*-[IrCl(CO)(PMe$_2$Ph)$_2$] is analogous to that described above for either formic or trifluoroacetic acid. However, with benzoic and 1-naphthoic acid the relative ease of formation of the various products differs from that found for formic acid. After addition of either benzoic or 1-naphthoic acid (1 mol equivalent) to a solution of *trans*-[IrCl(CO)(PMe$_2$Ph)$_2$] in [$^2H_8$]-toluene at −60 °C the ^1H n.m.r. spectrum contained only the lowest-field (δ −14.2 p.p.m. for benzoic and −14.0 p.p.m. for 1-naphthoic) hydride triplet resonance, indicating initial formation of the *cis* adduct. When the solution was allowed to warm to 28 °C two additional products were observed, *viz.* the dichloro-complex (6) and the dicarboxylato-complex (5). After the solution had been allowed to stand at room temperature for *ca.* 24 h the *trans* adduct (4) was observed in the n.m.r. spectrum of the mixture. Once the equilibrium mixture of complexes had been formed the relative ratio (see Table 4) was invariant to both temperature (−60 to 100 °C) and time (*ca.* 4 d). Thus, in contrast to the situation found with formic acid, with both benzoic and 1-naphthoic acid the *cis* adduct is the most easily formed and undergoes self-disproportionation to the dichloro- and dicarboxylato-complexes. Only after longer reaction times was the *trans* adduct, probably formed by slow isomerization of the *cis* adduct, observed. With acetic acid all the four complexes are rapidly formed at room temperature as evidenced by the ^1H n.m.r. spectrum of an equimolar mixture of $MeCO_2H$ and *trans*-[IrCl(CO)(PMe$_2$Ph)$_2$] in [$^2H_8$]toluene.

TABLE 4

90-MHz ^1H n.m.r. data for the complexes formed on addition of carboxylic acids RCO_2H to *trans*-[IrCl(CO)(PMe$_2$Ph)$_2$]

	Hydride resonances								
	δ/p.p.m. (±0.2)				$J(^{31}P-H)$/Hz (±0.5)				Ratio of complexes
R	(3)	(6)	(5)	(4)	(3)	(6)	(5)	(4)	(3) : (6) : (5) : (4)
CF_3	−14.2	−16.0	−18.5	−20.3 [a]	12.5	12.5	12.5	12.5	1 : 1 : 1 : 7
CF_3 [b]	−13.6	−15.7	−17.8	−19.5	11.0	12.0	11.0	12.5	0.9 : 1 : 1 : 1.7
Me [c]	−14.1	−16.1	−17.9	−19.4	12.5	12.5	12.5	14.0	1.3 : 1.3 : 1 : 1.3
Ph	−14.2 [d]	−16.1	−17.4	−19.2	13.0	13.0	13.0	13.0	1 : 1.5 : 1 : 1.5 [e]
1-Naphthyl	−14.0 [f]	−16.0	−17.2	−19.0	12.0	12.0	13.0	13.0	1 : 1 : 1 : 1 [g]

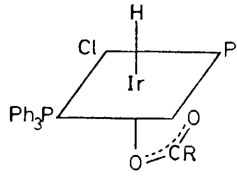
[a] Methyl groups of PMe$_2$Ph ligands in this complex give rise to two absorptions at δ 1.63 [$|^2J(P-H) + {}^4J(P-H)|$ 8 Hz] and 1.61 p.p.m. [$|^2J(P-H) + {}^4J(P-H)|$ 8 Hz]. [b] Complexes obtained using *trans*-[IrCl(CO)(PPh$_3$)$_2$], previously reported [2] with $CDCl_3$ as solvent. [c] Measured in [$^2H_8$]toluene; CH_3 signals of O_2CMe groups at δ 2.18 and 2.13 p.p.m. [d] Methyl groups of PMe$_2$Ph ligands in this complex give rise to two absorptions at δ 1.78 [$|^2J(P-H) + {}^4J(P-H)|$ 8 Hz] and 1.67 p.p.m. [$|^2J(P-H) + {}^4J(P-H)|$ 8 Hz]. [e] As observed after *ca.* 24 h, initially 10 : 1 : 1 : 0 (see text). [f] Methyl groups of PMe$_2$Ph ligands in this complex give rise to two absorptions at δ 1.78 [$|^2J(P-H) + {}^4J(P-H)|$ 8 Hz] and at 1.67 p.p.m. [$|^2J(P-H) + {}^4J(P-H)|$ 8 Hz]. [g] As observed after *ca.* 48 h, initially 9 : 1 : 1 : 0 (see text).

Deeming and Shaw [3] previously reported the absence of hydride resonances in the ^1H n.m.r. spectra of the adducts formed between weak carboxylic acids, *i.e.* acids with $pK_a > 4$, and complexes of the type *trans*-[IrCl(CO)L$_2$] (L = tertiary phosphine). They suggested that this was due to rapid exchange between the hydride-hydrogens and the hydrogens of the unchanged carboxylic acid. We have been unable to detect any such exchange on the n.m.r. time scale. The hydride resonances are invariant to temperature over the range −60 to 30 °C and addition of a three-fold excess of carboxylic acid has no effect on the n.m.r. linewidth. Thus, whereas we agree with their finding that with weak carboxylic acids (*e.g.* acetic and benzoic) conversion of the iridium(I) complex into the iridium(III) species is incomplete, our results indicate that although establishment of equilibrium (1) is rapid, hydride–acid exchange, if present, is slow on the n.m.r. time scale.

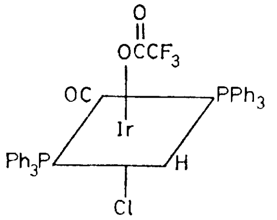
$$\text{iridium(I)} + \text{acid} \rightleftharpoons \text{iridium(III) complexes} \quad (1)$$

In their spectrophotometric experiments they observed the occurrence of a slow secondary process which was tentatively ascribed to a disproportionation since, on dissolving *trans*-[IrCl(CO)(PMe$_2$Ph)$_2$] in glacial acetic acid and diluting with water, the dichloro-species [IrCl$_2$H(CO)(PMe$_2$Ph)$_2$] was isolated in 47% yield based on iridium, *i.e.* 94% based on chlorine.[3] The results reported here confirm this suggestion since in the presence of excess of acid the disproportionation equilibrium is shifted in favour of the dichloro- and dicarboxylato-species.

(*d*) *An Alternative Route to Hydridoiridium Carboxylate Complexes.*—Smith *et al.*[18] have reported an alternative route to hydridoiridium carboxylate complexes *via* treatment of *trans*-[IrCl(N$_2$)(PPh$_3$)$_2$] (11) with the appropriate carboxylic acid followed by carbonylation. On the basis of i.r. spectral data it was shown that action of the carboxylic acid on (11) gives a carboxylato-hydrido-species of configuration (12) containing a bidentate carboxylate group, which on treatment with carbon monoxide forms a unidentate carboxylate complex having configuration (13). We have repeated this sequence of reactions with formic, acetic, trifluoroacetic, benzoic, and 1-naphthoic acids. The ^1H n.m.r. data in Table 5 support the configurational assignment originally proposed by Smith *et al.* The complexes of configuration (12) all give a high-field triplet signal in the n.m.r. spectrum corresponding to the hydride ligand *cis* to the two mutually *trans* tertiary phosphine ligands. The position of this signal is, unlike that observed for the complexes containing a unidentate carboxylate ligand (see above), strongly dependent on the nature of the acid. The dependence appears to be related to the bulk of the acid R group rather than to the pK_a of the free acid since, as can be seen from Table 5, the signal moves to lower field as the steric bulk of R increases.



(12)



(13)

Table 5

90-MHz ^{1}H n.m.r. data for complexes [$IrClH(O_2CR)(PPh_3)_2$], configuration (12)

R	pK_a of free acid	Hydride resonances δ ±0.2 p.p.m.	Hydride resonances $J(^{31}P–H)$ ±0.5 Hz
H	3.75	−11.6	14
Me	4.75	−10.0	14
CF_3	−0.26	−8.4	13
Ph	4.19	−5.9	14
1-Naphthyl	3.70	−6.1	15

Table 6

90-MHz ^{1}H n.m.r. data for the complexes formed by the action of carbon monoxide on [$IrCl(H)(O_2CR)(PPh_3)_2$], configuration (12)

	Hydride resonances				Ratio of (13) : (14)		
	δ/p.p.m. (±0.2)		$J(^{31}P–H)$/Hz (±0.5)		as formed initially at 20 °C	as formed after 3 h at 80 °C	as formed after 24 h at 80 °C
R	(13)	(14)	(15)	(16)			
H	−7.1	−7.6	14	14	5.5 : 1	*a*	
Me	−7.4	−7.7	14	14	*b*		2.7 : 1
CF_3 [c]	−7.3	−7.8	13	13	5 : 1 [d]	7 : 1 [e]	*f*
Ph [c]	−7.3	−7.7	14	14	*b*	34 : 1	*g*
1-Naphthyl	−7.1	−7.7	14	14	*b*	5 : 1	*g*

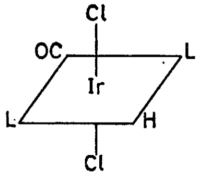
[a] Decomposes to give dihydrido-complex (2; L = PPh_3). [b] Only complex (13) formed at ambient temperature. [c] Measured in the presence of a two-fold excess of free acid. [d] Third hydrido-complex, thought to be [$IrH(O_2CCF_3)_2(CO)(PPh_3)_2$], configuration (15) (see text), also formed. Ratio (13) : (14) : (15) = 5 : 1 : 1.7. [e] Ratio (13) : (14) : (15) = 7 : 1 : 2.5. [f] Seven hydrido-species present in solution (see text). Ratio of signal area from low-to-high field = 2 : 5 : 5 : 1.5 : 1 : 4 : 3. [g] Extensive decomposition.

Treatment of the trifluoroacetic acid derivative (12; R = CF_3) with carbon monoxide at ambient temperature immediately gives three new hydrido-species. One of these species is, as previously reported,[18] the unidentate carboxylato-complex (13). Since the hydride chemical shift (see Table 6) of one of the remaining two species is essentially independent of the nature of the carboxylic acid used we consider that this is due to the dichloro-complex (14; L = PPh_3). {Analogous complexes with L = PMe_2Ph or PEt_2Ph have been reported [17,19] from the reaction between [$IrCl_3(CO)L_2$] and

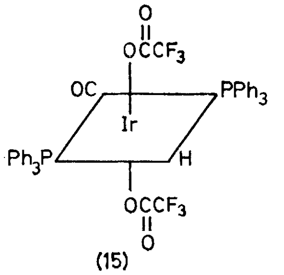
$$2\ (13) \rightleftharpoons (14) + (15) \qquad (2)$$

K[OH] in ethanol.} To the third species, which gives a triplet absorption in the ^{1}H n.m.r. spectrum at δ −6.6 p.p.m. [$J(^{31}P–H)$ 14 Hz], we assign structure (15) and tentatively suggest that both (14) and (15) arise *via* disproportionation of (13). With the formic acid derivative only (13) and (14) were observed in the ^{1}H n.m.r. spectrum after treating (12; R = H) with CO at ambient temperature. The failure to observe the *trans*-diformato-complex could be due its instability under the reaction conditions. Our attempts to prepare it *via* other routes have been unsuccessful.

Treatment of the acetic, benzoic, and 1-naphthoic acid derivatives (12; R = Me, Ph, or 1-naphthyl) with CO at ambient temperature leads to the exclusive formation of (13) in solution. Under forcing conditions, *ca.* 3 h at 80 °C, the second hydrido-species thought to be (14) (see above) is formed in small amounts (see Table 6). However, the latter reaction is accompanied by considerable decomposition.



(14)



(15)

Heating the mixture obtained on passing CO through a solution of (12; R = CF_3) in benzene for *ca.* 24 h at 80 °C leads to the formation of another four hydrido-species. The n.m.r. parameters of four of these complexes are identical to those of the complexes formed when CF_3CO_2H is added to *trans*-[$IrCl(CO)(PPh_3)_2$] [see section (*b*)], *i.e.* (3)—(6). For clarity, the latter sequence of reactions is summarized in Scheme 2. Although we have not followed this conversion as a

$$(12) \xrightarrow[25\ °C,\ 5\ min]{CO} (13)\text{—}(15) \xrightarrow[ca.\ 10\%\ conversion]{80\ °C,\ 24\ h} (3)\text{—}(6)$$

L = PPh_3, X = Cl, R = CF_3

Scheme 2

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[18] S. A. Smith, D. M. Blake, and M. Kubota, *Inorg. Chem.*, 1972, **11**, 660.

[19] J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 1964, 1625.

function of time, it appears to be a relatively slow process since after 3 h at 80 °C we observed only *ca.* 10% conversion into the final product mixture.

Conclusions.—The data presented above indicate that, although simple carboxylic acids react with iridium(I) complexes of the type *trans*-$[\mathrm{IrCl(CO)L_2}]$ (L = a tertiary phosphine) to give the expected oxidative-addition products, *i.e.* corresponding to formal *cis* and/or *trans* addition depending on the acid, the final products of the reaction are mediated by anion-exchange reactions. While oxidative-addition reactions of co-ordinatively unsaturated rhodium(I) and iridium(I) complexes have been extensively studied,[1-5,20,21] only passing reference has been made[3,5] to the possibility of anion-redistribution reactions among the rhodium(III) or iridium(III) products.* Our results demonstrate the important role such reactions can play in controlling the final products of these reactions.

EXPERIMENTAL

Materials and Physical Measurements.—All the operations involving air-sensitive materials were performed under an argon atmosphere. Complexes of the type *trans*-$[\mathrm{IrX(CO)L_2}]$ (L = PPh_3, PEt_3, or PMe_2Ph; X = Cl, Br, or I), $[\mathrm{IrCl_2H(CO)(PMe_2Ph)_2}]$, configuration (6; L = PMe_2Ph, X = Cl), $[\mathrm{IrClH_2(CO)(PMe_2Ph)_2}]$, configuration (2; L = PMe_2Ph), and *trans*-$[\mathrm{IrCl(N_2)(PPh_3)_2}]$ were prepared using published procedures.[10,17,23,24] The partially deuteriated formic acids, HCO_2D and DCO_2H, were obtained from their sodium salts.[25] Other materials were obtained commercially and used without prior purification.

Hydrogen-1 and ^{13}C n.m.r. spectra were recorded on Bruker WH 90 or WH 270 instruments, i.r. spectra on Perkin-Elmer 457 or 225 spectrophotometers. In the Tables of n.m.r. data an error of ±0.2 p.p.m. is quoted with respect to the chemical shift. This error refers not to the spectrometer accuracy, which is ±0.01 p.p.m., but rather to the degree of reproducibility experienced in conducting the experiments over a period of several months using different samples. Unless otherwise indicated, n.m.r. spectral data are quoted as obtained at 28 °C using C_6D_6 as solvent and tetramethylsilane as internal standard.

General Method of Preparation of the Adducts.—Solutions of the adducts for n.m.r. experiments were prepared by adding the acid (0.1—0.5 mmol) to a solution (suspension) of *trans*-$[\mathrm{IrX(CO)L_2}]$ (L = PEt_3, PMe_2Ph, or PPh_3; X = Cl, Br, or I) (0.1 mmol) in a deuteriated solvent (C_6D_6, $C_6D_5CD_3$, or CD_3NO_2) (0.5 cm^3).

Isolation of the Reaction Products.—(*a*) *trans*-$[\mathrm{IrCl(CO)(PMe_2Ph)_2}]$–$HCO_2H$ *System.* 97% Formic acid (0.03 cm^3, 0.8 mmol) was added to *trans*-$[\mathrm{IrCl(CO)(PMe_2Ph)_2}]$ (0.200 g, 0.38 mmol) in benzene (5 cm^3). The resulting white solution was set aside at ambient temperature for 30 min and subsequently freeze-dried *in vacuo* (0.01 Torr)† with liquid nitrogen (bath temperature 0 °C). The crystals were thoroughly washed with water and dried *in vacuo*; yield 0.183 g (83%).

(*b*) *trans*-$[\mathrm{IrCl(CO)(PMe_2Ph)_2}]$–$CF_3CO_2H$ *System.* Trifluoroacetic acid (0.05 cm^3, 0.67 mmol) was added to *trans*-$[\mathrm{IrCl(CO)(PMe_2Ph)_2}]$ (0.204 g, 0.38 mmol) in benzene (10 cm^3). The solvent and excess of acid were removed from the white solution *in vacuo*, leaving white crystals. The crystals were collected, thoroughly washed with pentane–diethyl ether (9 : 1), and subsequently dried *in vacuo*; yield 0.144 g (58%).

We thank Dr. A. J. Deeming, University College, London, for originally suggesting, on the basis of unpublished results, the possibility of intermolecular anion exchange in the systems reported here.

[7/1292 *Received, 19th July,* 1977]

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* While this work was in progress, halide exchange between complexes of the type $[\mathrm{MX(CO)L_2}]$ (M = Rh or Ir, X = Cl or Br, L = tertiary phosphine) was reported.[22]

† Throughout this paper: 1 Torr = (101 325/760) Pa.

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