Oxidative–Elimination Reactions of Zerovalent Iron and Ruthenium Complexes

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Ultraviolet irradiation of a solution of *trans*-$(Et_3P)_2Fe(CO)_3$ in liquid sulphur dioxide gives *trans*-$(Et_3P)_2Fe(CO)_2$-(SO_2), which reacts with hydrogen iodide to form *cis*-$(CO)_2$-*trans*-$(Et_3P)_2FeI_2$. Treatment of *trans*-$(PhPMe_2)_2$-$Fe(CO)_3$ with iodine or hydrogen iodide affords *cis*-$(CO)_2$-*trans*-$(PhPMe_2)_2FeI_2$. *trans*-$(Ph_2PMe)_2Ru(CO)_3$ and iodine react to give *cis*-$(CO)_2$-*trans*-$(Ph_2PMe)_2RuI_2$, whereas, a mixture of isomers of $(CO)_2[EtC(CH_2O)_3P]_2$-RuI_2 is obtained from *trans*-$[EtC(CH_2O)_3P]_2Ru(CO)_3$ and iodine. Trifluoroacetic acid reacts with *trans*-$[(MeO)_3P]_2Ru(CO)_3$ to form *cis*-$(CO)_2$-*trans*-$[(MeO)_3P]_2Ru(O_2CCF_3)_2$. Treatment of trifluoroiodomethane with *trans*-$[EtC(CH_2O)_3P]_2Ru(CO)_3$ gives *cis*-$(CO)_2$-*trans*-$[EtC(CH_2O)_3P]_2Ru(CF_3)I$, whereas, *trans*-$(PhPMe_2)_2$-$Fe(CO)_3$ gives an isomeric mixture $(CO)_2(PhPMe_2)_2Fe(CF_3)I$. *trans*-$L_2Ru(CO)_3$ (L = Ph_2PMe, or $PhPMe_2$) react with methylene chloride to give the respective dichlorides.

IN GENERAL,[1] zerovalent iron, ruthenium, and osmium complexes readily undergo oxidative-addition or -elimination reactions (d^8 to d^6) on treatment with electrophilic reagents. We have examined a number of oxidative-elimination reactions of complexes of the type *trans*-$L_2M(CO)_3$ [L = phosphine, phosphite; M = Fe, Ru], and herein report our observations.

The ability of the π-acceptor sulphur dioxide to co-ordinate to transition metals (molybdenum,[2] tungsten,[2] manganese,[3] rhodium,[4] iridium,[5] palladium,[6] and platinum [6]) has been widely recognised, and in view of the weak electrophilic nature of sulphur dioxide the formation of many of these complexes may formally be pictured as oxidative-addition or -elimination reactions. The complexes *trans*-$L_2M(CO)_3$ [L = phosphine; M = Fe or Ru] [7] undergo a very slow thermal reaction with sulphur dioxide; however, u.v. irradiation of a solution of *trans*-$(Et_3P)_2Fe(CO)_3$ in liquid sulphur dioxide led to rapid reaction and the formation of a yellow air-stable crystalline complex (I), characterised as $(Et_3P)_2Fe(CO)_2(SO_2)$ by elemental analysis [a mass spectrum with peaks at m/e 412 (P), 356 ($P - 2CO$), 348 ($P - SO_2$), 320 ($P - CO - SO_2$) and 292 ($P - 2CO - SO_2$)], and the presence of two equally intense terminal carbonyl bands in the i.r. region. The presence in the i.r. region of bands compatible [2,5,8] with sulphur dioxide co-ordinated through the sulphur atom, suggests a similar mode of bonding as has been established by *X*-ray crystallographic studies for sulphur dioxide in $(Ph_3P)Ir(CO)Cl(SO_2)$ [9] and $[RuCl(SO_2)(NH_3)_4]Cl$.[8] The ^1H n.m.r. spectrum showed two multiplets, and double-irradiation of the high field CH_3 resonance caused the collapse of the low field CH_2P resonance to an apparent triplet (J_{HP} 6·5 c./sec.), indicating [10,11] substantial ^{31}P–^{31}P coupling and a relative *trans*-configuration for the triethylphosphine ligands. Thus, the sulphur dioxide complex (I) probably has a trigonal-bipyramidal structure as depicted. The present evidence does not allow a decision as to the planarity of the $FeSO_2$ group.

It has been shown that the complexes $(CO)_2(Ph_3P)$-RuX_2 [12] and $(CO)_2(Ph_3P)_2OsX_2$ [13] (X = halogen) are formed on treatment of the corresponding zerovalent ruthenium and osmium complexes with halogen; whereas, there are conflicting reports with regard to the

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

related reactions of the iron complex *trans*-$(Ph_3P)_2Fe(CO)_3$, which is reported[14] to lose triphenylphosphine on reaction with bromine, and to form $(CO)_2(Ph_3P)_2FeI_5$ with iodine.[15]

A hexane solution of *trans*-tricarbonylbis(dimethylphenylphosphine)iron rapidly reacts with iodine to form a brown crystalline complex (II) (see Table). The stereochemistry is defined as depicted, *i.e.* *trans*-phosphine ligands, by the presence of two terminal carbonyl bands in the i.r. region, and by the ^1H n.m.r. CH_3 resonance, which appears as an apparent triplet. The same iron di-iodide (II), with identical stereochemistry, was obtained by treating *trans*-$(Me_2PhP)_2$-$Fe(CO)_3$ with anhydrous hydrogen iodide.

Therefore, in this case, the reaction of iron parallels those of ruthenium and osmium, and the reaction with iodine probably involves nucleophilic attack by the Fe(0) complex on iodine to form an octahedral cationic complex $[(Me_2PhP)_2Fe(CO)_3I]^+I^-$, which loses carbon monoxide to form the di-iodide (II). Hydrogen iodide probably reacts to form $[(Me_2PhP)_2Fe(CO)_3H]^+I^-$, from which carbon monoxide *cis* to FeH is displaced by iodide anion, to form the neutral complex $(Me_2PhP)_2Fe(CO)_2HI$. Further reaction with hydrogen iodide leads to the formation of hydrogen and the di-iodide (II). In both the reaction with iodine and hydrogen iodide the relative *trans*-configuration of the phospine ligands is retained.

The sulphur dioxide complex (I) also reacts with anhydrous hydrogen iodide, to form $(CO)_2(Et_3P)_2FeI_2$; the phosphines retain a relative *trans*-configuration. A similar reaction path involving the initial formation of the cationic hydride $[(Et_3P)_2Fe(CO)_2SO_2H]^+I^-$ followed by loss of sulphur dioxide, may be involved.

Although the stereochemistry of the di-iodide (II) is clearly defined, it is not clear whether this isomer is the kinetically or thermodynamically controlled product. This consideration equally applied to the related ruthenium and osmium systems, where even the stereochemistry of the products are not firmly established.[16,17] These considerations led us to examine the reaction of iodine with *trans*-$L_2Ru(CO)_3$ [L = $MePh_2P$, or $EtC(CH_2O)_3P$], of trifluoroacetic acid with *trans*-$[EtC(CH_2O)_3P]_2Ru(CO)_3$, and of trifluoroiodomethane with *trans*-$[EtC(CH_2O)_3P]_2Ru(CO)_3$ and *trans*-$(Me_2PhP)_2Fe(CO)_3$.

trans-Tricarbonylbis(methyldiphenylphosphine)-ruthenium reacts rapidly with a hexane solution of iodine to form (III) (see Table). The stereochemistry was defined by the presence of two terminal carbonyl bands in the i.r. spectrum, and the appearance in the ^1H n.m.r. spectrum of the CH_3P resonance as an apparent triplet, *i.e.* *trans*-phosphine ligands. Careful examination of the reaction mixture provided no evidence for other isomeric products. In contrast, the analogous reaction of *trans*-$[EtC(CH_2O)_3P]_2Ru(CO)_3$ with iodine gave an inseparable isomeric mixture of (IVa) and (IVb). The ^1H n.m.r. spectrum of the mixture showed two apparent triplet resonances corresponding to the CH_2OP resonances of two isomeric complexes both with phosphite ligands in a relative *trans*-configuration. The i.r. spectrum showed three bands suggesting the presence of (IVa) (two bands) with *cis*-iodines, and (IVb) (one band) with *trans*-iodines.

Although on the present evidence it is not possible to distinguish between the various alternative reaction paths available for the formation of (IVa) and (IVb), the lack of stereoselectivity shown in the reaction of the phosphite complex underlines the inherent danger in always assuming a *cis*-addition of the electrophile iodine.

Treatment of *trans*-$[(MeO)_3P]_2Ru(CO)_3$ with trifluoroacetic acid led to the slow formation of the white crystalline complex (V) (see Table), characterised as a bis(trifluoroacetate)ruthenium complex. The i.r. spectrum showed a band at 1685s cm.$^{-1}$ assignable to $RuO{\cdot}CO{\cdot}CF_3$ and two terminal carbonyl bands, suggesting the illustrated stereochemistry, which was confirmed by the appearance of the CH_3OP ^1H n.m.r. resonance as an apparent triplet. The reaction of *trans*-$(Ph_3P)_2Ru(CO)_3$ with trifluoroacetic acid has been previously shown[12] to give $(CO)_2(Ph_3P)_2Ru(O{\cdot}CO{\cdot}CF_3)_2$ of undefined stereochemistry; and $(Ph_3P)_2Ir(CO)Cl$ with CF_3CO_2H is reported[18] to give the iridium hydride $(Ph_3P)_2Ir(CO)ClH(O{\cdot}CO{\cdot}CF_3)$. Thus the formation of (V) probably involves initial protonation to form $[(MeO)_3P]_2Ru(CO)_3H^+$, displacement of carbon monoxide by trifluoroacetate anion, followed by protolysis of the Ru–H bond.

The perfluoroiodoalkanes have been previously shown[19] to undergo oxidative-addition and -elimination reactions with a variety of low-valent transition-metal complexes including $Fe(CO)_5$. Trifluoroiodomethane reacted (80°) with *trans*-$[EtC(CH_2O)_3P]_2Ru(CO)_3$ to form the first σ-bonded trifluoromethylruthenium compound (VI) (see Table). The ^{19}F n.m.r. spectrum showed a singlet resonance at 0·07 p.p.m. strongly shifted to low field, and corresponding to a CF_3Ru group. The i.r. spectrum showed the presence of two terminal carbonyl bands suggesting the illustrated stereochemistry with *trans*-phosphite ligands. This was confirmed by the appearance of the CH_2OP ^1H n.m.r. resonance as an apparent triplet.

The stereoselective formation of (VI) is probably closely related mechanistically to the iodine reaction, and may involve nucleophilic attack on the 'positive' iodine of trifluoroiodomethane to form a trifluoromethyl anion, which rapidly attacks the cationic complex $\{[EtC(CH_2O)_3P]_2Ru(CO)_3I\}^+$, with displacement of carbon monoxide.

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[16] See, however, unpublished work quoted as a footnote in ref. 13.

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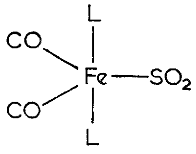
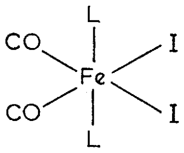
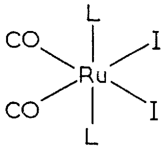


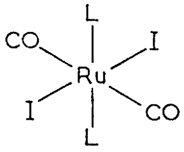
(I) L = Et_3P



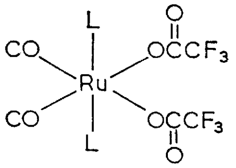
(II) L = Me_2PhP



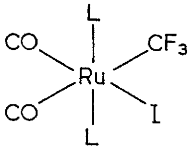
(III) L = $MePh_2P$
(IVa) L = $EtC(CH_2O)_3P$



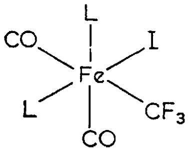
(IVb) L = $EtC(CH_2O)_3P$



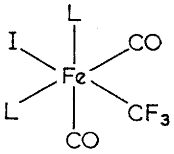
(V) L = $(MeO)_3P$



(VI) L = $EtC(CH_2O)_3P$



(VIIa) L = Me_2PhP



(VIIb) L = Me_2PhP

The analogous reaction of trifluoroiodomethane with *trans*-$(Me_2PhP)_2Fe(CO)_3$ occurred more rapidly to give the crystalline complex (VII) (see Table). The i.r. spectrum showed the presence of two terminal carbonyl bands indicating that (VII) has *cis*-carbonyl groups; however, the ^1H n.m.r. spectrum showed the presence of two isomeric complexes (1 : 5) both with *cis*-phosphine ligands, *i.e.* both CH_3P resonances appeared as doublets. The ^{19}F n.m.r. spectrum showed only one resonance, a triplet (J_{PF} 13·0 c./sec.) centred at 3·19 p.p.m., which together with the other evidence, indicates that the isomers are (VIIa) and (VIIb).

This structural assignment depends on the assumption that ^{31}P–^{19}F coupling occurs when Me_2PhP and CF_3 have a relative *cis*-configuration, whereas, in compound (VI) there is no evidence of such coupling (>0·5 c./sec.). Therefore, (VIIa) and (VIIb) are only tentative structures. Nevertheless, these results serve to emphasise the stereochemical dissimilarity between analogous reactions.

When *trans*-$L_2Ru(CO)_3$ (L = Ph_2PMe, or $PhPMe_2$) is dissolved in methylene chloride a relatively rapid reaction leads to the formation of the dichlorides (IX) and (X), where the phosphines retain their relative *trans*-configuration. This reaction may involve the generation of the carbene CH_2. A possibly related reaction occurs between *trans*-$[(MeO)_3P]_2Ru(CO)_3$ and trichlorosilane, when the dichloride (VIII) was formed, and not a Ru–Si compound.

EXPERIMENTAL

Fluorine-19 and ^1H n.m.r. spectra were measured at 94·1 Mc./sec. and 100 Mc./sec. respectively on a Varian HA 100 spectrometer. (Chemical shifts are measured relative to CCl_3F (0·0 p.p.m.) and Me_4Si (τ 10·00).) Mass-spectral determinations were made on a AEI MS 902 spectrometer. All reactions were conducted in a nitrogen atmosphere.

Reaction of trans-*Tricarbonylbis(triethylphosphine)iron with Sulphur Dioxide.*—*trans*-Tricarbonylbis(triethylphosphine)iron (0·10 g., 0·27 mmole) was introduced into a Pyrex tube (100 ml.), and an excess of sulphur dioxide (10 ml.) was condensed (−196°) into the tube. The tube and contents were allowed to warm to room temperature and irradiated (250 w Hanovia u.v. lamp) for 18 hr. to give a deep red solution. Volatile products were removed under reduced pressure and the hexane-soluble residue was recrystallised (−45°) three times from hexane to give (I) as yellow crystals (0·053 g., 48%), $\nu_{max.}$ (cyclohexane) 1966vs, 1907vs (CO), 1215s, 1073vs, and 1031s cm.$^{-1}$ (SO_2) The mass-spectrum showed peaks at m/e 412 (P, 1%), 356 (P − 2CO, 1%), 348 (P − SO_2), 320 (P − CO − SO_2, 17%), and 292 (P − 2CO − SO_2, 100%). ^1H N.m.r. resonances (in C_6F_6) occurred at τ 7·93 [12H, m, CH_3CH_2P] and 8·72 [18H, m, CH_3CH_2P]. Double irradiation of the high-field signal caused the low-field signal to collapse to a triplet (J_{HP} 6·5 c./sec.).

Reaction of trans-*Tricarbonylbis(dimethylphenylphosphine)-iron with Iodine.*—Treatment of a solution of *trans*-tricarbonylbis(dimethylphenylphosphine)iron (0·05 g., 0·12 mmole) in hexane (5 ml.) with iodine (0·031 g., 0·12 mmole) in hexane (10 ml.) led to an immediate reaction with

Iron and ruthenium complexes

		Found (%							Required (%						
Compound	M.p.°	C	H	Cl	F	P	I	M *	C	H	Cl	F	P	I	M
(I) $(CO)_2(Et_3P)_2FeSO_2$ [a]	80	40·7	7·2			15·1		412	40·8	7·3			15·1		412
(II) $(CO)_2(PhPMe_2)_2FeI_2$	117—119	33·8	3·2			9·9	39·4		33·7	3·4			9·7	39·6	
(III) $(CO)_2(Ph_2PMe)_2RuI_2$	220—224	42·1	3·2			7·3	31·4		41·8	3·2			7·7	31·2	
(IV) $(CO)_2[EtC(CH_2O)_3P]_2RuI_2$	150 (decomp.)	23·2	3·2			8·0	35·0		22·9	2·9			8·4	34·6	
(V) $(CO)_2[MeO)_3P]_2Ru(O_2CCF_3)_2$	125—128	25·0	3·0		18·1	9·9			24·8	2·9		18·1	9·8		
(VI) $(CO)_2[EtC(CH_2O)_3P]_2Ru(CF_3)I$	260 (decomp.)	23·4	3·2		8·7			677	23·1	3·3		8·4			677
(VII) $(CO)_2(PhPMe_2)_2Fe(CF_3)I$	95—97	39·1	3·8		9·8		21·6	584	39·1	3·8		9·8		21·8	584
(VIII) $(CO)_2[MeO)_3P]_2RuCl_2$	125—127	20·3	3·6			13·1		476	20·2	3·8			13·0		476
(IX) $(CO)_2(Ph_2PMe)_2RuCl_2$	220—224	54·0	4·4	11·5					53·6	4·2	11·3				
(X) $(CO)_2(PhPMe_2)_2RuCl_2$ [b]	129—131	42·8	4·4	14·1		12·0			42·8	4·4	14·1		12·3		

* Mass-spectrometric determination.

[a] Found: S, 7·9%. Reqd.: S, 7·7%. [b] Lit.[17] m.p. 129—135°.

precipitation of a brown crystalline solid which, on crystallisation (−78°) from methylene chloride–hexane, gave (II) (0·025 g., 33%), $\nu_{max.}$ (cyclohexane) 2025vs and 1973vs cm.$^{-1}$ (CO). The ^{1}H n.m.r. spectrum (in $CDCl_3$) showed resonances at τ 2·55 (m, 10H, C_6H_5P) and 7·62 (t, 12H, CH_3P, J_{HP} 3·5 c./sec.).

Reaction of trans-*Tricarbonylbis(dimethylphenylphosphine)-iron with Hydrogen Iodide*.—Hydrogen iodide (1·55 mmole) was condensed (−196°) into a tube containing *trans*-tricarbonylbis(dimethylphenylphosphine)iron (0·20 g., 0·48 mmole) in benzene (15 ml.). When the mixture was warmed to room temperature an immediate reaction occurred. Removal of solvent under reduced pressure and recrystallisation of the residue from methylene chloride–hexane gave (II) (0·1 g., 33%) identical (i.r. and ^{1}H n.m.r.) with that obtained in the iodine reaction.

Reaction of $(Et_3P)_2Fe(CO)_2(SO_2)$ *with Hydrogen Iodide*.—Hydrogen iodide (0·2 g., 1·55 mmole) was condensed (−196°) into a tube containing $(Et_3P)_2Fe(CO)_2(SO_2)$ (0·10 g., 0·24 mmole) dissolved in hexane (10 ml.). After ½ hr. at room temperature the solvent was removed under reduced pressure, and the residue recrystallised from hexane to give brown crystals of *dicarbonylbis(triethylphosphine)irondi-iodide* (0·05 g., 35%), m.p. 80° (Found: C, 27·6; H, 5·0. $C_{14}H_{30}FeI_2O_2P_2$: C, 27·9; H, 5·0), $\nu_{max.}$ (hexane) 2007vs and 1958vs cm.$^{-1}$. The ^{1}H n.m.r. spectrum (C_6F_6) showed peaks at τ 7·61 (m, 12H, CH_3CH_2P) and 8·69 (m, 18H, CH_3CH_2P). Double irradiation of the high-field band caused the low-field band to collapse to a triplet (J_{HP} 13·0 c./sec.).

Reaction of trans-*Tricarbonylbis(methyldiphenylphosphine)-ruthenium with Iodine*.—Reaction of *trans*-tricarbonylbis(methyldiphenylphosphine)ruthenium (0·025 g., 0·05 mmole) in methylene chloride (0·25 ml.)–hexane (5 ml.) with iodine (0·011 g., 0·05 mmole) in hexane (5 ml.) gave an immediate precipitate of a yellow crystalline product which, on recrystallisation from methylene chloride–hexane, gave (III) (0·01 g., 28%), $\nu_{max.}$ (cyclohexane) 2055vs and 1995vs cm.$^{-1}$ (CO). The ^{1}H n.m.r. spectrum (in $CDCl_3$) showed resonances at τ 2·50 (m, 20H, C_6H_5P) and 7·26 (t, 6H, CH_3P, J_{HP} 4·0 c./sec.).

Reaction of trans-*Tricarbonylbis(4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2,2,2]octane)ruthenium with Iodine*.—A solution of iodine (0·025 g., 0·1 mmole) in hexane (10 ml.) was added dropwise to *trans*-$[EtC(CH_2O)_3P]_2Ru(CO)_3$ (0·05 g., 0·1 mmole) in methylene chloride (0·25 ml.) and hexane (5 ml.). The resultant yellow, crystalline precipitate was recrystallised from methylene chloride–hexane to give (IV) (0·04 g., 50%), $\nu_{max.}$ (CH_2Cl_2) 2126m, 2108s, and 2056s cm.$^{-1}$ (CO). The ^{1}H n.m.r. spectrum (in $CDCl_3$) showed resonances at τ 5·43 (t, 12H, CH_2OP, J_{HP} 2·5 c./sec.), 5·71 (t, 12H, J_{HP} 2·5 c./sec.), 8·7 (q, 4H, CCH_2CH_3), and 9·2 (t, 6H, CCH_2CH_3, J_{HP} 7·0 c./sec.).

Reaction of trans-*Tricarbonylbis(trimethylphosphite)-ruthenium with Trifluoroacetic Acid*.—*trans*-Tricarbonylbis(trimethylphosphite)ruthenium (0·075 g., 0·17 mmole) was dissolved in anhydrous trifluoroacetic acid (5 ml.). After 7 hr. at room temperature the excess of trifluoroacetic acid was removed under reduced pressure; the residue was dissolved in methylene chloride and chromatographed on a Florisil packed column (1 × 15 cm.). The product was eluted with methylene chloride and recrystallised (−78°) from methylene chloride–hexane to give (V) (0·04 g., 37%), $\nu_{max.}$ ($CHCl_3$) 2091vs, 2021vs, 1685s (acyl), 1188m, 1139m, and 1022s cm.$^{-1}$. ^{1}H and ^{19}F n.m.r. resonances (in $CDCl_3$) occurred respectively at τ 6·29 (t, 18H, CH_3OP, J_{HP} 5·5 c./sec.) and 74·8 (s, 6F).

Reaction of trans-*Tricarbonylbis(4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2,2,2]octane)ruthenium with Trifluoroiodomethane*.—An excess of trifluoroiodomethane (2 mmoles) was condensed (−196°) into a tube containing *trans*-$[EtC(CH_2O)_3P]_2Ru(CO)_3$ dissolved in benzene (25 ml.). After 21 days at 80°, the pale yellow crystals which had been deposited in the tube, were recrystallised from methylene chloride–hexane to give (VI) (0·02 g., 35%), $\nu_{max.}$ (CH_2Cl_2) 2085vs, 2033vs, 1183w, 1150m, 1028s, 950m, 942m, 848m, 812m, and 637m cm.$^{-1}$. ^{1}H and ^{19}F n.m.r. resonances (in $CDCl_3$) occurred respectively at τ 5·70 (t, 12H, CH_2OP, J_{HP} 3·0 c./sec.), 8·7 (q, 4H, CCH_2CH_3) and 9·2 (t, 6H, CCH_2CH_3) and 0·07 (s, 3F).

Reaction of trans-*Tricarbonylbis(dimethylphenylphosphine)-iron with Trifluoroiodomethane*.—*trans*-Tricarbonylbis(dimethylphenylphosphine)iron (0·10 g., 0·24 mmole) dissolved in hexane (20 ml.) was introduced into a Carius tube (100 ml.). Trifluoroiodomethane (2 mmoles) was condensed (−196°) into the tube. When the mixture was warmed to room temperature an immediate reaction occurred with the formation of a brown crystalline precipitate, which was recrystallised from methylene chloride–hexane to give (VII) (0·03 g., 22%), $\nu_{max.}$ (CH_2Cl_2) 2036vs and 1982vs. ^{1}H and ^{19}F n.m.r. resonances (in $CDCl_3$) occurred respectively at 7·70 (d, 12H, CH_3P, J_{HP} 6·0 c./sec.) and 7·96 (d, 12H, CH_3P, J_{PP} 6·0 c./sec.) and 3·19 (t, 3F, CF_3Fe, J_{HP} 13·0 c./sec.).

Reaction of trans-*Tricarbonylbis(trimethylphosphite)-ruthenium with Silicochloroform*.—*trans*-Tricarbonylbis(trimethylphosphite)ruthenium (0·05 g., 0·12 mmole) in hexane (10 ml.) and trichlorosilane (1 mmole) were sealed together in a Carius tube (50 ml.). After 7 hr. at room temperature the white crystalline hexane-insoluble product was collected and recrystallised from methylene chloride–hexane to give VIII) (0·02 g., 37%), $\nu_{max.}$ (cyclohexane) 2079vs and 2017vs cm.$^{-1}$. The mass-spectrum showed peaks at *m*/*e* 477 (*P*), 449 (*P* − CO) and 421 (*P* − 2CO). The ^{1}H n.m.r. spectrum ($CDCl_3$) showed a resonance at τ 6·06 (t, 18H, CH_3OP, J_{HP} 5·8 c./sec.).

Reaction of trans-*Tricarbonylbis(methyldiphenylphosphine)-ruthenium with Methylene Chloride*.—A solution of *trans*-tricarbonylbis(methyldiphenylphosphine)ruthenium (0·10 g., 0·17 mmole) in methylene chloride (10 ml.) was heated under reflux (½ hr.). Addition of hexane (10 ml.) resulted in the crystallisation of (IX) (0·053 g., 51%), $\nu_{max.}$ ($CHCl_3$) 2057vs and 1993vs cm.$^{-1}$. The ^{1}H n.m.r. spectrum (in $CDCl_3$) showed resonances at τ 2·50 (m, 20H, C_6H_5P) and 7·75 (t, 6H, CH_3P, J_{HP} 5·0 c./sec.).

Reaction of trans-*Tricarbonylbis(dimethylphenylphosphine)-ruthenium with Methylene Chloride*.—*trans*-Tricarbonylbis-(dimethylphenylphosphine)ruthenium (0·07 g., 0·15 mmole) reacted immediately with methylene chloride to give white crystalline (X) (0·102 g., 100%), $\nu_{max.}$ ($CHCl_3$) 2050vs and 1986vs cm.$^{-1}$. ^{1}H N.m.r. resonances (in $CDCl_3$) appeared at τ 2·50 (m, 10H, C_6H_5P) and 8·31 (t, 12H, CH_3P, J_{HP} 3·0 c./sec.).

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