Reactions of Low-valent Metal Complexes with Fluorocarbons. Part XXIV.[1] Chloronitrosylbis(triphenyl-, methyldiphenyl- and dimethylphenyl-phosphine)ruthenium and Nitrosyltris(triphenylphosphine)iridium

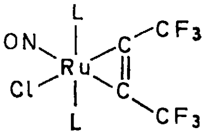
By **J. Clemens, M. Green, and F. G. A. Stone,*** Department of Inorganic Chemistry, The University, Bristol BS8 1TS

Tetrafluoroethylene and hexafluorobut-2-yne react with $RuCl(NO)L_2$ ($L = PPh_3, PMePh_2, PMe_2Ph$) to form the complexes $[Ru{\cdot}CF_2{\cdot}CF_2(Cl)(NO)L_2]$ and $[RuC(CF_3){:}C(CF_3)(Cl)(NO)L_2]$ respectively; the phosphine ligands have a relative *trans*-configuration. Chlorotrifluoroethylene and hexafluoropropene react with $RuCl(NO)(PMe_2Ph)_2$ to form adducts in which the phosphine ligands have a relative *cis*-configuration. Iodine adds *trans* to $RuCl(NO)(PMePh_2)$ to form $RuI_2Cl(NO)(PMePh_2)$ which isomerises in solution. Nitrosyltris(triphenylphosphine)iridium reacts with $CF_3C{\equiv}CCF_3$ to form di-μ-hexafluorobut-2-enylene-bis[*cis*-triphenylphosphine(nitrosyl)iridium(I)], whereas tetrafluoroethylene and hexafluoroacetone form $[IrCF_2{\cdot}CF_2(NO)(PPh_3)_2]$ and $[IrC(CF_3)_2{\cdot}O(NO)(PPh_3)]$. The ruthenium hexafluorobut-2-yne complexes undergo ring-opening reactions with CF_3CO_2H to form vinyl complexes.

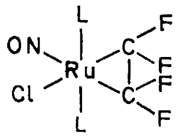
In previous papers in this series we have studied the reaction of fluoro-olefins, hexafluoroacetone, and hexafluorobut-2-yne with the square planar d^8 systems *trans*-$[IrCl(CO)L_2]$ ($L = PPh_3$ or $PMePh_2$),[2,3] and with the tetrahedral d^{10} molecules PtL_4 [$L = PPh_3$,[2] $Ph_2PCH_2CH_2PPh_2$,[4] $PMePh_2$,[2] $P(OMe)_3$[4] and $P(OPh)_3$[4]]. With the development of synthetic routes to chloronitrosylbis(triphenylphosphine)ruthenium[5] and nitrosyltris(triphenylphosphine)iridium,[6] which may be respectively considered as analogous to d^8 and d^{10} systems, an opportunity arose to study their comparative chemistry. The new compounds described in this paper were characterised by elemental analysis, solution molecular weights, and i.r., and ^1H and ^{19}F n.m.r. spectroscopy.

Chloronitrosylbis(triphenylphosphine)ruthenium $RuCl(NO)(PPh_3)_2$ (I) reacts with an excess of hexafluorobut-2-yne at room temperature to give complex (II), which showed bands in the i.r. spectrum at 1778s and 1742m cm^{-1} assigned respectively on the basis of their relative intensity, to the NO stretching frequency of a linear metal nitrosyl group and to the C⁚C frequency of co-ordinated hexafluorobut-2-yne. Although, in general, ν_{NO} is not diagnostic for structural assignment, because the mode of nitrosyl co-ordination is sensitive to the nature of the filled molecular orbitals regardless of the formal oxidation state of the metal, a linear mode of bonding corresponding to Ru^{II} is preferred for compound (II). This is because the position of $\nu_{C\equiv C}$ (max.) [with $\Delta\nu_{C\equiv C} = 558$ cm^{-1}, see ref. 7] implies extensive back bonding from the ruthenium into the π^* orbitals of the acetylene, and this would not occur if the ruthenium was already in a formal oxidation state of $+2$, as would be the case if the nitrosyl was bonded in the bent mode (NO^-).

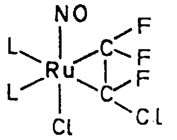
The ^{19}F n.m.r. spectrum of complex (II) showed two triplets of quartets arising from ^{31}P–^{19}F and ^{19}F–^{19}F coupling centred at 49·8 and 51·8 p.p.m. relative to CCl_3F. This pattern is compatible with the illustrated octahedral structure in which the triphenylphosphine ligands have a relative *trans*-configuration, and one CF_3 group is *trans* to a chlorine and the other *trans* to a nitrosyl.[3,8] Interestingly, the F–F coupling (*ca.* 4 Hz) between the non-equivalent *cis*-CF_3 groups in (II), and related complexes (see below), is greater than that observed in the spectrum of $[IrC(CF_3){:}C(CF_3)(CO)(Cl)(PPh_3)_2]$ (0 Hz) but less than that found in the spectrum of $[IrC(CF_3){:}C(CF_3)(CO)(Cl)(PPh_2Me)_2]$ (15 Hz).[3,8] In complexes containing a σ bonded *cis*$[CF_3(R)C{:}C(CF_3){\cdot}Metal]$ group $J_{CF_3-CF_3}$ is generally of the order of 10—15 Hz.[9,10] This suggests that this coupling increases as the metal-bonded carbon atoms become more sp^2 like. The observed temperature invariance of the ^{19}F spectrum of (II) implies a high barrier to rotation, as expected for extensive electron transfer from ruthenium to the antibonding orbitals of the acetylene; as discussed above this accords with a linear RuNO group.



(II) $L = PPh_3$
(VI) $L = PMePh_2$
(IX) $L = PMe_2Ph$



(III) $L = PPh_3$
(VII) $L = PMePh_2$
(X) $L = PMe_2Ph$



(XI) $L = PMe_2Ph$

Tetrafluoroethylene also reacts with (I) to give orange crystals of a 1 : 1 adduct (III), which showed a nitrosyl

---

[1] Part XXIII, J. Ashley-Smith, M. Green, and F. G. A. Stone, *J.C.S. Dalton*, 1972, 1805.

[2] B. A. Clarke, M. Green, R. B. L. Osborn, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 168.

[3] B. A. Clarke, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1970, 951.

[4] J. Browning, H. D. Empsall, M. Green, and F. G. A. Stone, following paper.

[5] M. H. B. Stiddard and R. E. Townsend, *Chem. Comm.*, 1969, 1372.

[6] C. A. Reed and W. R. Roper, *Chem. Comm.*, 1969, 155; *J. Chem. Soc.* (*A*), 1970, 3054.

[7] E. O. Greaves, C. J. L. Lock, and P. M. Maitlis, *Canad. J. Chem.*, 1968, **46**, 3879.

[8] G. W. Parshall and F. N. Jones, *J. Amer. Chem. Soc.*, 1965, **87**, 5356.

[9] H. C. Clark and W. S. Tsang, *J. Amer. Chem. Soc.*, 1967, **89**, 533.

[10] R. Burt, M. Cooke, and M. Green, *J. Chem. Soc.* (*A*), 1970, 2981.

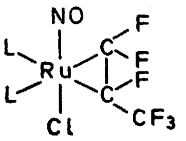
stretching frequency of 1730 cm^{-1}. In contrast with the acetylene adduct, complex (III) readily dissociated in solution with the result that the ^{19}F n.m.r. spectrum could not be examined. Similar relative stabilities have been observed previously for the isostructural adducts of $CF_3C{\equiv}CCF_3$ and C_2F_4 with *trans*-$[IrCl(CO)(PPh_3)_2]$.[8]

It was found previously that in contrast to $[IrCl(CO)(PPh_3)_2]$, the compound $[IrCl(CO)(PPh_2Me)_2]$ forms a stable adduct with tetrafluoroethylene.[3] A similar stabilisation due to an increased nucleophilicity of the metal was found with the ruthenium nitrosyl system. Reaction of (I) with methyldiphenylphosphine or dimethylphenylphosphine in refluxing benzene led to displacement of triphenylphosphine and the formation of $[RuCl(NO)(PPh_2Me)_2]$ (IV) and $[RuCl(NO)(PPhMe_2)_2]$ (V). However, due to the oxygen sensitivity of these complexes difficulty was experienced in obtaining pure materials, and therefore it was necessary to carry out reactions without isolation of the starting materials. In this context it is interesting that a stable dioxygen adduct $[\overline{Ru\cdot O\cdot O}(Cl)(NO)(PPh_3)_2]$ is formed by displacement of carbon monoxide from $[RuCl(CO)(NO)(PPh_3)_2]$ with molecular oxygen.[11]

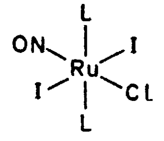
Hexafluorobut-2-yne and tetrafluoroethylene react with (IV) to give the stable crystalline 1 : 1 adducts (VI) and (VII) respectively. The acetylene complex showed only one broad band in its i.r. spectrum at 1770 cm^{-1} which is ascribed to overlapping NO and C⋮C stretching frequencies. The ^1H n.m.r. spectrum shows the CH_3P resonance as an apparent triplet, which is consistent with *trans*-phosphine ligands in an octahedral structure.[12] The presence in the ^{19}F n.m.r. spectrum of (VI) of two signals due to CF_3 groups provides further support for this stereochemistry. The ^1H n.m.r. spectrum of (VII) implies a similar stereochemistry with *trans*-phosphine ligands. This contrasts with the corresponding iridium system;[3] *trans*-$[IrCl(CO)(PPh_2Me)_2]$ and tetrafluoroethylene form an adduct with *cis*-phosphine ligands, although the initially formed complex has a *trans*-arrangement of phosphine groups.[13] The ^{19}F n.m.r. spectrum of (VII) showed a complex multiplet centred at 112·9 p.p.m., which was not sufficiently well resolved to allow analysis.

Hexafluoropropene, trifluoroethylene, and chlorotrifluoroethylene did not form stable adducts with (IV), however, complex (V) reacts with $CF_3C{\equiv}CCF_3$, C_2F_4, $CF_2{:}CFCl$, $CF_2{:}CFCF_3$, and $CF_2{:}CFH$ to form respectively (IX), (X), (XI), (XII), and (XIII) as stable crystalline adducts; only the trifluoroethylene adduct showed instability in solution.

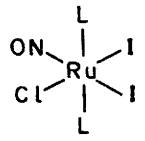
The complexes (IX) and (X) are isostructural with the other hexafluorobut-2-yne and tetrafluoroethylene complexes; the ^1H n.m.r. spectra showed two apparent triplet resonances due to *trans*-phosphine ligands; the methyl groups on the same phosphorus atom appeared as unequivalent because there is no plane of symmetry through the two *trans*-phosphorus atoms.[12] In contrast a different stereochemistry was observed for (XI) and (XII). The ^1H n.m.r. spectrum of the chlorotrifluoroethylene complex showed four apparent doublet signals indicating a relative *cis*-configuration for the phosphine ligands; different chemical shifts were observed for CH_3P *trans* to CFCl and *trans* to the CF_2 of the fluoro-olefin, the absence of a symmetry plane through the phosphorus resulting in a further inequivalence. The ^1H n.m.r. spectrum of the hexafluoropropene complex showed the same features except that different CH_3P shifts were not observed for the ligands *cis* and *trans* to the $CFCF_3$ group of the fluoro-olefin.



(XII) L = PMe_2Ph



(VIIIa) L = $PMePh_2$



(VIIIb) L = $PMePh_2$

The ^{19}F n.m.r. spectra of (XI) and (XII) showed respectively three and four resonances, demonstrating stereospecificity in the formation of these compounds. In addition the magnitude of J (F_1F_2) implies, as has been previously discussed,[14,15] a change in the geometry of the fluoro-olefin, the substituents being pushed away from the metal on co-ordination.

The reactions leading to the formation of the complexes described above may be considered to be of the oxidative–addition type. It was therefore of some interest to study the reaction of complex (IV) with a typical oxidising agent, iodine. It has previously been shown[11] that $[RuCl(CO)(NO)(PPh_3)_2]$ reacts with halogens to form complexes of the type $[RuX_2Cl(NO)(PPh_3)_2]$. Addition of iodine to $[RuCl(NO)(PMePh_2)_2]$ in benzene led to an immediate colour change and formation of orange crystals of (VIII) [ν_{NO} (max.) 1870 cm^{-1}]. On recrystallisation from methylene chloride partial isomerisation occurred to give a mixture showing nitrosyl stretching frequencies at 1870 and 1840 cm^{-1}. The ^1H n.m.r. spectrum showed two apparent triplet resonances centred at τ 7·10 and 7·40 with relative intensities 1 : 5. It has been shown[16,17] that in the series of compounds $[RuX_3(NO)L_2]$ the inductive effect of the halogen dominates in determining the position of the nitrosyl stretching frequency; ν_{NO} (max.) for the iodo-complexes being lower than that of the corresponding chloro-compounds. Apparently, reaction of iodine with (IV) involves a kinetically controlled *trans*-addition to afford (VIIIa); the latter then undergoes a thermodynamically controlled isomerisation to (VIIIb), the

---

[11] K. R. Laing and W. R. Roper, *Chem. Comm.*, 1968, 1556.

[12] B. L. Shaw and J. M. Jenkins, *J. Chem. Soc.* (*A*), 1966, 1787.

[13] P. J. Maples, private communication.

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

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

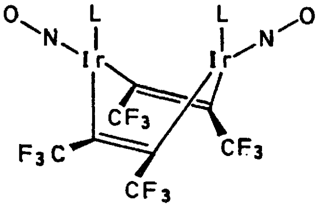
[16] M. B. Fairy and R. J. Irving, *J. Chem. Soc.* (*A*), 1966, 475.

[17] J. Chatt and B. L. Shaw, *J. Chem. Soc.* (*A*), 1966, 1811.

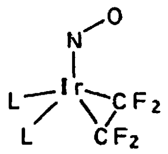
relative *trans*-configuration of the phosphine ligands being retained throughout. Interestingly, reaction of halogens with *trans*-$[\text{IrCl(CO)(PMePh}_2)_2]$ involves an analogous *trans*-addition.[18]

Hexafluorobut-2-yne reacts in benzene solution with nitrosyltris(triphenylphosphine)iridium to give the green complex (XIV). Although the analytical data and the i.r. [assuming coincidence of ν_{NO} (max.) and $\nu_{\text{C:C}}$ (max.)] and ^{19}F n.m.r. spectra are consistent with a formulation for (XIV) of $[\overline{\text{IrC(CF}_3)\text{:C}}\text{(CF}_3\text{)(NO)(PPh}_3)]$, unsuccessful attempts to displace the acetylene moiety with iodine in benzonitrile and a solution molecular weight of twice the required magnitude indicated the possibility of an unusual structure. A single-crystal *X*-ray diffraction study[19] revealed that (XIV) was, in fact, di-μ-hexafluorobut-2-enylene-bis[*cis*-triphenylphosphine(nitrosyl)-iridium(I)]. As shown in the illustrated structure the geometry about each iridium is essentially square planar with NO, P, and one carbon atom of each of the hexafluorobut-2-enylene ligands in this plane. The iridium atoms are formally co-ordinatively unsaturated, and are considered to be in an oxidation state of (1+) with co-ordination of the nitric oxide as NO$^+$.

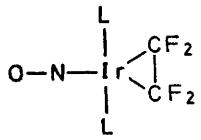
Tetrafluoroethylene and hexafluoroacetone react with $[\text{Ir(NO)(PPh}_3)_3]$ to form respectively (XV) and (XVII). However, the initial adduct (XV) from C_2F_4 on recrystallisation from benzene–hexane decomposed to give $[\text{Ir(NO)(PPh}_3)_3]$ and a stable complex $[\overline{\text{IrCF}_2\text{CF}_2}\text{-(NO)(PPh}_3)_2]$ (XVI) [ν_{NO} (max.) 1680 cm^{-1}]. The ^{19}F n.m.r. spectrum showed an apparent triplet centred at 117·4 p.p.m.



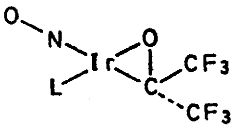
(XIV) L = PPh_3



(XVIa) L = PPh_3



(XVIb) L = PPh_3



(XVII) L = PPh_3

If (XVI) has a square based pyramidal structure (XVIa), then the NO ligand should be in a bent mode, following a recent discussion[20] of correlation diagrams for the bending of nitrosyls in five-co-ordinate tetragonal systems. Although ν_{NO} (max.) is *ca.* 120 cm^{-1} higher than in related complexes $[\text{IrX}_2\text{(NO)(PPh}_3)_2]$ (X = Cl, I) where a bent nitrosyl mode and square pyramidal structure has been established by *X*-ray crystallography,[21] this difference could conceivably be due to the high back-bonding capability of tetrafluoroethylene. However, for the structure (XVIa) more than one ^{19}F chemical shift environment might have been expected. This difficulty does not arise with (XVIb) where the different spatial arrangement allows a linear mode of nitric oxide bonding. In the light of these considerations structure (XVIb) is tentatively preferred.

Complex (XVII) had an i.r. spectrum with ν_{NO} (max.) at 1820 cm^{-1}, and a ^{19}F n.m.r. spectrum with a single resonance at 64·9 p.p.m. (d, $J_{\text{P-F}}$ 6·5 Hz). This strongly suggests the illustrated square planar structure,[2,4] with co-ordination around the iridium being somewhat similar to that in (XIV). It is not possible from the data available to determine whether in (XVII) the triphenylphosphine ligand is *cis* or *trans* to the oxygen of the hexafluoroacetone moiety. The magnitude of $J_{\text{P-F}}$ is intermediate between those generally observed for *cis* and *trans* ^{13}P–^{19}F couplings in square planar complexes of the type $[\overline{\text{M·C(CF}_3)_2\text{O}}\text{L}_2]$ (M = Ni, Pd, Pt; L = phosphine or phosphite).[2,4,22,23]

Treatment of (XVI) or (XVII) with iodine in benzonitrile led to the displacement of tetrafluoroethylene or hexafluoroacetone, as well as nitric oxide, and the formation of the five-co-ordinate iridium(III) complex $[\text{IrI}_3\text{(PhCN)(PPh}_3)]$ (XVIII). As previously mentioned, (XIV) does not lose hexafluorobut-2-yne on reaction with iodine–benzonitrile; instead, the nitrosyl group is lost and a brown crystalline material (XIX) is formed. On the basis of the elemental analysis and i.r. and ^{19}F n.m.r. spectral results it is suggested that the six-membered di-iridium ring remains intact and that the compound has structure (XIX).

The mechanism of formation of the dinuclear complex (XIV) merits comment. It seems likely that the d^{10} system $\text{Ir(NO)(PPh}_3)_3$ reacts as a nucleophilic reagent with $\text{CF}_3\text{C}{\equiv}\text{CCF}_3$ to form the ionic dipolar species $\text{CF}_3\overset{-}{\text{C}}{=}\text{C(CF}_3)\overset{+}{\text{Ir}}\text{(NO)(PPh}_3)_2$, which could dimerise with loss of triphenylphosphine to give (XIV).[19]

The ruthenium nitrosyl hexafluorobut-2-yne complexes (II) and (VI) readily react with trifluoroacetic acid to form, respectively, (XX) and (XXI) as stable yellow crystalline nitrosyl complexes. It is suggested, by analogy with related reactions, that these complexes have the illustrated structures. In agreement, the i.r. spectra show bands corresponding to a linearly bonded nitrosyl group and to a $\text{Ru·C(CF}_3)\text{:C(CF}_3)\text{H}$ group;

---

[18] J. P. Collman and C. T. Sears, *Inorg. Chem.*, 1968, **7**, 27.

[19] J. Clemens, M. Green, Ming-Cheng Kuo, C. J. Fritchie, J. T. Mague, and F. G. A. Stone, *Chem. Comm.*, 1972, 53.

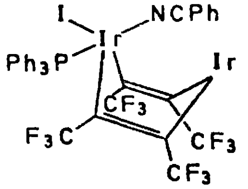
[20] C. G. Pierpont and R. Eisenberg, *J. Amer. Chem. Soc.*, 1971, **93**, 4905.

[21] D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, 1971, **10**, 1035.

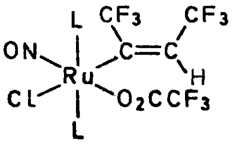
[22] H. D. Empsall, M. Green, and F. G. A. Stone, *J.C.S. Dalton*, 1972, 96.

[23] J. Browning, C. S. Cundy, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1971, **448**.

the ^{1}H and ^{19}F n.m.r. spectra support this formulation. In the formation of (XXI) from (VI) the *trans*-relative configuration of the methyldiphenylphosphine ligands is



(XIX) (Ligands omitted around one Ir for clarity)



(XX) L = PPh_3
(XXI) L = $PMePh_2$

retained. The magnitude of the ^{19}F–^{19}F coupling between vicinal-trifluoromethyl groups suggests a relative *cis*-configuration,[9] and therefore the ruthenium and hydrogen must also have a *cis*-configuration. The same stereochemistry for the formal ring opening of complexes of the type $\overline{\mathrm{M{\cdot}C(CF_3){:}C}}\mathrm{(CF_3)}$ with HX has been observed in both osmium[24] and platinum chemistry.[25-27]

EXPERIMENTAL

^{1}H and ^{19}F N.m.r. spectra were recorded on a Varian Associates HA 100 spectrometer at 100 and 94·1 MHz respectively. Chemical shifts are relative to Me_4Si (τ 10·00) and CCl_3F (0·00 p.p.m.). I.r. spectra were recorded with a Perkin-Elmer 257 spectrophotometer using Nujol and hexachlorobutadiene mulls. All operations were carried out under dry oxygen-free nitrogen. Light petroleum refers to the fraction b.p. 40—60°.

Reactions of Chloronitrosylbis(triphenylphosphine)ruthenium (I).—(a) *With hexafluorobut-2-yne.* An excess of hexafluorobut-2-yne (5·0 mmol) was condensed (−196°) into a Carius tube containing complex (I) (0·35 g, 0·50 mmol) in benzene (30 ml). After 5 h at room temperature the volume of the solvent was reduced (5 ml) *in vacuo*, and hexane added to give red *crystals* of (II) (0·30 g, 70%), m.p. 209—212° (dec.) (Found: C, 56·3; H, 3·5; N, 1·7. $C_{40}H_{30}ClF_6NOP_2Ru$ requires C, 56·3; H, 3·5; N, 1·6%); $\nu_{max.}$ 3040w, 1778s, 1742m, 1590w, 1575w, 1483m, 1437s, 1256s, 1225s, 1200s, 1155m, 1123s, 1092s, 1032w, 1005w, 930w, 915w, 817m, 764m, 750s, 748s, 700s, 680m, and 674m cm^{-1}. The ^{19}F n.m.r. spectrum (C_6H_6) showed resonances at 49·8 p.p.m. (t of q, 3F, J_{PF} 1·9 Hz, J_{FF} 3·8 Hz) and 51·8 (t of q, 3F, J_{PF} 2·8 Hz, J_{FF} 3·8 Hz).

(b) *With tetrafluoroethylene.* Similarly, tetrafluoroethylene (2·50 mmol) was treated (2 h) at room temperature with a solution of complex (I) (0·46 g, 0·60 mmol) in benzene (20 ml). Rapid removal of the benzene *in vacuo* and addition of hexane gave orange *crystals* of (III) (0·24 g, 50%), m.p. 157—158° (dec.) (Found: C, 57·5; H, 3·9; N, 1·9. $C_{38}H_{30}ClF_4NOP_2Ru$ requires C, 57·7; H, 3·8; N, 1·8%); $\nu_{max.}$ 3050w, 1730s, 1590w, 1575w, 1480m, 1434s, 1421m, 1396w, 1311w, 1187w, 1160w, 1122s, 1100m, 1091s, 1040s, 998w, 810s, 744m, 738m, 720w, and 690s cm^{-1}.

Reactions of Chloronitrosylbis(methyldiphenylphosphine)ruthenium (IV).—(a) *With hexafluorobut-2-yne.* A solution of complex (IV) was prepared by refluxing (10 min) a solution of complex (I) (0·35 g, 0·49 mmol) in benzene (20 ml) with methyldiphenylphosphine (0·32 g, 1·62 mmol). Hexafluorobut-2-yne (2·00 mmol) was condensed (−196°) into a Carius tube containing the above solution. After 15 min at room temperature, the solutions was filtered, the solvent removed *in vacuo*, and the residue chromatographed on a Florisil-packed column. Elution with diethyl ether–hexane (1 : 9) gave red *crystals* of (VI) (0·15 g, 40%), m.p. 125° (dec.) (Found: C, 48·8; H, 3·6; F, 15·9; N, 1·9; P, 8·6. $C_{30}H_{26}ClF_6NOP_2Ru$ requires C, 49·4; H, 3·6; F, 15·6; N, 1·9; P, 8·5%); $\nu_{max.}$ 3050w, 1770s, 1586w, 1575w, 1485m, 1445s, 1414w, 1344w, 1310w, 1290w, 1252s, 1240m, 1222s, 1193w, 1160m, 1132s, 1114s, 1030w, 1002w, 975w, 930w, 895s, 856w, 815m, 760m, 746s, 712s, 700s, 680m, and 675m cm^{-1}. The ^{19}F n.m.r. spectrum (C_6H_6) showed resonances at 49·8 p.p.m. (t of q, 3F, J_{PF} 2·0 Hz, J_{FF} 4·0 Hz) and 52·7 (t of q, 3F, J_{PF} 3·3 Hz, J_{FF} 4·0 Hz). The ^{1}H n.m.r. spectrum (C_6D_6) showed peaks at τ 2·2—3·1 (m, 20H, C_6H_5P) and 8·10 (apparent t, 6H, CH_3P, $|J|_{PCH}$ 8·0 Hz).

(b) *With tetrafluoroethylene.* Similarly, reaction of complex (IV) (0·90 mmol) in benzene (40 ml) with tetrafluoroethylene (3·00 mmol) gave after 14 h at room temperature an orange solution. Removal of the solvent *in vacuo* followed by chromatography on Florisil gave an orange powder which crystallised from benzene to give orange *crystals* of (VII) (0·17 g, 2·9%), m.p. 132° (dec.) (Found: C, 50·1; H, 3·9; F, 11·5; P, 9·4. $C_{28}H_{26}P_2NOClF_4Ru$ requires C, 50·5; H, 3·9; F, 11·4; P, 9·3%); $\nu_{max.}$ 3060w, 1725s, 1590w, 1575w, 1485m, 1435s, 1421m, 1390m, 1332w, 1309w, 1290w, 1123s, 1092s, 1082s, 1045s, 1030w, 1000w, 900s, 895s, 848w, 810s, 795m, 750s, 748s, and 700s cm^{-1}. The ^{19}F n.m.r. spectrum (C_6H_6) showed a signal at 112·9 p.p.m. (m, 4F). The ^{1}H n.m.r. spectrum (C_6D_6) showed resonances at τ 2·1—2·8 (m, 10H, C_6H_5P) and 7·90 (apparent t, 6H, CH_3P, $|J|_{PCH}$ 8·0 Hz).

(c) *With Iodine.* Addition of iodine (0·31 g, 1·25 mmol) to a solution of complex (IV) (1·12 mmol) in benzene (20 ml) led to an immediate colour change and the deposition of orange *crystals* of (VIII) (0·80 g, 86%), m.p. 231—234° (dec.) (Found: C, 38·2; H, 3·4; I, 30·7. $C_{26}H_{26}ClI_2NOP_2Ru$ requires C, 38·1; H, 3·2; I, 31·0%); $\nu_{max.}$ 3060w, 1870s, 1585w, 1570w, 1480m, 1432s, 1420w, 1410w, 1330w, 1277m, 1192w, 1160w, 1100m, 1093m, 1074w, 1030w, 1000w, 904s, 894s, 887s, 750m, 738s, 701s, and 695s cm^{-1}. On recrystallisation from methylene chloride two nitrosyl stretching frequencies were observed at 1870s and 1840s cm^{-1}. The ^{1}H n.m.r. spectrum (C_6D_6) showed resonances at τ 2·0—3·1 (m, 20H, C_6H_5P), 7·10 (apparent t, 6H, CH_3P, $|J|_{PCH}$ 8·0 Hz), and 7·40 (apparent t, 6H, CH_3P, $|J|_{PCH}$ 8·0 Hz); the latter two peaks had relative intensities of 1 : 5.

Reactions of Chloronitrosylbis(dimethylphenylphosphine)ruthenium (V).—(a) *With hexafluorobut-2-yne.* An excess of hexafluorobut-2-yne (3·00 mmol) was condensed (−196°) into a Carius tube containing complex (V) prepared from (I) (0·55 g, 0·80 mmol) dimethylphenylphosphine (0·22 g, 1·60 mmol) in benzene (25 ml). After 2 h at room tem-

[24] M. Cooke, M. Green, and T. A. Kuc, *J. Chem. Soc.* (*A*), 1971, 1200.

[25] B. E. Mann, B. L. Shaw, and N. I. Tucker, *J. Chem. Soc.*, (*A*), 1971, 2667.

[26] P. B. Tripathy, B. W. Renoe, K. Adzamli, and D. M. Roundhill, *J. Amer. Chem. Soc.*, 1971, **93**, 4406.

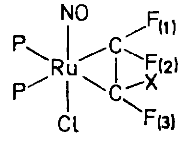
[27] D. M. Barlex, R. D. W. Kemmitt, and G. W. Littlecott, *Chem. Comm.*, 1971, 199.

perature, polymer was filtered off, the solvent removed *in vacuo*, and the residue chromatographed on a Florisil-packed column. Elution with diethyl ether–hexane (1 : 9) gave red *crystals* of (IX) (0·07 g, 15%), m.p. 87—89° (dec.) (Found: C, 39·8; H, 4·1; N, 2·6. $C_{20}H_{22}ClF_6NOP_2Ru$ requires C, 39·7; H, 3·7; N, 2·3%); $\nu_{max.}$ 3050w, 1740s, 1590w, 1575w, 1480m, 1438s, 1420w, 1409w, 1342w, 1304w, 1285w, 1257s, 1245s, 1225s, 1158s, 1132s, 1110s, 1030w, 1004w, 950s, 906s, 849w, 810m, 751s, 748s, 726m, 700s, and 680s cm^{-1}. The ^{19}F n.m.r. spectrum (CH_2Cl_2) showed resonances at 50·9 p.p.m. (t of q, 3F, J_{PF} 1·7 Hz, J_{FF} 4·0 Hz) and 54·0 (t of q, 3F, J_{PF} 2·8 Hz, J_{FF} 4·0 Hz). The ^1H n.m.r. spectrum (C_6D_6) showed peaks at τ 2·1—3·2 (m, 10H, C_6H_5P), 8·40 (apparent t, 6H, CH_3P, $|J|_{PCH}$ 8·0 Hz) and 8·70 (apparent t, 6H, CH_3P, $|J|_{PCH}$ 8·0 Hz). Further elution with diethyl ether–hexane (1 : 8) gave crystals of dinitrosylbis(triphenylphosphine)ruthenium (0·06 g, 0·08 mmol) (Found: C, 63·4; H, 4·6; N, 3·9. Calc. for $C_{36}H_{30}N_2O_2P_2Ru$: C, 63·1; H, 4·4; N, 4·1%); ν_{NO} (Nujol) 1665m and 1615s cm^{-1}.

(b) *With tetrafluoroethylene*. Similarly, reaction of tetrafluoroethylene (3·00 mmol) with complex (V) (1·00 mmol) in benzene (30 ml.) gave after 6 h at room temperature followed by removal of the solvent and chromatography (eluted with diethyl ether–hexane 1 : 8) orange *crystals* of (X) (0·35 g, 40%), m.p. 142—144° (dec.) (Found: C, 40·0; H, 4·1; Cl, 6·7; F, 14·3; N, 2·9. $C_{18}H_{22}ClF_4NOP_2Ru$ requires C, 39·8; H, 4·1; Cl, 6·5; F, 14·0; N, 2·6%). $\nu_{max.}$ 3060w, 1730s, 1590w, 1575w, 1490w, 1438m, 1415m, 1386m, 1345w, 1328w, 1305w, 1292w, 1280m, 1110s, 1096s, 1038s, 1030s, 1000m, 960m, 951m, 912s, 870m, 848m, 811s, 796s, 750s, 722s, 700s, and 681w cm^{-1}. The ^{19}F n.m.r. spectrum (CH_2Cl_2) showed resonances at 113·6 p.p.m. (m, 2F) and 115·1 (m, 2F). The ^1H n.m.r. spectrum (C_6D_6) showed peaks at τ 2·5—3·1 (m, 10H, C_6H_5P), 8·46 (apparent t, 6H, CH_3P, $|J|_{PCH}$ 8·0 Hz) and 8·64 (apparent t, 6H, CH_3P, $|J|_{PCH}$ 8·0 Hz).

(c) *With chlorotrifluoroethylene*. Reaction of chlorotrifluoroethylene (3·00 mmol) with complex (V) (0·75 mmol) in benzene (25 ml) gave (6 h, room temperature) after chromatography (eluted with diethyl ether–hexane 1 : 9), yellow *crystals* of (XI) (0·22 g, 53%), m.p. 99—100° (dec.) (Found: C, 38·6; H, 4·2; Cl, 12·8; F, 10·4. $C_{18}H_{22}Cl_2F_3NOP_2Ru$ requires C, 38·6; H, 4·0; Cl, 12·7; F, 10·2%); $\nu_{max.}$ 3080w, 1715s, 1570w, 1490w, 1475m, 1430s, 1410w, 1350s, 1328w, 1310w, 1296w, 1280m, 1160w, 1100s, 1010s, 950s, 912s, 906s, 845w, 778s, 750s, 716s, 708s, 692s, and 670w cm^{-1}. The ^{19}F n.m.r. spectrum (CH_2Cl_2) showed resonances at 99·5 p.p.m. (F_1), 104·8 (F_2), and 111·7 (F_3) where J (F_1F_2) 132·0 Hz, J (F_1F_3) 23·0 Hz, J (F_2F_3) 15·0 Hz, J_{trans} (PF_1) 45·0 Hz, J_{trans} (PF_2) 15·0 Hz. The ^1H n.m.r. spectrum (C_6D_6) showed peaks at τ 2·5—3·1 (m, 10H, C_6H_5P), 8·44 (apparent d, 3H, CH_3P, $|J|_{PCH}$ 8·0 Hz), 8·45 (apparent d, 3H, CH_3P, $|J|_{PCH}$ 8·0 Hz), 8·62 (apparent d, 3H, CH_3P, $|J|_{PCH}$ 8·0 Hz), and 8·64 (apparent d, 3H, CH_3P, $|J|_{PCH}$ 8·0 Hz).

(d) *With hexafluoropropene*. Similarly, reaction of hexafluoropropene (5·00 mmol) with complex (V) (1·40 mmol) in benzene (30 ml.) gave (5 h, 60°) after chromatography (eluted with diethyl ether–hexane 1 : 8), yellow *crystals* of (XII) (0·21 g, 25%), m.p. 114—116° (dec.) (Found: C, 38·3; H, 3·7; F, 19·5. $C_{19}H_{22}ClF_6NOP_2Ru$ requires C, 38·5; H, 3·7; F, 19·2%); $\nu_{max.}$ 3060w, 1715s, 1480w, 1435m, 1380s, 1325w, 1304w, 1280s, 1200w, 1180s, 1147m, 1110s, 1050s, 975s, 951m, 920s, 850w, 790m, 778w, 750s, 742s, 720m, and 692s cm^{-1}. The ^{19}F n.m.r. spectrum (CH_2Cl_2) showed resonances at 66·8 p.p.m. (CF_3), 96·8 (F_1), 99·8 (F_2), and 146·0 (F_3) where J (F_1F_2) 142·0 Hz, J (F_1F_3) 10·5 Hz, and J_{trans} (PF_1) 10·5 Hz. The ^1H n.m.r. spectrum (C_6D_6) showed signals at τ 2·5—3·2 (m, 10H, C_6H_5P), 8·46 (apparent d, 6H, CH_3P, $|J|_{PCH}$ 8·0 Hz) and 8·60 (apparent d, 6H, CH_3P, $|J|_{PCH}$ 8·0 Hz).



(e) *With trifluoroethylene*. Reaction of trifluoroethylene (5·00 mmol) with complex (V) (1·80 mmol) in benzene (30 ml) gave (18 h, 60°) after chromatography orange *crystals* of (XIII) (0·21 g, 22%), m.p. 105—107° (dec.) (Found: C, 41·5; H, 4·4; F, 10·9. $C_{18}H_{23}ClF_3NOP_2Ru$ requires C, 41·2; H, 4·4; F, 10·9%); $\nu_{max.}$ 3060w, 1705s, 1575w, 1480w, 1440m, 1420w, 1395m, 1330w, 1310w, 1300w, 1285w, 1265s, 1114m, 1088m, 1020s, 1008m, 958m, 910s, 870s, 861s, 750s, 722s, 713s, 702s, and 685w cm^{-1}. The complex was unstable in solution and both ^{19}F and ^1H n.m.r. spectra indicated a mixture of isomers.

Reactions of Nitrosyltris(triphenylphosphine)iridium.—(a) *With hexafluorobut-2-yne*. An excess of hexafluorobut-2-yne (5·00 mmol) was condensed (−196°) into a Carius tube (100 ml) containing a solution of nitrosyltris(triphenylphosphine)iridium (0·80 g, 0·80 mmol) in benzene (30 ml). After 24 h at 50° the volume of the solvent was reduced *in vacuo* and hexane added to give green *crystals* of (XIV) (0·30 g, 58%), m.p. 198—199° (dec.) (Found: C, 41·0; H, 2·6; F, 17·3; N, 2·3%. *M* (osmometry $CHCl_3$) 1260. $C_{44}H_{30}F_{12}N_2O_2P_2Ir_2$ requires C, 40·9; H, 2·3; F, 17·6; N, 2·2%. *M*, 1292), $\nu_{max.}$ 3070w, 1780s, 1600w, 1580w, 1556w, 1482m, 1440m, 1315m, 1240s, 1229s, 1191m, 1168m, 1142s, 1125s, 1113s, 1100s, 1076m, 1031w, 1003w, 858w, 843w, 760m, 753m, 748m, 700s, and 686w cm^{-1}. The ^{19}F n.m.r. spectrum (CH_2Cl_2) showed resonances at 51·8 p.p.m. (q, 6F, CF_3, J_{FF} 11·5 Hz) and 53·8 (m, 6F, CF_3, J_{FF} 11·5 Hz).

(b) *With tetrafluoroethylene*. Similarly, reaction (6 days, 80°) of an excess of tetrafluoroethylene (4·00 mmol) with nitrosyltris(triphenylphosphine)iridium (0·45 g, 0·45 mmol) gave, on removal of solvent and addition of hexane, orange *crystals* of (XV) (0·26 g, 53%), m.p. 151—155° (dec.), $\nu_{max.}$ 3060w, 1600s, 1580m, 1570w, 1480m, 1435s, 1367m, 1316w, 1288w, 1190m, 1161w, 1100m, 1093m, 1085m, 1070m, 1036m, 1005, 814s, 754s, 749s, 742s, 702s, and 690s cm^{-1}. On recrystallisation from benzene–hexane complex (XV) decomposed to give $[IrNO(PPh_3)_3]$ and brown *crystals* of (XVI) (0·14 g, 29%), m.p. 163—164° (dec.) (Found: C, 54·0; H, 3·7; F, 9·1; N, 1·8; P, 6·9. $C_{38}H_{30}F_4IrNOP_2$ requires C, 53·9; H, 3·6; F, 9·0; N, 1·7; P, 6·6%); $\nu_{max.}$ 3080w, 3050w, 1680s, 1590w, 1575w, 1480m, 1438s, 1408m, 1380m, 1310w, 1290w, 1185w, 1160w, 1100s, 1074m, 1036s, 1002w, 857w, 850w, 803s, 765m, 760m, 750s, and 700s cm^{-1}. The ^{19}F n.m.r. spectrum (CH_2Cl_2) showed a resonance at 117·4 p.p.m. (apparent t, $|J\ (PF) + J\ (PF')|$ 42·0 Hz).

(c) *With hexafluoroacetone*. An excess of hexafluoroacetone (3·00 mmol) was added to a solution of nitrosyltris(triphenylphosphine)iridium (0·24 g, 0·24 mmol) in benzene (20 ml). After 7 days at 80° the volume of the solvent was reduced *in vacuo* and addition of ethanol and hexane gave orange *crystals* of (XVII) (0·11 g, 67%), m.p. 157° (dec.) (Found: C, 38·6; H, 2·1; F, 17·8%, *M* ($CHCl_3$) 588. $C_{21}H_{15}F_6IrNO_2P$ requires C, 38·8; H, 2·3; F, 17·5; *M*, 680), $\nu_{max.}$ 3080w, 3050w, 1820s, 1585w, 1572w, 1480m, 1440s, 1333w, 1318s, 1300m, 1280s, 1251m, 1216m, 1173s, 1160s, 1144s, 1111m, 1102s, 1000w, 950s, 880s, 856w, 755s, 721m, 708s, 700s, and 665m cm^{-1}. The ^{19}F n.m.r. spectrum (CH_2Cl_2) showed a single resonance at 64·9 p.p.m. (d, 6F, CF_3, J_{PF} 6·5 Hz).

Reaction of Complex (II) *with Trifluoroacetic Acid*.—An excess of trifluoroacetic acid (2 ml) was added (room temperature) to a stirred solution of complex (II) (0·20 g, 0·24 mmol) in methylene chloride (20 ml). After 10 min the volume was reduced *in vacuo* and hexane added. The resultant oil was crystallised from methylene chloride–hexane to give yellow *crystals* of (XX) (0·17 g, 74%), m.p. 179—180° (dec.) (Found: C, 52·0; H, 3·3; F, 17·9; N, 1·6. $C_{42}H_{31}ClF_9NO_3P_2Ru$ requires C, 52·1; H, 3·2; F, 17·7; N, 1·5%); $\nu_{max.}$ 3070w, 1880s, 1680s, 1615w, 1590w, 1575w, 1485m, 1437s, 1394m, 1350m, 1320w, 1254s, 1218s, 1205s, 1180s, 1161s, 1130s, 1120s, 1093s, 1031w, 1003w, 850w, 790w, 751m, 730m, 712m, 700s, and 645w cm^{-1}. The ^{19}F n.m.r. spectrum (CH_2Cl_2) showed resonances at 55·4 p.p.m. (overlapping m, 6F, CF_3) and 74·0 (s, 3F, CF_3CO_2). The ^1H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 2·2—2·7 (m, 30H, C_6H_5P) and 4·2 (m, 1H, $CF_3\cdot C\mathit{H}=$).

Reaction of Complex (VI) *with Trifluoroacetic Acid*.—Crystals of complex (VI) (0·13 g, 0·20 mmol) were added to trifluoroacetic acid (2 ml; excess) with stirring; the colour changed from red to yellow. After 5 min at room temperature the excess CF_3CO_2H was removed *in vacuo* and the residue chromatographed on a Florisil-packed column. Elution with diethyl ether–hexane (30% ether) gave yellow *crystals* of (XXI) (0·08 g, 50%), m.p. 163—164° (dec.) (Found: C, 45·6; H, 3·2; F, 19·9; N, 1·7. $C_{32}H_{27}ClF_9NO_3P_2Ru$ requires C, 45·6; H, 3·2; F, 20·3; N, 1·7%), $\nu_{max.}$ 3060w, 1865s, 1685s, 1610m, 1575w, 1488m, 1440s, 1412m, 1368m, 1298w, 1250s, 1221m, 1200s, 1166m, 1139s, 1126s, 1115s, 1005w, 900s, 850w, 819w, 800w, 751s, 742s, 712s, 702s, and 654, cm^{-1}. The ^{19}F n.m.r. spectrum (C_6H_6) showed resonances at 55·7 p.p.m. (m, 3F, J_{FF} 13·0 Hz), 56·1 (m, 3F, J_{FF} 13·0 Hz), and 74·2 (s, 3F, CF_3CO_2). The ^1H n.m.r. spectrum (C_6D_6) showed resonances at τ 2·2—3·1 (m, 20H, C_6H_5P), 3·50 (q, 1H, $CF_3\cdot C\mathit{H}=$, J_{HF} 10·0 Hz) and 80·4 (apparent t, 6H, CH_3P, $|J|_{PCH}$ 8·0 Hz).

Reaction of Complex (XVII) *with Iodine*.—An excess of iodine (0·20 g), was added too a stirred solution (benzonitrile, 20 ml) of Complex (XVII) (0·028 g, 0·04 mmol) *in vacuo*. After 5 min at room temperature the volatile material was collected and identified by i.r. spectroscopy as hexafluoroacetone. The benzonitrile was slowly removed *in vacuo* and the residue recrystallised from methylene chloride–hexane to give red *crystals* of (XVIII) (0·03 g, 75%), m.p. 205—206° (dec.) (Found: C, 31·9; H, 2·1; N, 1·7. $C_{25}H_{20}I_3IrNP$ requires C, 32·0; H, 2·1; N, 1·5%); $\nu_{max.}$ 3080w, 2290w, 1595w, 1590w, 1575w, 1480w, 1450s, 1440s, 1432m, 1428w, 1345w, 1318w, 1295w, 1268w, 1203w, 1190w, 1178w, 1165w, 1105m, 1096m, 1075w, 1030w, 1005w, 930w, 828w, 765s, 760s, 752s, 745m, 720m, 710s, 700s, and 689s cm^{-1}.

Reaction of Complex (XVI) *with Iodine*.—A similar reaction to that described above gave tetrafluoroethylene and (XVIII).

Reaction of Complex (XIV) *with Iodine*.—A solution of (XIV) (0·06 g, 0·10 mmol) in benzonitrile (5 ml) was treated *in vacuo* with iodine (0·03 g, 0·10 mmol) at room temperature. Benzonitrile was removed *in vacuo* and the residue recrystallised from methylene chloride to give brown *crystals* of (XIX) (0·07 g, 80%), m.p. 179—181° (dec.) (Found: C, 41·1; H, 2·1; F, 13·3; I, 15·0; N, 1·8. $C_{58}H_{40}F_{12}I_2Ir_2N_2P_2$ requires C, 41·2; H, 2·3; F, 13·5; I, 15·0; N, 1·7%); $\nu_{max.}$ 3060w, 2300w, 2280w, 1600w, 1590w, 1575w, 1480m, 1450s, 1439m, 1432m, 1230s, 1219s, 1181m, 1162m, 1132s, 1115s, 1100s, 1087s, 1030w, 1005w, 855m, 760s, 751m, 705m, 690m, and 672w cm^{-1}. The ^{19}F n.m.r. spectrum (CH_2Cl_2) showed an A_3B_3 system centred at 48·7 p.p.m. [J_{FF} 19·0 Hz, J_{PF} 8·0 Hz].

We thank the S.R.C. for a research studentship (J. C.) and the U.S.A.F. Office of Scientific Research through its European Office for support.

[2/1572 *Received*, 4*th July*, 1972]