Metal Carbonyl Chemistry. Part XXI.[1] A Comparison of the Reactivities of the Anions $[M(CO)_2(PPh_3)_2]^-$ (M = Co, Rh, or Ir) Towards Fluoroaromatic Compounds

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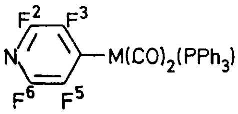
The preparations are described of the compounds 4-C_6F_4NM', 4-$CN{\cdot}C_6F_4M'[M' = Co(CO)_2(PPh_3)_2$ or $Ir(CO)_2(PPh_3)_2]$, 4-$EtO_2C{\cdot}C_6F_4M'$, 3,4-$(CN)_2C_6F_3M'$, 4-$(2\text{-}CN{\cdot}C_5F_3N)M'$, and 5-$(2\text{-}CN{\cdot}C_5F_3N)M'[M' = Ir(CO)_2(PPh_3)_2]$ by reaction between the corresponding perfluoroaromatic compound and the respective carbonylmetal anion. A comparison of the relative reactivities of the cobalt and iridium anions, and the analogous rhodium anion, towards pentafluoropyridine has established the order $[Rh(CO)_2(PPh_3)_2]^- > [Ir(CO)_2(PPh_3)_2]^- > [Co(CO)_2(PPh_3)_2]^-$.

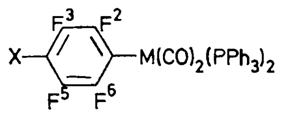
RELATIVE reactivities of a number of carbonylmetal anions have been established previously by kinetic studies [2] or, more generally, by qualitative observations based on their reactivities towards unsaturated fluorocarbons.[3-7] These investigations have shown that the reactivity depends markedly upon the nature of the coordinated ligands, and increases when carbonyl ligands are replaced by more basic ligands such as phosphines or a π-cyclopentadienyl group. Little information is available, however, as to how the metal atom affects nucleophilic reactivity. It is difficult to make a comparison of the nucleophilic properties of the metal atoms in different groups since there are differences in the coordination numbers and the electronic configurations of the metal atoms. It has been established that $[Mn(CO)_5]^-$ is a much stronger nucleophile than either $[Fe(CO)_4]^{2-}$ or $[Co(CO)_4]^-$ and a similar trend is also apparent on comparison of the relative basicities of these anions.[8] It is not yet known, however, whether this trend is repeated for the second and third row transition metals. Rather more information is available on how the reactivities change within a group. The nucleophilic strengths of the anions $[(\pi\text{-}C_5H_5)M(CO)_3]^-$ (M = Cr, Mo, or W) have been shown to be in the order W > Mo > Cr,[2-4] and this trend may be repeated in group VIIB in that $[Re(CO)_5]^-$ is a stronger nucleophile than $[Mn(CO)_5]^-$. However, the reverse trend is apparent for the iron triad in that $[(\pi\text{-}C_5H_5)Fe(CO)_2]^-$ is a stronger nucleophile than $[(\pi\text{-}C_5H_5)Ru(CO)_2]^-$, although information on the osmium analogue is still lacking. We now report on the relative reactivities of the anions $[M(CO)_2(PPh_3)_2]^-$ (M = Co, Rh, or Ir) in nucleophilic aromatic substitution reactions, and the preparations of a number of new perfluoroaromatic-cobalt and -iridium complexes.

Cobalt Complexes.—The anion $[Co(CO)_2(PPh_3)_2]^-$ (ref. 9) is readily obtained in quantitative yield (i.r. spectroscopy) by reduction of $[CoI(CO)_2(PPh_3)_2]$ [10] with 1% sodium amalgam in dry tetrahydrofuran under an atmosphere of carbon monoxide.

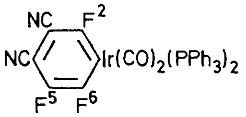
Solutions of this anion in tetrahydrofuran react with pentafluoropyridine and pentafluorobenzonitrile at room temperature to afford compounds (Ia) and (IIa) in 16 and 17% yields respectively. These compounds could only be obtained as green-yellow, amorphous solids which are unstable in air. Despite several attempts at purification, using various techniques, satisfactory analyses could not be obtained, and the structural assignments are made on the basis of spectroscopic data only. The ^{19}F n.m.r. spectra (Table 1) each show a typical AA'XX' pattern expected for the assigned structures and the chemical-shift values are in agreement with those of similar complexes, and in particular the rhodium [7] and iridium analogues. The i.r. spectra show only one very strong band in the metal carbonyl region



(Ia) M = Co
(Ib) M = Ir



(IIa) M = Co; X = CN
(IIb) M = Ir ; X = CN
(III) M = Ir ; X = CO_2Et



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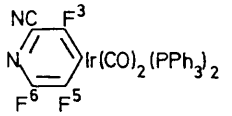
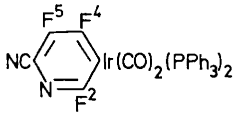


(V)



(VI)

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[1] Part XX, B. L. Booth, R. N. Haszeldine, and T. Inglis, *J.C.S. Dalton*, 1975, 1449.

[2] R. E. Dessy, R. L. Pohl, and R. B. King, *J. Amer. Chem. Soc.*, 1966, **88**, 512.

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

[4] M. I. Bruce, D. N. Sharrocks, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1970, 680.

[5] M. I. Bruce, B. L. Goodall, D. N. Sharrocks, and F. G. A. Stone, *J. Organometallic Chem.*, 1972, **39**, 139.

[6] B. L. Booth, R. N. Haszeldine, and M. B. Taylor, *J. Chem. Soc.* (*A*), 1970, 1974.

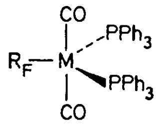
[7] B. L. Booth, R. N. Haszeldine, and I. Perkins, *J. Chem. Soc.* (*A*), 1971, 927.

[8] D. F. Shriver, *Accounts Chem. Res.*, 1970, **3**, 231.

[9] W. Hieber and H. Duchatsch, *Chem. Ber.*, 1965, **98**, 2933.

[10] A. Sacco, *Gazzetta*, 1963, **93**, 542.

(Table 1) indicating that in the solid state the compounds have the structure shown (M = Co).



Unlike $[Rh(CO)_2(PPh_3)_2]^-$ (ref. 7), the cobalt anion does not react with hexafluorobenzene even after 15 h at the reflux temperature of tetrahydrofuran.

TABLE 1

Spectroscopic data

Complex	I.r. spectra $\nu(CO)/cm^{-1}$	^{19}F n.m.r. spectra[a] (chemical shifts p.p.m. relative to $CF_3{\cdot}CO_2H$)[b]				
		$\delta(2)$	$\delta(3)$	$\delta(4)$	$\delta(5)$	$\delta(6)$
(Ia)	1 996vs[c]	19.8	34.8		34.8	19.8
(Ib)	1 968vs	22.6	41.5		41.5	22.6
(IIa)	2 000vs[c]	26.3	58.6		58.6	26.3
(IIb)	1 969vs	34.3	60.8		60.8	34.3
(III)	1 970vs	36.9	66.1		66.1	36.9
(IV)	1 975vs	−1.6			58.6	18.0
(V)	1 969vs		11.8		25.4	17.2
(VI)	1 970vs	−37.7		18.1	70.9	

[a] Spectra were recorded in dichloromethane solution. [b] Coupling constants could not be determined owing to the limited solubility of the complexes and low intensity of the spectra obtained. [c] Nujol mull.

Iridium Complexes.—A convenient route to the anion $[Ir(CO)_2(PPh_3)_2]^-$ is the reduction of $[IrCl(CO)_2(PPh_3)_2]$ [11] with 1% sodium amalgam under 1 atm of carbon monoxide in tetrahydrofuran at room temperature. The reaction is quantitative. A carbon monoxide atmosphere is essential since reversible loss of CO from $[IrCl(CO)_2(PPh_3)_2]$ occurs readily at room temperature.[11] The pressure of carbon monoxide and the reaction temperature are also important since reduction of the chloro-complex at 60 °C and a CO pressure of 15 atm is reported to give the anion $[Ir(CO)_3(PPh_3)]^-$ [ν(CO) 1 840s and 1 860s cm^{-1}].[12] Attempts to prepare $[Ir(CO)_2(PPh_3)_2]^-$ by the alternative reduction of $[IrH(CO)_2(PPh_3)_2]$ [13] with sodium amalgam under an atmosphere of carbon monoxide gave only recovered starting material indicating the weakly acid character of this hydride.

Solutions of $[Ir(CO)_2(PPh_3)_2]^-$ in tetrahydrofuran react readily at room temperature with pentafluoropyridine and pentafluorobenzonitrile to afford complexes (Ib) and (IIb) respectively, and with ethyl pentafluorobenzoate, tetrafluorophthalodinitrile, and 2-cyanotetrafluoropyridine to give compounds (III)—(VI). The compounds are all yellow crystalline solids, which are stable in the solid state in air for several days, and are soluble in most organic solvents to give solutions which are only moderately air sensitive. Satisfactory elemental analyses were obtained on all these compounds.

The i.r. spectra of these iridium compounds (Table 1) all show only one strong band in the metal carbonyl region indicating that arrangement of the ligands around the metal atom is similar to that observed for the rhodium [7] and cobalt analogues. The ^{19}F n.m.r. spectra (Table 1) are again consistent with the assigned structures, and chemical-shift assignments are made by analogy with those reported previously for the rhodium analogues.[7]

The reaction with 2-cyanotetrafluoropyridine at room temperature gives an approximately equimolar mixture of the 4- and 5-substituted complexes (V) and (VI) respectively. It is now apparent from further work [14] carried out on the similar reaction of the analogous rhodium anion that at this temperature the product distribution is thermodynamically controlled. At room temperature the rate of displacement of $[Rh(CO)_2(PPh_3)_2]^-$ by F^- must be appreciable and the final product distribution reflects the approximately equal free energies of compounds (V) and (VI). When this reaction is carried out at a lower temperature (−60 °C) only the kinetically controlled product (V) is obtained.[14]

The iridium anion does not react with hexafluorobenzene after 17 h at the reflux temperature of tetrahydrofuran. The only product isolated from this reaction is $[IrH(CO)_2(PPh_3)_2]$ (24% yield) which is presumed to arise by abstraction of a proton by the anion either from the solvent or possibly from water on the chromatography column during work up.

TABLE 2

Competition reactions with pentafluoropyridine[a]

Competing anions	Products (% yield)[b]	
$[(\pi\text{-}C_5H_5)Fe(CO)_2]^- + [Rh(CO)_2(PPh_3)_2]^-$	$[(NC_5F_4)Fe(CO)_2(\pi\text{-}C_5H_5)]$[c]	(52)
	+	
	$[(NC_5F_4)Rh(CO)_2(PPh_3)_2]$[d]	(24)
$[Ir(CO)_2(PPh_3)_2]^- + [Rh(CO)_2(PPh_3)_2]^-$	$[(NC_5F_4)Rh(CO)_2(PPh_3)_2]$[d]	(51)[e]
	+	
	(Ib)	(26)[e]
$[Ir(CO)_2(PPh_3)_2]^- + [Co(CO)_2(PPh_3)_2]^-$	(Ib)	(40)[f]

[a] All reactions were carried out at room temperature for 18 h under an atmosphere of carbon monoxide using a 1 : 1 : 1 molar ratio of the two anions and pentafluoropyridine in tetrahydrofuran. [b] Based on amount of anion taken. [c] Identified by m.p. and i.r. spectroscopy [J. Cooke, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1966, 1837]. [d] Identified by m.p. and i.r. spectroscopy.[7] [e] Estimated from the ^{19}F n.m.r. spectrum of the mixture. [f] No evidence for the formation of any compound (Ia) was obtained.

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[11] L. Vaska, *Science*, 1966, **152**, 769.

[12] J. P. Collman, F. D. Vastine, and W. R. Roper, *J. Amer. Chem. Soc.*, 1968, **90**, 2282.

[13] G. Yagupsky and G. Wilkinson, *J. Chem. Soc.* (*A*), 1969, 725.

[14] R. E. Banks, R. N. Haszeldine, and K. Legge, unpublished observations.

Kinetic Studies.—It is clear from these results that the rhodium anion, which does react with hexafluorobenzene,[7] is a stronger nucleophile than either the iridium or the cobalt anions, which do not. These conclusions are confirmed by a series of competition experiments (Table 2) in which the reactivities of these anions and the anion $[(\pi\text{-}C_5H_5)Fe(CO)_2]^-$ towards pentafluoropyridine were compared. This showed the order of reactivities to be $[(\pi\text{-}C_5H_5)Fe(CO)_2]^- > [Rh(CO)_2(PPh_3)_2]^- > [Ir(CO)_2(PPh_3)_2]^- > [Co(CO)_2(PPh_3)_2]^-$.

In an attempt to define more exactly the relative reactivities of these anions in the cobalt triad with those of other known anions further kinetic investigations were undertaken. Second-order rate constants have been obtained for the reactions of the cobalt, rhodium, and iridium anions and the anion $[Mn(CO)_5]^-$ with pentafluoropyridine at 25 °C (Table 3), which were followed by i.r. spectroscopy. The reaction of $[(\pi\text{-}C_5H_5)Fe(CO)_2]^-$ under similar conditions occurs almost instantaneously on mixing the reactants. These results confirm the order given above and show that both the rhodium and iridium anions are stronger nucleophiles than $[Mn(CO)_5]^-$. If the rather tenuous extrapolation is made between these rate constant values and those obtained by Dessy *et al.*[2] for S_N2 substitution of an alkyl halide, then if $k_2^* = 77$ for $[Mn(CO)_5]^-$ is equated with $k_2 = 0.173 \times 10^{-2}$ (Table 3) the rhodium anion ($k_2^* = 2.2 \times 10^3$) is found to be of similar reactivity to $[Re(CO)_5]^-$ ($k_2^* = 2.5 \times 10^4$) while the iridium anion ($k_2^* = 8.7 \times 10^2$) is rather more reactive than $[(\pi\text{-}C_5H_5)W(CO)_3]^-$ ($k_2^* = 500$), which, in turn, is more reactive than the cobalt anion ($k_2^* = 2.5$). Since this comparison is between mechanistically different reactions too much reliance can not be placed on the numerical values. Nevertheless, the order obtained does agree quite well with the experimental observations.

TABLE 3

Second-order rate constants for the reactions of carbonylmetal anions with pentafluoropyridine at 25.0 ± 0.25 °C[a]

Anion	k_2/l mol^{-1} s^{-1} [b]
$[(\pi\text{-}C_5H_5)Fe(CO)_2]^-$	Too rapid to measure
$[Rh(CO)_2(PPh_3)_2]^-$	0.478×10^{-1}
$[Ir(CO)_2(PPh_3)_2]^-$	0.195×10^{-1}
$[Co(CO)_2(PPh_3)_2]^-$	0.564×10^{-4}
$[Mn(CO)_5]^-$	0.173×10^{-2}

[a] Determined by i.r. spectroscopy using 0.04M-solutions of the anions and pentafluoropyridine in tetrahydrofuran. [b] Standard deviation 5% or less.

It is interesting that this reactivity order of Rh > Ir > Co for these d^{10} metal anions differs from the order established for d^8 complexes of these same metals. A study of some S_N2 reactions[15] and some displacement reactions[16] of bis(dimethylglyoximinato)pyridine-rhodium(I) and -cobalt(I) ions has shown that Co^I is a better nucleophile than Rh^I. A more recent kinetic investigation of some oxidative-addition reactions of $[M(cis\text{-}Ph_2P{\cdot}CH{:}CH{\cdot}PPh_2)_2]^+$ complexes (M = Co, Rh, and Ir)[17] has also shown the reactivity order Co > Ir > Rh. There appears to be no obvious correlation of trends in reactivities between metal atoms in different Periodic groups, and, moreover, it is apparent that the order of reactivities of metals in the same group are affected by the oxidation states of the atoms.

It has been shown in this work and previously[7] that reaction of 2-cyanotetrafluoropyridine with carbonylmetal anions leads to substitution in the 4- and 5-positions. For reasons which have been discussed above substitution occurs to approximately the same extent in both positions at room temperature. It was of interest, therefore, to explore the possibility that further reaction of the 4- or 5-substituted complexes with carbonylmetal anions could lead to disubstituted compounds. Consequently the reactions of $[Rh(CO)_2(PPh_3)_2]^-$ and $[Rh(CO)_2(Ph_3P)_2$(2-cyanotrifluoro-4-pyridyl)][7] were examined. No reaction occurs at room temperature and on heating in refluxing diglyme for 18 h under carbon monoxide only decomposition occurred. The similar reaction of the rhodium anion with $[Rh(CO)_2(Ph_3P)_2$(6-cyanotrifluoro-3-pyridyl)][7] at the reflux temperature of tetrahydrofuran for 18 h gave an 80% recovery of the starting material and some decomposition products. These experiments demonstrate that replacement of fluorine by a transition metal-containing group greatly deactivates an aromatic ring to nucleophilic attack. This is entirely consistent with previous observations[18,19] that similar groups have powerful electron-donating effects. Polysubstitution of aromatic hydrocarbons by nucleophilic attack of carbonylmetal anions will probably only be achieved under extremely forcing conditions and, as demonstrated above, under these conditions thermal decomposition of the reactants becomes a problem.

EXPERIMENTAL

^{19}F N.m.r. spectra were recorded on a Hitachi–Perkin-Elmer R20A spectrometer at 56.4 MHz or with a Varian HA 100 instrument at 94.1 MHz. I.r. spectra were recorded on a Perkin-Elmer 257 instrument, and except where stated the spectra in the metal–carbonyl stretching region were obtained for dichloromethane solutions using full scale expansion. Chromatographic separations utilised Florisil-packed columns. All reactions were carried out under an atmosphere of carbon monoxide.

Dicarbonyliodobis(triphenylphosphine)cobalt (m.p. 98 °C with decomp.; reported[10] 97—100 °C with decomp.) was prepared in 56% yield by a previously reported method[10]

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[*] Dessy's scale.[2]

[15] J. H. Weber and G. N. Schrauzer, *J. Amer. Chem. Soc.*, 1970, **92**, 726.

[16] D. Dodd and M. D. Johnson, *Chem. Comm.*, 1971, 1371.

[17] L. Vaska, L. S. Chen, and W. V. Miller, *J. Amer. Chem. Soc.*, 1971, **93**, 6671.

[18] M. D. Johnson and N. Winterton, *J. Chem. Soc.* (*A*), 1970, 507; S. N. Anderson, D. H. Ballard, and M. D. Johnson, *J.C.S. Perkin II*, 1972, 311.

[19] A. N. Nesmeyanov, I. F. Lescheva, I. V. Polovyanysik, Yu. A. Ustynyk, and L. G. Markarova, *J. Organometallic Chem.*, 1972, **37**, 159.

from tricarbonylbis(triphenylphosphine)cobalt(+1) tetracarbonylcobaltate(−1), which was obtained in 86% yield from octacarbonyldicobalt.[20] Dicarbonylchlorobis(triphenylphosphine)iridium (98% yield) was prepared in tetrahydrofuran solution by the method of Vaska.[11]

Reactions of $[\mathrm{Co(CO)_2(PPh_3)_2}]^-$.—A solution of dicarbonyliodobis(triphenylphosphine)cobalt and an excess of 1% sodium amalgam stirred in tetrahydrofuran (50 ml) for 4 h gave a green solution of the anion [ν(CO) 1 874vs and 1 844m cm^{-1}], which was used without further purification after removal of the excess of amalgam. Conversion was assumed to be quantitative as measured by the complete disappearance of the characteristic metal–carbonyl bands of the iodo-complex [ν(CO) 1 970s and 1 910vs cm^{-1} (Nujol)].

(a) *With pentafluoropyridine.* Pentafluoropyridine (1.0 g, 5.9 mmol) added to a solution of the anion (1.3 g, 2.0 mmol) in tetrahydrofuran (20 ml) and stirred at room temperature for 18 h gave *dicarbonyl(tetrafluoro-4-pyridyl)bis(triphenylphosphine)cobalt* (Ia) (0.21 g, 0.25 mmol, 16%) as a greenish yellow powder, m.p. 114—116 °C with decomposition, isolated by chromatography (50% light petroleum–diethyl ether eluant), and recrystallisation from a 1 : 1 mixture of light petroleum–diethyl ether (Found: C, 58.3; H, 3.9; F, 14.2; N, 2.6. $\mathrm{C_{43}H_{30}CoF_4O_2P_2}$ requires C, 65.4; H, 3.8; F, 9.6; N, 1.8%).

(b) *With pentafluorobenzonitrile.* Reaction between the anion (1.2 g, 1.9 mmol) and pentafluorobenzonitrile (1.0 g, 5.2 mmol) in tetrahydrofuran (50 ml) at room temperature for 18 h gave *dicarbonyl(4-cyanotetrafluorophenyl)bis(triphenylphosphine)cobalt* (IIa) (0.25 g, 0.31 mmol, 17%) as a yellow powder, m.p. 154—156 °C with decomposition, after chromatography (50% light petroleum–diethyl ether) and recrystallisation from the same solvent mixture (Found: C, 58.5; H, 2.9; F, 14.3. $\mathrm{C_{45}H_{30}CoF_4NO_2P_2}$ requires C, 66.4; H, 3.9; F, 9.4%).

(c) *With hexafluorobenzene.* When a mixture of hexafluorobenzene (1.0 g, 5.4 mmol) and the anion (1.3 g, 2.0 mmol) in tetrahydrofuran (50 ml) was refluxed for 15 h, the only product isolated was a black solid (1.2 g) which showed no metal–carbonyl bands in its i.r. spectrum and no fluorine atoms in the ^{19}F n.m.r. spectrum. It was assumed to be a decomposition product and was not investigated further.

Reactions of $[\mathrm{Ir(CO)_2(PPh_3)_2}]^-$.—When a pale yellow suspension of dicarbonylchlorobis(triphenylphosphine)iridium in tetrahydrofuran was stirred with an excess of 1% sodium amalgam for 4 h under 1 atm of carbon monoxide at room temperature a green solution of the sodium salt [ν(CO) 1 842vs and 1 800 cm^{-1}] was obtained. I.r. spectroscopy showed that bands due to the starting material [ν(CO) 1 923s and 1 976vs cm^{-1}] had completely disappeared after this period. The solution of the anion was used without further purification after removal of the excess of amalgam.

(a) *With pentafluoropyridine.* Reaction between the anion (1.98 g, 2.56 mmol) and pentafluoropyridine (1.0 g, 6.0 mmol) in tetrahydrofuran (20 ml) stirred at room temperature for 18 h gave bright yellow crystals of *dicarbonyl(tetrafluoro-4-pyridyl)bis(triphenylphosphine)iridium* (Ib) (1.15 g, 1.22 mmol, 49%), m.p. 211—213 °C, after chromatography (diethyl ether eluant), and recrystallisation from a 1 : 2 mixture of diethyl ether–hexane (Found: C, 56.1; H, 3.0; F, 8.4; N, 1.8. $\mathrm{C_{43}H_{30}F_4IrNO_2P_2}$ requires C, 56.0; H, 3.3; F, 8.3; N, 1.5%).

(b) *With pentafluorobenzonitrile.* A similar reaction between the anion (1.59 g, 2.05 mmol) and pentafluorobenzonitrile (1.0 g, 5.2 mmol) in tetrahydrofuran (50 ml) gave yellow crystals of *dicarbonyl(4-cyanotetrafluorophenyl)bis(triphenylphosphine)iridium* (IIb) (1.14 g, 1.2 mmol, 61%), m.p. 238—240 °C, isolated by chromatography (dichloromethane eluant) and recrystallisation from a 1 : 1 dichloromethane–hexane mixture (Found: C, 57.4; H, 3.3; F, 8.0; N, 1.6. $\mathrm{C_{45}H_{30}F_3IrNO_2P_2}$ requires C, 57.1; H, 3.2; F, 8.0; N, 1.5%).

(c) *With ethyl pentafluorobenzoate.* A solution of the anion (1.59 g, 2.05 mmol) and ethyl pentafluorobenzoate (1.0 g, 4.2 mmol) in tetrahydrofuran (50 ml) stirred at room temperature for 18 h gave, after chromatography (1 : 4 mixture of diethyl ether–dichloromethane eluant) and recrystallisation from a mixture of dichloromethane–diethyl ether, yellow crystals of *dicarbonyl(4-ethoxycarbonyltetrafluorophenyl)bis(triphenylphosphine)iridium* (III) (0.7 g, 0.7 mmol, 34%), m.p. 198 °C (Found: C, 57.1; H, 3.6; F, 8.0. $\mathrm{C_{47}H_{35}F_4IrO_4P_2}$ requires C, 56.8; H, 3.5; F, 7.7%).

(d) *With tetrafluorophthalodinitrile.* Chromatography (diethyl ether eluant) of the product from the reaction of the anion (1.59 g, 2.05 mmol) and tetrafluorophthalodinitrile (0.62 g, 3.11 mmol) at room temperature for 18 h in tetrahydrofuran (50 ml), gave bright yellow crystals, m.p. 233—235 °C, of *dicarbonyl(3,4-dicyanotrifluorophenyl)bis(triphenylphosphine)iridium* (IV) (1.12 g, 1.17 mmol, 57%), which were recrystallised from a 1 : 2 diethyl ether–hexane mixture (Found: C, 58.2; H, 3.3; F, 6.4; N, 3.0. $\mathrm{C_{46}H_{30}F_3IrN_2O_2P_2}$ requires C, 57.9; H, 3.1; F, 6.0; N, 2.9%).

(e) *With 2-cyanotetrafluoropyridine.* When the anion (1.29 g, 1.68 mmol) and 2-cyanotetrafluoropyridine * (0.4 g, 2.1 mmol) were caused to react in tetrahydrofuran (50 ml) at room temperature for 18 h, chromatography of the product using a 1 : 1 mixture of light petroleum–diethyl ether as eluant gave yellow crystals of *dicarbonyl(2-cyanotrifluoro-4-pyridyl)bis(triphenylphosphine)iridium* (V) (0.54 g, 0.58 mmol, 35%), m.p. 197 °C, which were recrystallised from diethyl ether (Found: C, 56.5; H, 3.5; F, 6.1; N, 3.1. $\mathrm{C_{44}H_{30}F_3IrN_2O_2P_2}$ requires C, 56.8; H, 3.2; F, 6.1; N, 3.0%).

Further elution with a 50% diethyl ether–dichloromethane mixture gave yellow crystals of *dicarbonyl(6-cyanotrifluoro-3-pyridyl)bis(triphenylphosphine)iridium* (VI) (0.5 g, 0.5 mmol, 33%) (Found: C, 56.5; H, 3.5; F, 5.8; N, 3.3. $\mathrm{C_{44}H_{30}F_3IrN_2O_2P_2}$ requires C, 56.8; H, 3.2; F, 6.1; N, 3.0%).

(f) *With hexafluorobenzene.* Hexafluorobenzene (1.0 g, 5.4 mmol) was added to a solution of the anion (1.11 g, 1.44 mmol) in tetrahydrofuran (50 ml) and the mixture was refluxed for 17 h. Filtration and chromatography of the brown filtrate using 50% light petroleum–diethyl ether as eluant gave only pale yellow needles of dicarbonylhydridobis(triphenylphosphine)iridium (0.27 g, 0.35 mmol, 24%), m.p. 134 °C (reported,[13] 135—136°), which was identified by i.r. and ^{1}H n.m.r. spectroscopy.

Reaction of Dicarbonyl(2-cyanotrifluoro-4-pyridyl)bis(triphenylphosphine)rhodium with $[\mathrm{Rh(CO)_2(PPh_3)_2}]^-$.—A solution of the fluoroheterocyclic complex (0.1 g, 0.1 mmol) and the anion (0.35 g, 0.51 mmol) in diglyme (30 ml) was refluxed for 18 h to give a black solution which on chromatography (dichloromethane eluant) gave a black solid (0.15 g) which could not be identified, but which did not contain any carbonyl groups or fluorine atoms. Further elution with

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* Thanks are due to Dr. R. E. Banks and Mr. K. Legge for supplying us with a sample of this compound.

[20] A. Sacco, *Ann. Chim. (Italy)*, 1953, **43**, 495.

acetone gave a trace of another black solid. An appreciable amount of decomposition material remained on the column.

Reaction of Dicarbonyl(6-cyanotrifluoro-3-pyridyl)bis(triphenylphosphine)rhodium with $[Rh(CO)_2(PPh_3)_2]^-$.—When a solution of the anion (0.4 g, 0.6 mmol) and dicarbonyl(6-cyanotrifluoro-3-pyridyl)bis(triphenylphosphine)rhodium (0.1 g, 0.1 mmol) in tetrahydrofuran was refluxed for 18 h the heterocyclic complex starting material was recovered in 80% yield. Some decomposition products remained on the column after chromatography.

Competition Reactions.—In a typical experiment a solution of anion X (1.00 mmol) in tetrahydrofuran (50 ml), and a solution of anion Y (1.00 mmol) in tetrahydrofuran (50 ml) were added simultaneously to a solution of pentafluoropyridine (1.00 mmol) in tetrahydrofuran (20 ml), and the reactants were stirred at room temperature for 16 h. The solution was then filtered and chromatographed. In cases where chromatography did not separate the mixture then the relative proportions of the components of the mixture were estimated from the ^{19}F n.m.r. spectrum. Where separation could be achieved then the separated components were further purified by recrystallisation and the percentages quoted are percentage yields based on amount of pure complex isolated. The results are given in Table 2.

Kinetic Studies.—The kinetic investigations were carried out in a variable-temperature i.r. cell maintained at a temperature of 25 ± 0.25 °C, and reaction rates were followed by observing the rate of appearance of the metal-carbonyl band of the product (*ca.* 2 000 cm^{-1}) and the rate of disappearance of the carbonyl band of the anion (*ca.* 1 850 cm^{-1}). Kinetic runs were carried out under second-order conditions using a 1 : 1 ratio of pentafluoropyridine to anion. Good Beer's law behaviour was observed for all the systems investigated, and in all cases excellent linear plots of $1/A_t$ *vs.* time were obtained.

The results are given in Table 3.

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