

Some Oxidative Elimination Reactions of Zerovalent Osmium Complexes

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Tetrafluoroethylene, trifluoroethylene, and chlorotrifluoroethylene react on irradiation with *trans*-Os(CO)₃[(MeO)₃P]₂ to afford the complexes Os[fluoro-olefin](CO)₂[(MeO)₃P]₂, where the phosphite ligands have a relative *cis*-configuration. In contrast, *trans*-Os(CO)₃(PhPMe₂)₂ reacts with trifluoroethylene to give Os[C₂F₃H](CO)₂(PhPMe₂)₂ where the phosphine groups have a relative *trans*-configuration. The corresponding reactions with hexafluoroacetone gives OsC(CF₃)₂O(CO)₂(PhPMe₂)₂. Reaction of Os(CF₃C₂CF₃)(CO)₂[(MeO)₃P]₂ with HCl gives OsCl[C(CF₃) = C(CF₃)H](CO)₂[(MeO)₃P]₂. The reaction of iodine with *trans*-Os(CO)₃(PhPMe₂)₂ is described.

In previous papers the oxidative-elimination reactions of electronegatively substituted unsaturated systems such as hexafluoroacetone,^{1,2} fluoro-olefins,^{1,2} and hexafluorobut-2-yne³ with iron(0) and ruthenium(0) carbonyl complexes have been studied. Since significant differences were observed in the stereochemistry and nature of the products from Fe⁰ and Ru⁰ complexes it was important to carry out comparative studies with analogous osmium compounds. The synthesis of tricarbonylcyclo-octatetraene osmium and the observation that the hydrocarbon could be readily displaced by trimethyl phosphite provided a synthetic route to the required osmium(0) complexes *trans*-Os(CO)₃L₂ [L = (MeO)₃P, or PhPMe₂]. Previously,⁵ only *trans*-tricarbonylbis(triphenylphosphine)osmium had been prepared, and this system clearly has limitations with regard to the determination of the stereochemistry of the products of oxidative reactions. In this paper we describe the reaction of tetrafluoroethylene, trifluoroethylene, chlorotrifluoroethylene, hexafluoroacetone and iodine with *trans*-Os(CO)₃L₂ [L = (MeO)₃P, or PhPMe₂]. The products of these oxidative reactions were characterised by elemental analysis, mass, i.r. and ¹H and ¹⁹F n.m.r. spectroscopy.

Tetrafluoroethylene displaces carbon monoxide from *trans*-tricarbonylbis(trimethyl phosphite)osmium on u.v. irradiation of a hexane solution of the reactants. The product of the reaction, a white crystalline compound, was identified as (I) tetrafluoroethylene-*trans*-dicarbonyl-*cis*-bis(trimethyl phosphite)osmium. The i.r. spectrum of (I) showed two closely spaced terminal carbonyl bands indicating *trans*-carbonyls in an octahedral complex; in agreement the ¹H n.m.r. spectrum showed an apparent doublet centred at τ 6.30 assignable⁶ to the CH₃OP protons of trimethyl phosphite ligands in identical environments with a relative *cis*-configuration, i.e. the stereochemistry found^{1,2} for the corresponding iron and ruthenium systems.

The ¹⁹F n.m.r. spectrum showed a temperature invariant XX'AA'X''X'' system centred at 117.5 p.p.m., which, as previously discussed² for the analogous ruthenium system, suggests a rigid 3-ring structure, in which the π^* -antibonding level of the olefin is populated, resulting in an apparent change in the hybridization of the olefin carbon atoms from *sp*² to *sp*³.

Attempts to react tetrafluoroethylene with *trans*-tricarbonylbis(dimethylphenylphosphine)osmium, prepared by reacting C₈H₈Os(CO)₃ with PhPMe₂ were un-

¹ M. Cooke and M. Green, *J. Chem. Soc. (A)*, 1969, 651.

² R. Burt, M. Cooke, and M. Green, *J. Chem. Soc. (A)*, 1970, 2975.

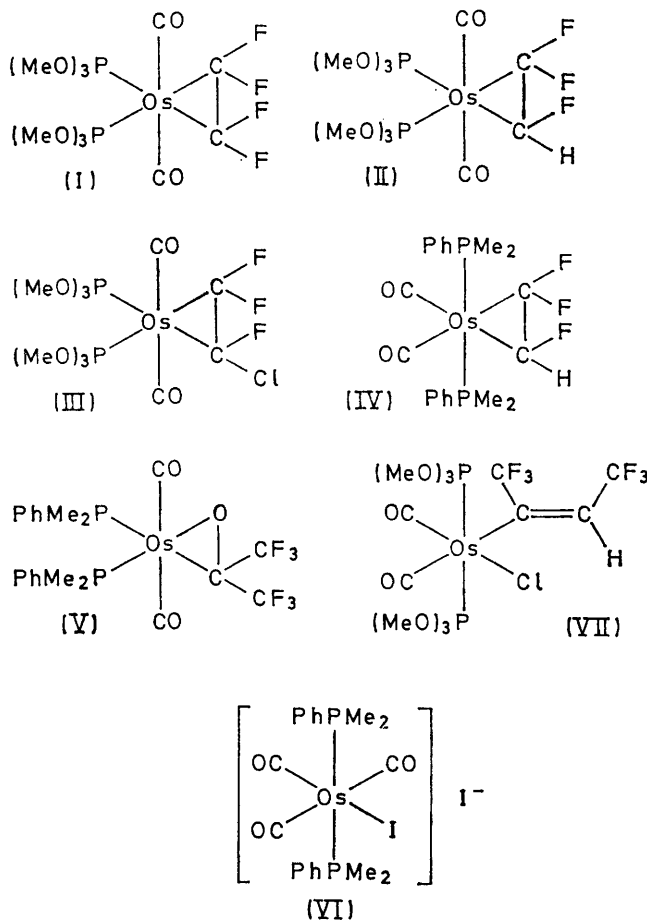
³ R. Burt, M. Cooke, and M. Green, *J. Chem. Soc. (A)*, 1970, 2981.

⁴ M. I. Bruce, M. Cooke, M. Green, and D. J. Westlake, *J. Chem. Soc. (A)*, 1969, 987.

⁵ J. P. Collman and W. R. Roper, *J. Amer. Chem. Soc.*, 1966, **88**, 3504.

⁶ J. M. Jenkins and B. L. Shaw, *J. Chem. Soc. (A)*, 1966, 770.

successful, however, trifluoroethylene reacted with both *trans*-Os(CO)₃[(MeO)₃P]₂ and *trans*-Os(CO)₃(PhPMe₂)₂ to form respectively the stable white crystalline complexes (II) trifluoroethylene-*trans*-dicarbonyl-*cis*-bis(trimethyl phosphite)osmium and (IV) trifluoroethylene-*cis*-dicarbonyl-*trans*-bis(dimethylphenylphosphine)osmium; the i.r. spectra of (II) and (IV) showing respectively one and two terminal carbonyl bands. The ¹H n.m.r. spectrum of (II) showed two doublet resonances assignable to trimethyl phosphite ligands *cis* and *trans* to the CHF group of trifluoroethylene and *cis* to each other.



The spectrum of (IV) showed two overlapping apparent triplets corresponding to the CH₃P resonances of PhPMe₂ ligands in different environments as required by structure (IV).

The ¹H n.m.r. spectra of (II) and (IV) also showed resonances due to CHF protons; values for *J*_{gem-HF} of 66.0 and 64.0 Hz respectively being observed. As has been previously discussed² values of this magnitude indicate an apparent change in the hybridization of the olefinic carbon atoms towards *sp*³; however, the stereochemistry of (II) and (IV) is very different, the phosphines adopting a relative *cis*-configuration and the

⁷ A. Greco, S. K. Shakshooki, M. Green, and F. G. A. Stone, *Chem. Comm.*, 1970, 1374.

⁸ B. Clarke, M. Green, R. B. L. Osborn, and F. G. A. Stone, *J. Chem. Soc. (A)*, 1968, 168.

phosphines remaining in a *trans*-configuration on reaction with trifluoroethylene. Therefore, it is surprising that a greater difference in *J*_{gem-HF} for the two complexes is not observed.

For the reaction with trifluoroethylene there was no evidence for the formation of hexafluoro-osmiumcyclopentanes indicating a parallel with the corresponding ruthenium chemistry. It would appear, therefore, that on ascending a triad there is an increased tendency for 5-ring compounds to be formed. This same trend is also discernible⁷⁻¹⁰ in the Ni, Pd, Pt triad.

On irradiation chlorotrifluoroethylene reacts with *trans*-tricarbonylbis(trimethyl phosphite)osmium to afford (III) chlorotrifluoroethylene-*trans*-dicarbonyl-*cis*-bis(trimethyl phosphite)osmium, a stable white crystalline complex the stereochemistry of which was established by the appearance in the i.r. spectrum of two closely spaced terminal carbonyl bands, and by the presence in the ¹H n.m.r. spectrum of two doublet resonances corresponding to mutually *cis*-trimethyl phosphite ligands *cis* and *trans* to the CFCI group of the co-ordinated chlorotrifluoroethylene.

A first-order ¹⁹F n.m.r. spectrum was obtained for (III) and in the Table the derived coupling constants

¹⁹F Chemical shifts (p.p.m.) and coupling constants (Hz) for co-ordinated and free chlorotrifluoroethylene

Compound	Chemical shifts		
	δ_1	δ_2	δ_3
Chlorotrifluoroethylene	120.5	104.5	144.5
(CO) ₂ [(MeO) ₃ P] ₂ Os[C ₂ F ₃ Cl]	99.8	115.0	123.0
(CO) ₂ [(MeO) ₃ P] ₂ Ru[C ₂ F ₃ Cl]	95.7	104.8	122.0
Compound	Coupling constants		
	<i>J</i> _{F(1)F(2)}	<i>J</i> _{F(1)F(3)}	<i>J</i> _{F(2)F(3)}
Chlorotrifluoroethylene	78.0	115.0	58.0
(CO) ₂ [(MeO) ₃ P] ₂ Os[C ₂ F ₃ Cl]	178.0	35.0	8.0
(CO) ₂ [(MeO) ₃ P] ₂ Ru[C ₂ F ₃ Cl]	163.0	44.0	7.5

are compared with those found for the ruthenium analogue and unco-ordinated chlorotrifluoroethylene. There are clearly large changes in the *J* values on co-ordination, and it is interesting that these are greater for the osmium complex indicating a more substantial change in the geometry of C₂F₃Cl co-ordinated onto osmium compared with ruthenium. This suggests that even with what might be thought to be an extreme bonding situation, *i.e.* two σ -bonded structure, there are still gradations in bond type dependent on the nature of the metal.

The osmium complex (III) is stable and showed no tendency to undergo a 'vinyl rearrangement.'

Hexafluoroacetone has been found^{7,8} to react with low valent group VIII complexes to give either 3-ring

MC(CF₃)₂O, or 5-ring MC(CF₃)₂OC(CF₃)₂O, complexes. In the case of the Fe, Ru, Os triad we have previously^{1,2}

⁹ M. Green, A. J. Rest, R. B. L. Osborn, and F. G. A. Stone, *J. Chem. Soc. (A)*, 1968, 2525.

¹⁰ C. S. Cundy, M. Green, and F. G. A. Stone, *J. Chem. Soc. (A)*, 1970, 1647.

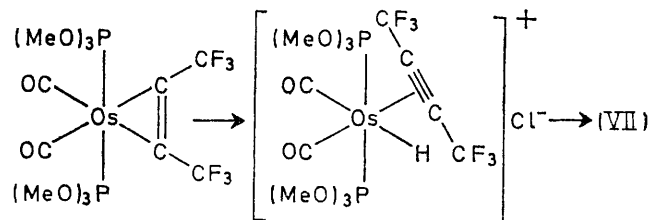
shown that *trans*-Ru(CO)₃L₂ [L = (MeO)₃P or PhPMe₂] reacts with (CF₃)₂C=O to form only the 3-ring complexes

RuC(CF₃)₂O(CO)₂L₂, where the ligands L adopt a *cis*-configuration in the case of the phosphite and a *trans*-configuration with the phosphine. Treatment of *trans*-Os(CO)₃[(MeO)₃P]₂ with excess hexafluoroacetone in hexane led to a rapid thermal reaction to give (V) hexafluoroacetone-*trans*-dicarbonyl-*cis*-bis-(dimethylphenylphosphine)osmium, a white stable crystalline compound; there being no evidence for the formation of a 5-ring complex. The presence in the i.r. spectrum of (V) of a single terminal carbonyl peak, and the appearance in the ¹H n.m.r. spectrum of the CH₃P resonance as overlapping doublets established for (V) the illustrated stereochemistry. Thus, the hexafluoroacetone osmium complex has a different stereochemistry from the analogous ruthenium system. This is also reflected in the ¹⁹F n.m.r. spectrum of (V), which shows a doublet centred at 66.2 p.p.m. [unco-ordinated (CF₃)₂C=O, 77.2 p.p.m.]; the splitting arising due to coupling with the ³¹P nucleus of the phosphine *trans* to the C(CF₃)₂ group. The chemical shift of the ruthenium complex occurs at some 10 p.p.m. to higher field implying a shielding effect by the phosphines *cis* to the hexafluoroacetone.

Complexes of the type M(fluoro-olefin)(CO)₂L₂ (M = Fe, Ru, or Os, L = phosphine or phosphite) react with HX (X = Cl, Br, or I) to give inseparable mixtures of the complexes MX₂(CO)₂L₂ and MR_F(X)(CO)₂L₂ (R_F = fluoroethyl). However, hexafluorobut-2-yne-*cis*-dicarbonyl-*trans*-bis(trimethyl phosphite)osmium,³ prepared by reaction of the acetylene with *trans*-Os(CO)₃[(MeO)₃P]₂ reacts with hydrogen chloride in hexane to give only one product, a vinyl complex (VII). The i.r. spectrum of (VII) showed terminal carbonyl bands at 2063 and 2000 cm⁻¹ indicating that the carbonyl groups remain in a relative *cis*-configuration on ring-opening, and this is supported by the appearance in the ¹H n.m.r. spectrum of the CH₃OP resonance as an apparent triplet. In addition the ¹H spectrum showed a signal at τ 3.18 due to the vinylic proton CHCF₃. The ¹⁹F n.m.r. spectrum showed two signals of equal intensity at 54.6 and 57.7 p.p.m. due to CF₃ groups in different environments; the low-field signal which showed no ¹H-¹⁹F coupling being assigned to the CF₃ adjacent to the osmium. The presence of ¹⁹F-¹⁹F coupling of the order of 14.0 Hz established ¹¹ a relative *cis*-configuration for the two CF₃ groups. Thus the formal ring-opening reaction proceeds with the retention of the stereochemistry of both the phosphite ligands and the CF₃ groups.

It has been suggested ¹² that co-ordinated O₂ in PtO₂(PPh₃)₂ has dipolar character, due to population of π*-orbitals. If this argument is extended to acetylene complexes, then it is possible that the formation of (VII) involves direct protonation of the co-ordinated

hexafluorobut-2-yne. Alternatively, the initial formation of an osmium hydride may be involved, with subsequent hydrogen transfer within the co-ordination sphere; the character of the bonding between the metal and the acetylene changing from a two σ-bonded structure to a π-bonding system during the course of the reaction.



A previous interest ¹³ in the stereochemistry of the reaction $M(CO)_3L_2 \xrightarrow{I_2} MI_2(CO)_2L_2$ (M = Fe, or Ru, L = phosphine or phosphite) led us to examine the reaction of *trans*-Os(CO)₃(PhPMe₂)₂ with iodine. Reaction occurred immediately at room temperature in hexane to give the ionic crystalline complex (VI) [OsI(CO)₃(PhPMe₂)₂]⁺I⁻. The i.r. spectrum showed three terminal carbonyl bands at 2136, 2066, and 2042 cm⁻¹ as was previously reported ⁵ for the complexes [OsX(CO)₃(PPh₃)₂]⁺X⁻ (X = Br or I), but this does not define the stereochemistry of (VI). However, the ¹H n.m.r. spectrum of (VI) shows a single CH₃P resonance as an apparent triplet suggesting the illustrated stereochemistry with *trans*-phosphines, *i.e.* the oxidation reaction Os⁰ → Os^{II} proceeds with retention of the relative stereochemistry of the phosphine and carbon monoxide ligands. Whereas the complexes [OsX(CO)₃(PPh₃)₂]⁺X⁻ (X = Br, or I) decarbonylate on being heated,⁵ attempts to effect decarbonylation of (VI) were unsuccessful.

EXPERIMENTAL

¹H and ¹⁹F N.m.r. spectra were measured on a Varian Associates HA 100 spectrometer at 100 MHz and 94.1 MHz respectively; chemical shifts are relative to Me₄Si (τ 10.00) and CCl₃F (0.00 p.p.m.). I.r. spectra were recorded on a Perkin-Elmer 257 spectrophotometer. Mass spectra were measured on an AEI MS 902 spectrometer and counted using the ¹⁹²Os isotope peak. All reactions were carried out in a dry atmosphere of oxygen-free nitrogen.

Preparation of *trans*-Tricarbonylbis(dimethylphenylphosphine)osmium.—A solution of tricarbonylcyclo-octatetraene-osmium (0.03 g, 0.08 mmol) and dimethylphenylphosphine (0.05 g, 0.36 mmol) in methylcyclohexane (15 ml) was heated under reflux (1 h). Volatile material was removed *in vacuo* and the residue was crystallised from hexane (0°) to give pale yellow crystals of *trans*-tricarbonylbis(dimethylphenylphosphine)osmium (0.033 g, 80%), m.p. 83.5° [Found: C, 41.6; P, 11.2%; M (mass-spectrum), 552. C₁₉H₂₃P₂OsO₃ requires C, 41.4; P, 11.2%; M, 552], γ_{max} (cyclohexane) 1889s, 1252w, 1030w, br, 1010m, br, 940w, 899br, 850w, 740m, and 685w cm⁻¹; m/e 552 (P, 66%), 524 (P - CO, 31%), 414 (P - CO-2CH₃, 100%), 492 (P - 4CH₃, 80%).

¹³ R. Burt, M. Cooke, and M. Green, *J. Chem. Soc. (A)*, 1969, 2645.

¹¹ S. Ng and C. H. Sederholm, *J. Chem. Phys.*, 1964, 40, 2090.

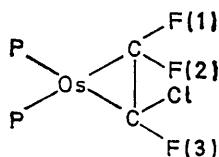
¹² R. Ugo, F. Conti, S. Cenini, R. Mason, and G. B. Robertson, *Chem. Comm.*, 1968, 1498.

and 468 ($P - 3CO$, 15%); τ ($CDCl_3$) 2.7 (m, 10H, C_6H_5P) and 7.92 (t, 12H, CH_3P , $|J|_{POCH}$ 8.0 Hz).

Reactions of trans-Tricarbonylbis(trimethyl phosphite)-osmium.—(a) *With Tetrafluoroethylene.*—An excess of tetrafluoroethylene (2.1 mmol) was condensed (-196°) into a Carius tube containing *trans*-tricarbonylbis(trimethyl phosphite)osmium (0.038 g, 0.073 mmol) in hexane (10 ml), and the solution was irradiated with u.v. light (250 W Hanovia 1 amp.) for 6 h. Volatile material was removed *in vacuo* and the residue was crystallised (0°) from hexane (2 ml) to give white needle crystals of (I) *tetrafluoroethylene-trans-dicarbonyl-cis-bis(trimethyl phosphite)osmium* (0.026 g, 62%), m.p. 128° [Found: C, 20.4; H, 3.4; P, 10.4%; M (mass spec.), 596. $C_{10}H_{18}F_4P_2OsO_8$ requires C, 20.2; H, 3.0; P, 10.4%; M , 596], ν_{max} (cyclohexane) 2015s, 2010sh, 1180w, 1088sh, 1056sh, 1045sh, 1031s, 823m, 795m, br, 756m, and 738m cm^{-1} ; m/e 596 (P , 49%), 577 ($P - F$, 7%), 568 ($P - CO$, 70%), 540 ($P - 2CO$, 42%), 496 ($P - C_2F_4$, 100%), and 468 ($P - C_2F_4 - CO$, 58%); τ ($CDCl_3$) 6.30 (d, 18H, CH_3OP , $|J|_{POCH}$ 12.3 Hz); the ^{19}F n.m.r. spectrum ($CDCl_3$) showed a resonance at 117.5 p.p.m. (m, 4F, $|J_{PF} + J_{PF}| = 51.5$ Hz).

(b) *With trifluoroethylene.* Ultraviolet irradiation (18 h) of a solution of *trans*-tricarbonylbis(trimethyl phosphite)-osmium (0.10 g, 0.19 mmol) and trifluoroethylene (2.5 mmol) in hexane (15 ml) gave on recrystallisation (-78°) from hexane white crystals of (II) *trifluoroethylene-trans-dicarbonyl-cis-bis(trimethyl phosphite)osmium* (0.032 g, 29%), m.p. $142-144^\circ$ [Found: C, 21.1; F, 9.9; P, 10.8%; M (mass spec.), 576. $C_{10}H_{18}F_3P_2OsO_8$ requires C, 20.8; F, 9.9; P, 10.8%; M , 576], ν_{max} ($CHCl_3$) 2052s cm^{-1} ; m/e 578 (P , 21%), 550 ($P - CO$, 30%), 522 ($P - 2CO$, 60%), and 496 ($P - C_2F_3H$, 80%); τ [$(CD_3)_2CO$] 4.30 (d of m, 1H, CHF , J_{gem-HF} 66.0 Hz), 6.25 (d, 9H, CH_3OP , J_{HF} 11.0 Hz), and 6.45 (d, 9H, CH_3OP , J_{HF} 10.0 Hz); the ^{19}F n.m.r. spectrum ($CDCl_3$) showed only complex multiplets at 101 and 205 p.p.m.

(c) *With chlorotrifluoroethylene.* An excess of chlorotrifluoroethylene (1.1 mmol) was condensed (-196°) into a Carius tube containing *trans*-tricarbonylbis(trimethyl phosphite)osmium (0.05 g, 0.10 mmol) in hexane (15 ml), and irradiated for 18 h. Removal of the solvent followed by crystallisation (0°) of the residue from hexane gave white crystals of (III) *chlorotrifluoroethylene-trans-dicarbonyl-cis-bis(trimethyl phosphite)osmium* (0.044 g, 70%), m.p. 136° [Found: C, 19.5; H, 3.6; P, 10.1%; M (mass spec.), 612. $C_{10}H_{18}F_3P_2ClOsO_8$ requires C, 19.6; H, 3.0; P, 10.1%; M , 612], ν_{max} (cyclohexane) 2015s, and 2011s, sh cm^{-1} ; m/e 612 (P , 24%), 584 ($P - CO$, 24%), 556 ($P - 2CO$, 86%), 496 ($P - C_2F_3Cl$, 100%), 465 ($P - C_2F_3Cl - OMe$, 52%), and 434 ($P - C_2F_3Cl - 2OMe$, 49%); τ ($CDCl_3$) 6.29 (d, 9H, CH_3OP , J_{HF} 12.0 Hz) and 6.34 (d, 9H, CH_3OP , J_{HF} 12.0 Hz); the ^{19}F n.m.r. spectrum ($CDCl_3$) showed resonances at 99.8 p.p.m. [F(1)], 115.0 [F(2)], and 123.0 [F(3)] where $J_{F(1)F(2)}$ 178.0 Hz, $J_{F(1)F(3)}$ 35.0 Hz, $J_{F(2)F(3)}$ 8.0 Hz, $J_{trans-PF}$ 53.0 Hz, $J_{trans-PF}$ 32.0 Hz, $J_{cis-PF} < 0.2$ Hz, $J_{cis-PF} < 0.2$ Hz.



Reactions of trans-Tricarbonylbis(dimethylphenylphosphine)osmium.—(a) *With trifluoroethylene.* Irradiation (18 h) of a solution of *trans*-tricarbonylbis(dimethylphenylphosphine)osmium (0.10 g, 0.18 mmol) and trifluoroethylene (2.5 mmol) in hexane (25 ml) gave after removal of solvent *in vacuo* a residue, which was recrystallised (-78°) from hexane to give white crystals of (IV) *trifluoroethylene-cis-dicarbonyl-trans-bis(dimethylphenylphosphine)osmium* (0.027 g, 25%), m.p. $171-173^\circ$ [Found: C, 41.4; F, 7.6; P, 9.8%; M (mass spec.), 604. $C_{20}H_{22}F_3OsO_2P_2$ requires C, 41.1; F, 7.9; P, 10.0%; M , 604], ν_{max} ($CHCl_3$) 1997s and 1926vs cm^{-1} ; m/e 606 (P , 15%), 578 ($P - CO$, 100%), 550 ($P - 2CO$, 50%) and 524 ($P - C_2F_3H$, 50%); τ ($CDCl_3$) 2.65 (m, 10H, C_6H_5P), 5.50 (d of m, 1H, CHF , J_{gem-FH} 64.0 Hz) and τ 8.15 (overlapping apparent triplets, CH_3P , $|J|_{POCH}$ 8.0 Hz).

(b) *With hexafluoroacetone.* An excess of hexafluoroacetone (2.5 mmol) was condensed (-196°) into a Carius tube containing a solution of *trans*-tricarbonylbis(dimethylphenylphosphine)osmium (0.10 g, 0.18 mmol) in hexane (20 ml). As the mixture warmed to room temperature a white solid was deposited, which on recrystallisation (-78°) from methylene chloride-hexane gave white crystals of (V) *hexafluoroacetone-trans-dicarbonyl-cis-bis(dimethylphenylphosphine)osmium* (0.07 g, 56%), m.p. $115-117^\circ$ [Found: C, 36.7; F, 16.6; P, 9.1. $C_{21}H_{22}F_6P_2OsO_3$ requires C, 36.7; F, 16.6; P, 9.0%; ν_{max} ($CHCl_3$) 1986vs cm^{-1} ; τ ($CDCl_3$) 2.63 (m, 10H, C_6H_5P) and 8.07 (m, 12H, CH_3P); the ^{19}F n.m.r. spectrum ($CHCl_3$) showed a resonance at 66.2 p.p.m. (d, 6F, CF_3C , $J_{trans-PF}$ 4.0 Hz).

(c) *With iodine.* A solution of iodine (0.10 g, 0.04 mmol) in hexane (2 ml) was added dropwise to a stirred solution (0°) of *trans*-tricarbonylbis(trimethylphenylphosphine)osmium (0.03 g, 0.039 mmol) in hexane (10 ml). The resultant yellow precipitate was collected and crystallised from methylene chloride-hexane to white crystals of (VI) *di-iodotricarbonylbis(dimethylphenylphosphine)osmium* (0.03 g, 72%), m.p. $152-153^\circ$ [Found: C, 28.0; H, 2.8; P, 7.9%; M (mass spec.), 778; M (acetone), 380. $C_{10}H_{22}I_2OsO_3P_2$ requires C, 28.4; H, 2.7; P, 7.2%; M , 804], ν_{max} (CH_2Cl_2) 2136s, 2066s, and 2042s cm^{-1} ; m/e 778 ($P - CO$, 37%), 750 ($P - 2CO$, 1%), 722 ($P - 3CO$, 4%), 651 ($P - CO - I$, 46%), and 625 ($P - CO - I$, 100%); τ ($CDCl_3$) 2.60 (m, C_6H_5P) and 7.48 (apparent triplet, 12H, CH_3P , $|J|_{POCH}$ 8.5 Hz).

Reaction of Hexafluorobut-2-yne-cis-dicarbonyl-trans-bis(trimethylphosphite)osmium with Hydrogen Chloride.—A solution of hexafluorobut-2-yne-cis-dicarbonyl-trans-bis(trimethyl phosphite)osmium (0.070 g, 0.10 mmol) and hydrogen chloride (2.0 mmol) in hexane (15 ml) was heated (80°) for 24 h. The solvent was removed *in vacuo* to give after recrystallisation from methylene chloride-hexane a low-melting solid (VII) (0.02 g, 34%), ν_{max} (hexane) 2063vs and 2000 cm^{-1} ; m/e 694 (P , 20%), 664 ($P - CO$, 12%), 638 ($P - 2CO$, 16%), 531 ($P - C_4F_6H$, 25%), and 503 ($P - CO - C_4F_6H$, 100%); τ ($CDCl_3$) 3.18 (q of m, 1H, $CHCF_3$, J_{HF} 11.2 Hz, J_{HP} 1.0 Hz) and 6.24 (apparent triplet, 18H, CH_3OP , $|J|_{POCH}$ 10.6 Hz); the ^{19}F n.m.r. spectrum ($CDCl_3$) showed resonances at 54.6 p.p.m. (q, 3F, $CClCF_3$, J_{FF} 14.0 Hz) and 57.7 (q of t of d, 3F, $CHCF_3$, J_{FF} 14.0 Hz, J_{HP} 2.8 Hz, J_{HF} 11.2 Hz).