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Preparation and Properties of Complexes of Osmium(II) with Carbonyl, Nitrosyl, Organic Cyanide and Organic Isocyanide Ligands

By J. Chatt, D. P. Melville, and R. L. Richards,* A.R.C. Unit of Nitrogen Fixation, University of Sussex, Brighton BN1 9QJ, Sussex

The new complexes $[OsX_2(Y)(PR_3)_3]$, $[OsX_2(Y)_2(PR_3)_2]$, and $[Os_2X_3(PR_3)_6]^+$ (X = Cl or Br; Y = CO, MeNC, PhNC, MeCN or PhCN; PR_3 = tertiary phosphine or $AsMe_2Ph$) have been prepared by the zinc reduction of $[OsX_3(PR_3)_3]$ in presence of Y. Under these conditions, nitrogen oxide gives the complexes $[OsCl_2(NO_2)(NO)-$ (PMe₂Ph)₂] and [OsCl(NO₂)(NO)(PMe₂Ph)₃]⁺. The ¹H and ³¹P n.m.r. spectra of the complexes are discussed and used in conjunction with i.r. data to assign configurations. The osmium–chlorine stretching frequencies of the complexes are recorded and discussed. Reactions of $[OSX_2(Y)(PR_3)_3]$ and $[OSX_2(Y)_2(PR_3)_2]$ with dichlorine, tertiary phosphine, and carbon monoxide are described. The compound [OsCl₂(PMe₂Ph)₃MeNC]Cl results from dichlorine oxidation of [OsCl₂(PMe₂Ph)₃MeNC]. The bonding characteristics of the ligands Y are compared with those of dinitrogen.

THE reduction of halido-complexes of the transition metals by zinc or sodium amalgams in the presence of

¹ J. Chatt, G. J. Leigh, and R. L. Richards, *Chem. Comm.*, 1969, 515; J. Chatt, G. J. Leigh, and R. L. Richards, *J. Chem.* Soc. (A), 1970, 2243.

the ligand has proved a very convenient route to complexes containing dinitrogen,^{1,2} carbon monoxide,^{1,2} hydride,^{1,2} organic cyanide,³ and related ligands Y.

² B. Bell, J. Chatt, and G. J. Leigh, Chem. Comm., 1970, 842.
 ³ R. E. Clarke and P. C. Ford, Inorg. Chem., 1970, 9, 227.

The stability of the complexes formed with the ligands Y is dependent upon the inter-relationship of the ligand σ -donor and π -acceptor, and the metal σ -acceptor and π -donor functions. For ligands such as dinitrogen, this inter-relationship is very subtle and the σ -donor and π -acceptor functions are satisfied in relatively few cases,

formed (see text).] Bromide may replace chloride in certain steps in the Scheme. The compounds prepared and analytical data *etc.* are shown in Table 1.

The initial step in the reaction, with or without added ligand, is the formation of a green solution.¹ It is possible that this colour corresponds to the presence of a

| TABLE 1 | |
|-----------------------------|--|
| Complex compounds of osmium | |

| | *** 11 | | | | Analysis » | | | | |
|--|--------------|---------|--------------------------|------------------------|---|------------|----------|----------|-----------|
| Complex ^a | (%) | Colour | C | н | N | Cl | | Mc | Mnď |
| $[O_{SC}]_{(CO)}(PMe, Ph)_{1}(B)$ | 70 | White | 42.5(42.7) | 4.8(4.7) | | | Ũ | 691(704) | 101 109 |
| $\left[OsCl_{2}(CO)(PPhPr^{\mathbf{a}})\right](B)$ | 59 | White | 49.7(50.0) | 6.7(7.0) | | | | 021(704) | 191-192 |
| $[OsBr_{2}(CO)(PMe_{2}Ph)_{2}](B)$ | 80 | White | 38.7(38.7) | $4 \cdot 3(4 \cdot 7)$ | | | | | 220 |
| $\left[OsCl_2(CO)(PMe_Ph)_2\right](A)$ | 85 | Vellow | 42.9(42.7) | 4.8(4.7) | | 9.8(10.1) | | 691(704) | /160108\ |
| $\left[OsCl_{2}(CO)(PFt,Ph)_{2}\right](A)$ | 31 | Vellow | 47.7(47.3) | 5.9(5.8) | | 0 0(10 1) | | 801(788) | (103 |
| $\left[O_{S}Br_{*}(CO)(PMe_{*}Ph)_{*}\right](A)$ | 65 | Orange | 37.8(37.9) | $4 \cdot 3(4 \cdot 2)$ | | | 2.2(2.0) | 759(703) | (105911) |
| $\left[OsCl_{2}(CO), (PMePh_{2}), 1/C\right]$ | 69 | Vellow | 46.4(46.9) | 3.8(3.7) | | | 22(20) | 884(718) | (150 |
| [03012(00)2(1 M01 M2/2](0) | 00 | 10100 | 10 1(10 0) | 00(01) | | | | 004(110) | 174.5) |
| $[OsCl_{2}(CO)_{2}(PEtPh_{2})_{2}](C)$ | 59 | Yellow | 48.6(48.3) | $4 \cdot 2(4 \cdot 0)$ | | 9.1(9.5) | 4.5(4.3) | 722(744) | (170) |
| $[OsCl_2(CO)_2(PEt_2Ph)_2](C)$ | 14 | Vellow | 41.2(40.7) | 4.7(4.6) | | 0 1(0 0) | 10(10) | 717(649) | (145-159) |
| $\left[OsCl_{2}(CO)_{2}(PPhPr^{n}_{2})_{2}\right](C)$ | 41 | Yellow | 44.3(44.3) | 5.6(5.4) | | 10.3(10.1) | 4.6(4.5) | 706(706) | (165-175) |
| $[OsCl_2(CO)_2(PBu^n Ph)_2](C)$ | 71 | Yellow | 47.5(47.3) | $6 \cdot 2(6 \cdot 1)$ | | 10 0(10 1) | 10(10) | 688(761) | 149.5 |
| | | | | • -(• -) | | | | 000(101) | 151(157) |
| $[OsCl_{a}(CO)_{a}(PEt_{a})_{a}](C)$ | 40 | Yellow | 31.0(30.4) | 5.6(5.5) | | | | | 110- |
| | | 10100 | 01 0(00 1) | 0 0(0 0) | | | | | 122(170) |
| [OsCl _a (CO) _a (AsMe _a Ph) _a](C) | 411 | Yellow | 31.9(31.7) | $3 \cdot 3(3 \cdot 3)$ | | | | | 160 - 162 |
| $[OsBr_{o}(CO)_{o}(PEtPh_{o})_{o}](C)$ | 58 | Yellow | $43 \cdot 2(43 \cdot 2)$ | 3.8(3.6) | | | | | (195) |
| $\left[OsCl_{2}(CO)\right]$ (PEtPh_)](D) | 80 | White | 48.6(48.3) | $4 \cdot 3(4 \cdot 0)$ | | | | 603(649) | 254-256 |
| $[OsCl_2(CO)_2(PPhPr^n_2)_2](D)$ | 80 | White | 44.1(44.2) | 5.8(5.4) | | | | 000(010) | 175 - 178 |
| $[OsCl_2(CO)_2(PFt_1)_2](D)$ | 60 | White | 31.0(30.4) | 5.6(5.5) | | | | 510/553) | 102 - 103 |
| $[O_{3}O_{2}(O_{2$ | 40 | White | $43 \cdot 3(43 \cdot 2)$ | 3.7(3.6) | | | | 010(000) | 286-288 |
| $[OsCl_{2}(WeNC)(PMe_{Ph})_{a}](A)$ | 85 | Yellow | 43.3(43.6) | 5.3(5.1) | $2 \cdot 1 (2 \cdot 0)$ | | | 740(717) | 199-201 |
| [OsCl ₂ (MeNC)(PMe ₂ Ph) ₂](B) | 50 | White | 43.2(43.6) | $5\cdot 2(5\cdot 1)$ | 2.1(2.0) | | | 666(717) | 181-183 |
| $[OsCl_{2}(MeNC)_{2}(PEt_{2})_{3}(D)]$ | 58 | Vellow | 33.2(33.2) | 6.4(6.3) | 4.8(4.8) | | | 000(111) | 176-177 |
| $fac_{-}[OsCl_{(MeNC)}(PMe_{-}Ph)_{-}]$ | 62 | V. pale | 43.5(43.6) | $5 \cdot 2(5 \cdot 1)$ | $2 \cdot 2(2 \cdot 0)$ | | | 717(717) | (128) |
| / // [00012(1101/0)(11102111/3] | 02 | green | 20 0(20 0) | 0 =(0 =) | (- •) | | | | (120) |
| [OsCl _a (PhNC)(PMe ₂ Ph) ₂](A) | 58 | Vellow | 47.8(47.8) | $5 \cdot 2(4 \cdot 9)$ | $2 \cdot 2(1 \cdot 8)$ | 9.0(9.1) | | 698(779) | 161-163 |
| [OsCl ₂ (PhNC)(PMe ₂ Ph) ₂](B) | 63 | White | 48.0(47.8) | 5.1(4.9) | $2 \cdot 1 (1 \cdot 8)$ | 9.2(9.1) | | 000(110) | 169-1900 |
| [OsCl _a (MeCN)(PMe _a Ph) _a](A) | 60 | Yellow | 43.8(43.6) | 5.3(5.1) | $\bar{2} \cdot \bar{1} (\bar{2} \cdot \bar{0})$ | · -(• -/ | | 685(717) | 173-1751 |
| [OsCl _a (PhCN)(PMe ₂ Ph) ₂](A) | 9 | Yellow | 47.7(47.8) | $5 \cdot 2(4 \cdot 9)$ | 1.9(1.8) | | | | 203-206 |
| $[OsCl_{o}(NO_{o})(NO)(PMe_{o}Ph)_{o}]$ | 15 | Orange | 31.8(31.3) | 3.9(3.6) | 4.7(4.6) | | | 602(603) | 176-178 |
| [OsCl(NO ₂)(NO)(PMe ₂ Ph) ₂]BPh | -ğ | Yellow | 55.6(55.8) | 5.2(5.2) | 2.4(2.7) | | | 002(000) | 208 |
| [OsCl _o (MeNC)(PMe _s Ph) _s]Cl | $2\tilde{7}$ | Green | 41.5(41.5) | 5.2(4.8) | 1.9(1.9) | | | | 133 / |
| trans-[OsCl. (PMe.Ph).] | 42 | Yellow | 47.0(47.2) | 5.4(5.4) | | | | 707(813) | 232-238 |
| | | | ~() | -() | | | | | -55 200 |

^a Configurations in parentheses. ^b Calc. values in parentheses. ^c In $C_2H_4Cl_2$ solution. ^d In vacuo, isomerisation point in parentheses. ^e Crystals contain two molecules of methanol. ^f Obtained under pressure of CO. ^e With decomposition.

when compared with, for example, carbon monoxide. The σ -donor function appears to be particularly important for dinitrogen.⁴ Osmium(II) in certain of its phosphine complexes is able to satisfy the requirements for binding dinitrogen ¹ and therefore we now describe a variety of complexes of the above related ligands Y, which were prepared in order to gain knowledge of the nature of this dinitrogen-binding metal site.

Preparation of Complexes.—The complexes were prepared by the reduction, in presence of the ligand Y, of the compounds mer- $[OsX_3(PR_3)_3]$ (X = Cl or Br; PR_3 = tertiary phosphine or $AsMe_2Ph$) by amalgamated zinc, illustrated in the Scheme for a trichloro-compound. Various isomers are possible as shown, but the number of isomers formed is dependent upon the ligand. Carbon monoxide gave the largest variety of isomers, but dinitrogen and organic cyanides gave only one. [With methyl isocyanide as ligand, a fac-isomer may also be

⁴ J. Chatt, D. P. Melville, and R. L. Richards, *J. Chem. Soc.* (*A*), 1969, 2841.



Inorg. Phys. Theor.

compound $[OsCl_2(THF)(PR_3)_3]$ but we have been unable to isolate any compound of this type by carrying out the reduction under argon; only intractable oils or complexes of the type [Os₂Cl₃(PR₃)₆][anion] (see text) resulted. Pure complexes were obtained when Y = CO, RNC, and RCN, and are described below. Nitrogen oxide gave a more complicated reaction in which halogen was replaced by an NO₂ group (see text). Complexes where $Y = N_2$ or H_2^* are described elsewhere.1,5

phosphorus coupling; those of configuration (B) two (sometimes overlapping) triplets (intensity 2) and a doublet (intensity 1); those of configuration (C) a triplet and those of configuration (D) a triplet (Table 2). Confirmation of assignments may also be obtained from the i.r. spectra of the complexes; for example complexes of configuration (D) ($C_{2\nu}$) should show two ν (Os-Cl), two ν (Os-L), two ν (Os-Y), and two bands from the internal stretching of the Y ligand. In general the number of (C=O) or (C=N) absorptions, determined in solution, is

| | initi speecha er es | | |
|---|---|--|--|
| | Resonance | $ ^{2} f(PH) + [^{2} f(PH)]$ | |
| Compound | $(\tau \pm 0.01)$ | $(Hz \pm 0.2)$ | Assignment |
| $[OsCl_2(CO)(\hat{PMe_2Ph})_3](A)$ | 8·24 8·73 | $7 \cdot 2$ $7 \cdot 7$ | trans P-Me triplet cis P-Me doublet |
| $[\mathrm{OsBr}_2(\mathrm{CO})(\mathrm{PMe}_2\mathrm{Ph})_3](\mathrm{A})$ | 8·21 8·54 | 7·2 8·2 | <i>trans</i> P- <i>Me</i> triplet <i>cis</i> P- <i>Me</i> doublet |
| $[OsCl_2(MeCN)(PMe_2Ph)_3](A)$ | 8·43 8·26 8·76 9·43 ⁵ | 6·4 8·7 | trans P-Me-triplet cis-P-Me doublet MeCN singlet MeCN singlet |
| $[OsCl_2(MeNC)(PMe_2Ph)_3](A)$ | 8·37 8·45 7·25 7·80 b | 5·4 8·0 | trans P-Me triplet cis P-Me doublet MeNC singlet MeNC singlet |
| $[OsCl_2(PhNC)(PMe_2Ph)_3](A)$ | $\begin{array}{c} 8 \cdot 29 \\ 8 \cdot 62 \end{array}$ | 7·2 8·1 | trans P-Me triplet cis P-Me doublet |
| $[OsCl_2(CO)(PMe_2Ph)_3](B)$ | 8.08 ° 8.67 | 7·8 9·7 | <i>trans</i> P- <i>Me</i> triplet <i>cis</i> -P- <i>Me</i> doublet |
| $[\mathrm{OsBr_2(CO)(PMe_2Ph)_3](B)}$ | 7·95 • 8·59 | 8·3 9·6 | <i>trans</i> P- <i>Me</i> triplet <i>cis</i> P- <i>Me</i> doublet |
| $[OsCl_2(MeNC)(PMe_2Ph)_2](B)$ | 8·16 ° 8·62 6·76 7·26 » | 8·0 9·0 | trans P-Me triplet cis P-Me doublet MeNC singlet MeNC singlet |
| $[OsCl_2(PhNC)(PMe_2Ph)_3](B)$ | 8·12 ¢ 8·60 | $\begin{array}{c} \mathbf{7\cdot2}\\ \mathbf{9\cdot1} \end{array}$ | trans P-Me triplet cis P-Me doublet |
| $[OsCl_2(CO)_2(PMe_2Ph_2)](C)$ | 7.92 | $4 \cdot 2$ | trans P-Me triplet |
| $[OsCl_2(CO)_2(AsMe_2Ph)_3](C)$ | 8.12 | | trans As-Me singlet |
| $[OsCl_2(CO)_2(PEt_3)_2](C)$ | 7·9 8·8 | 3·6 ª 7·4 ª | trans $P-CH_2$ nonatet trans $P-Me$ quintet |
| $[OsCl_2(MeNC)_2(PEt_3)_2](C)$ | 7·9 8·8 6·27 6·91 » | 3.6 đ 7.4 đ | trans P-CH ₂ nonatet trans P-CH ₃ quintet MeNC singlet MeNC singlet |
| $[OsCl_2(CO)_2(PEt_3)_2](D)$ | 7·9 8·8 | 3.7 đ 7.7 đ | trans P- CH_2 nonatet trans P- CH_3 quintet |
| fac-[OsCl ₂ (MeNC)(PMe ₂ Ph) ₃] | 8·12 8·36 8·51 | 8·3 8·8 8·9 | P- <i>Me</i> doublet P- <i>Me</i> doublet P- <i>Me</i> doublet |

| | | TABLE 2 |
|----|--------|--|
| ιH | N.m.r. | spectra of osmium complexes ^a |
| | | $ ^{2}I(PH) + ^{4}I(PH)$ |

• In deuteriochloroform solution with tetramethylsilane as internal reference. ^bIn deuteriobenzene solution. ^c Two overlapping triplets. ⁴ Separation of adjacent resonances of the multiplets, see Figure.

Assignment of Configurations.—Assignment of configuration has been made chiefly on the basis of the ${}^{1}H$ n.m.r. spectra of complexes with $PMe_xPh_{(3-x)}$ ligands (Table 2), using the method developed by Shaw and his co-workers.⁶ Complexes of configuration (A) show a triplet (intensity 2) and a doublet (intensity 1) for the methyl resonance as a result of strong phosphorus-

⁵ D. P. Melville, D.Phil. Thesis, Sussex, 1970; J. Chatt, D. P. Melville, and R. L. Richards, *J. Chem. Soc.* (A), 1971, 895. ⁶ B. L. Shaw and A. C. Smithies, *J. Chem. Soc.* (A), 1968, 2784; P. G. Douglas and B. L. Shaw, *J. Chem. Soc.* (A), 1969, 1491 1491.

the expected number for the various symmetries (Table 3) and (Os-Cl) bands, which were easily assigned, are the number expected (Table 4). The exception is configuration (A) where only one (Os-Cl) band is observed, but probably for this (C_{2v}) configuration the A_1 vibration will have a low dipole moment change and absorption will be weak and in this case unobservable. Only one ν (Os-Cl) was observed for analogous compounds with amine ligands.7 Reliable assignment of (Os-C) or 7 J. Chatt, G. J. Leigh, and R. J. Paske, J. Chem. Soc. (A), 1969, 854.

(Os-P) vibrational modes cannot be made because other ligand vibrations obscure the region $(500-200 \text{ cm}^{-1})$ where they are likely to occur (Table 4).

Carbonyl Complexes.—Carbon monoxide is the most versatile ligand of the series and air-stable complexes of configurations (A), (B), (C), and (D) may be obtained. The compounds of configuration (A) are quite stable but are converted into the (B) isomers when heated. When

TABLE 3

I.r. spectra of osmium compounds

| | ν(AΞB) | ^b cm ⁻¹ |
|---|--------------------|-------------------------------|
| | | Chloro- |
| Compound a | Benzene | form |
| $OsCl_{o}(CO)(PMe_{Ph})_{o}](A)$ | 1947 | 1957 |
| $OsCl_{o}(CO)(PEt_{o}Ph)_{o}(A)$ | 1941 | 1938 |
| $OsBr_{o}(CO)(PMe_{o}Ph)_{o}](A)$ | 1979 | 1962 |
| OsCl _a (CO)(PMe _a Ph) _a](B) | 1930 | 1929 |
| OsCl _a (CO)(PPhPr ⁿ _a), (B) | 1915 | 1921 |
| OsCl.(CO)(PEt.).1(B) | 1916 ° | |
| OsBr. (CO) (PMePh) .1(B) | 1932 | 1939 |
| OsCl, (CO), (PMePh,), (C) | 1980 | 1984 |
| OsCl, (CO), (PEtPh,), (C) | 1980 | 1982 |
| OsCl ₂ (CO) (PEt ₂ Ph) (C) | 1980 | 1981 |
| $OsCl_2(CO)_2(PPhPrn_2)_2(C)$ | 1981 | 1981 |
| $OsCl_{4}(CO)_{2}(PBu^{n}_{2}Ph)_{2}](C)$ | 1978 | 1981 |
| $[OsCl_2(CO)_2(PEt_3)_2](C)$ | 1979 | 1972 |
| $OsCl_2(CO)_2(AsMe_2Ph)_2](C)$ | 1981 | 1981 |
| $OsBr_2(CO)_2(PEtPh_2)_2](C)$ | 1982 | 1982 |
| $OsCl_2(CO)_2(PEtPh_2)_2(D)$ | 2037, 1971 | 2043, 1971 |
| $[OsCl_2(CO)_2(PPhPrn_2)_2](D)$ | 2031, 1961 | 2035, 1961 |
| $[OsCl_2(CO)_2(PEt_3)_2](D)$ | 2019, 1960, | 2029, 1953 |
| | $1958 \mathrm{sh}$ | |
| $[OsBr_2(CO)_2(PEtPh_2)_2](D)$ | 2041, 1983 | 2046, 1977 |
| $[OsCl_2(MeNC)(PMe_2Ph)_3](A)$ | 2136 | 2140 |
| $[OsCl_2(MeNC)(PMe_2Ph)_3](B)$ | 2064, 1998w | 2068, 1999w |
| $[OsCl_2(MeNC)_2(PEt_3)_2](C)$ | 2110 | 2121 |
| $fac-[OsCl_2(MeNC)(PMe_2Ph)_3]$ | 2176 | 2171 |
| $[OsCl_2(PhNC)(PMe_2Ph)_3](A)$ | 2067 | 2071 |
| $[OsCl_2(PhNC)(PMe_2Ph)_3](B)$ | 2016 | 2017 |
| $[OsCl_2(MeCN)(PMe_2Ph)_3](A)$ | 2280 | 2278 |
| $[OsCl_2(PhCN)(PMe_2Ph)_3](A)$ | 2191 | 2196 |
| $[OsCl_2(NO_2)(NO)(PMe_2Ph)_3](A)$ | 1852 | |
| $[OsCl(NO_2)(NO)(PMePh)_3][BPh_4]$ | 1834 ° | 2210 |
| $[OsCl_2(MeNC)(PMe_2Ph)_3]Cl$ | | 2218 |
| CO gas | 21 | 43 |
| N ₂ gas | 23 | 31 |
| PRINC | 2134 | |
| Menu | 2168 | |
| PIUN | 2230 | 0054 |
| MeUN | 2254 | 2254 |
| | • | 1 (A-D) |

^a Configuration of complex in parentheses. ^b $\nu(A \equiv B) = \nu(C \equiv O)$, $\nu(N \equiv N)$, $\nu(N \equiv C)$ or $\nu(C \equiv N)$ as appropriate. ^c Nujol mull, w = weak, sh = shoulder; all other bands are strong.

dinitrogen is the ligand, only complexes of configuration (B) are obtained, where dinitrogen is trans to halide.¹ This is to be expected, since dinitrogen, a weaker ligand than carbon monoxide in both the σ - and π -capacities,^{4,8} will prefer to bind trans to the weak trans-influence halide ligand rather than, in configuration (A), trans to the phosphine ligand of high trans-influence. The v(CO) value for the (B) isomer is lower than for the (A) isomer, suggesting a greater overlap of osmium nonbonding *d*-orbitals with π^* -carbon monoxide orbitals when CO is trans to the weaker trans-influence ligand.

Organic Isocyanide Complexes.—These complexes,

- ⁸ K. F. Purcell, Inorg. Chim. Acta, 1969, 3, 540.
 ⁹ K. Nakamoto, J. Fujita, and H. Murato, J. Amer. Chem. Soc., 1958, 80, 4817.

J. Chem. Soc. (A), 1971

which are the first of osmium to be prepared, of configurations (A), (B), and (C) are easily formed and closely resemble their carbonyl analogues. Again, it is noticeable that $v(N \equiv C)$ for the (B) isomer is lower than for the (A) isomer. When the yellow compound [OsCl₂(MeNC)(PMe₂Ph)₃] {configuration (A)} was kept in benzene solution, pale green fac-[OsCl2(MeNC)-(PMe₂Ph)₃] slowly formed. Its configuration was assigned since the n.m.r. spectrum shows a pattern of three doublets for the Me resonances of the phosphine (Table 2).

Organic Cyanides.—These compounds gave only complexes of configuration (A), and in this respect resemble primary amines,7 which, unlike dinitrogen, are moderate σ -donor ligands and have a low π -acceptor capacity. The compound [OsCl₂(PhCN)(PMe₂Ph)₃] {configuration (A)} has a lower ν (C=N) value (2191 cm⁻¹) than the free ligand (2230 cm⁻¹) suggesting as strong a d_{π} - π^* overlap, as is usually observed when a dinitrogen binding site is occupied by the organic cyanide.³ Thus, the corrolary, that sites which cause a lowering of $\nu(C=N)$ will bind to dinitrogen, does not follow. Methyl cyanide, bound to the same site, exhibits an increased $\nu(C=N)$.

Nitrogen Oxide.---Nitrogen oxide reacted in a more complicated fashion than the other ligands and the complexes [OsCl₂(NO₂)(NO)(PMe₂Ph)₂] and [OsCl(NO₂)-(NO)(PMe₂Ph)₃][BPh₄] were obtained. Bands in the i.r. spectra of these compounds at 583 and 605 cm^{-1} respectively, indicate that the NO₂ is bound as a nitrogroup.9 The nitrogen oxide used for these reactions was shown by mass spectrometry to contain less than 100 p.p.m. of nitrogen dioxide. It seems likely that the nitro-ligands result from the reaction of nitrogen dioxide or dinitrogen oxide formed by disproportionation of nitrogen oxide during the course of reaction, as also occurs for rhodium(I) complexes.¹⁰ The n.m.r. spectrum of [OsCl₂(NO₂)(NO)(PMe₂Ph)₂] (in CDCl₃) gave a pattern of two overlapping triplets at τ 8.0, indicating trans-PMe₂Ph ligands not in a mirror plane, and probably the



configuration is (E). The v(NO) values for both compounds (Table 3) are in the range found for related ruthenium compounds where the NO is considered to bind as NO^{+.11}

Dimethylphenylphosphine.—Dimethylphenylphosphine gave a yellow complex formulated as trans-[OsCl₂-(PMe₂Ph)₄] since its ¹H n.m.r. spectrum is a broad singlet for the PCH_3 protons as might be expected for such a system.6

- ¹⁰ W. B. Hughes, Chem. Comm., 1969, 1126.
- ¹¹ J. Chatt and B. L. Shaw, J. Chem. Soc. (A), 1966, 1811.

| 11 | 73 |
|----|----|
|----|----|

| Far-i.r. spectra (400-100 cm ⁻¹) of osmium compounds | | | | | | | |
|--|----------------------|--|--|--|--|--|--|
| Compound b | ν(Os-X) • | Other bands | | | | | |
| [OsCl _a (CO)(PMe _a Ph) _a](A) | 303vs | 355m, 346m, 337m, 321m, 244w, 220w | | | | | |
| OsBr. (CO) (PMe. Ph), (A) | ca. 200br | 345s, 322s, 236w | | | | | |
| OsCl, (CO) (PEt, Ph), (A) | 300vs | 396m, 386m, 291sh | | | | | |
| OsCl _a (MeNC)(PMe ₂ Ph) ₃ (A) | 296vs | 347m, 338s, 317s, 229w, 206m, 185w | | | | | |
| OsCl ₂ (PhNC)(PMe ₂ Ph) ₃ (A) | 297s | 345w, 339w, 322m, 236s, br | | | | | |
| $[OsCl_2(MeCN)(PMe_2Ph)_3](A)$ | 298vs | 352s, 328w br, 318m, 272m, 240w | | | | | |
| $[OsCl_2(PhCN)(PMe_2Ph)_3](A)$ | 292vs,br | 364s, 348w, 337w, 249m, 230w | | | | | |
| $[OsCl_2(N_2)(PMe_2Ph)_3](B)^d$ | (283) • | | | | | | |
| $[OsCl_2(CO)(PMe_2Ph)_3](B)$ | 290vs, 261vs (276) • | 363s, 345m, 320m, 156w, 108w | | | | | |
| $[OsBr_2(CO)(PMe_2Ph)_3](B)$ | 173m | 362m,br, 348m, 318m | | | | | |
| $[OsCl_2(CO)(PPr^n_2Ph)_3](B)$ | 286vs, 258vs | 243s, 171w, 139w | | | | | |
| $[OsCl_2(MeNC)(PMe_2Ph)_3](B)$ | 278vs, 251s (265) • | 367s, 343w, 320w, 242m, 236sh, 232 sh, 155w, 139w | | | | | |
| $[OsCl_2(PhNC)(PMe_2Ph)_3](B)$ | 284s, 248vs (267) • | 362s, 335w, 328w, 243sh, 237sh, 232sh | | | | | |
| $[OsCl_2(CO)_2(PMePh_2)_2](C)$ | 313vs | 360s, 347ssh, 304w | | | | | |
| $[OsCl_2(CO)_2(PEtPh_2)_2](C)$ | 312vs | 357sbr, 337m, 303m | | | | | |
| $[OsCl_2(CO)_2(PPr^n_2Ph)_2](C)$ | 308vs | 352s, 363s, 303m | | | | | |
| $[OsCl_2(CO)_2(PEt_3)_2](C)$ | 312vs | 391s, 362s, 336m, 304m | | | | | |
| $[OsCl_2(CO)_2(AsMe_2Ph)_2](C)$ | 311vs | 365s, 287s, 252m | | | | | |
| $[OsBr_2(CO)_2(PEtPh_2)_2](C)$ | 234vs | 363m, 334m, 308w | | | | | |
| $[OsCl_2(MeNC)_2(PEt_3)_2](C)$ | 314vs | 385m, 336s, 290vs, 264s, 218w, 189w | | | | | |
| $[OsCl_2(CO)_2(PPr^n_2Ph)_3](D)$ | 305s, 277vs | 229w, 157m | | | | | |
| $[OsCl_2(CO)_2(PEt_3)_2](D)$ | 304s, 279w | 382m, 337m, 188m, 145m | | | | | |
| $[OsBr_2(CO)_2(PEt_2Ph)_2](D)$ | 212vs, 193vs | 385s, 354w, 273m, 265m | | | | | |
| $fac-[OsCl_2(MeNC)(PMe_2Ph)_3]$ | 273vs, 240vs | 384w, 371w, 362m, 342m, 332m, 309w, 245sh, 188w | | | | | |
| $[OsCl_2(NO_2)(NO)(PMe_2Ph)_2]$ | 321vs, 302vs | 342s, 208w, 202w, 148w | | | | | |

TABLE 4

^a As Nujol mulls. ^b Configuration in parentheses. ^c X = Cl or Br. ^d Included from ref. 1 for comparison. ^e Mean ν (Os-Cl) value. s = Strong, sh = shoulder, m = medium, w = weak, br = broad.

Reaction under argon gave the intermediate green solution which slowly became yellow, and yellow, halogen-bridged, crystalline complexes of the type $[Os_2Cl_3(PR_3)_6]X$ [X = Cl, BPh₄, PF₆, or ZnCl₃ (ligand)]

TABLE 5

³¹P N.m.r. of $[OsX_2(Y)(PMe_2Ph)_3]$ (Y = CO, N₂, MeNC or PhNC)

| Compound a | δ(p.p.m. abo | ove P_4O_6) ^b |
|--|------------------|-----------------------------|
| $[OsCl_2(CO)(PMe_2Ph)_3](A)$ | 157.0(2) • | 159·0(1) ° |
| $\left[OsBr_{2}(CO)(PMe_{2}Ph)_{3}\right](A)$ | $163 \cdot 4(2)$ | 168-8(1) |
| $[OsCl_2(MeNC)(PMe_2Ph)_3](A)$ | 154.0(2) | $159 \cdot 4(1)$ |
| [OsCl ₂ (PhNC)(PMe ₂ Ph) ₃](A) | 155.7(2) | $159 \cdot 9(1)$ |
| $[OsCl_2(N_2)(PMe_2Ph)_3](B)$ | 148.5 4 | |
| $[OsCl_2(CO)(PMe_2Ph)_3](B)$ | 144.4 • | |

^a Configuration in parentheses. ^b Approximate relative intensities in parentheses; P_4O_6 internal reference. ^c Overlapping absorptions. ^d Broad singlet. • Sharp singlet.

were obtained by concentrating the solution or upon addition of a precipitating anion. Analytical data *etc.* for these diamagnetic complexes are shown in Table 6 which also includes some assignments of Os-Cl stretching frequencies for these compounds. It is noticeable that all the ligands which bind to the $OsX_2(PR_3)_3$ unit (CO, RCN, RNC, PR_3 , and NH_2R) are able to occupy a co-ordination position *trans* to a tertiary phosphine, whereas dinitrogen cannot. Since this series of ligands vary in their π -acceptor capacity, from strong (CO) to negligible (RNH₂) the binding of these ligands must be largely σ in character; thus, it seems very likely that dinitrogen cannot bind *trans* to the tertiary phosphine ligand (of high *trans*-influence) because its σ -donor function is too weak. Thus, the site which binds dinitrogen must have the ability to act as a strong σ -acceptor as well as a strong π -donor.

N.m.r. Spectra.—The ¹H n.m.r. spectra of complexes which contain phosphines having methyl groups have already been discussed and are shown in Table 2. For complexes of the type $[OsX_2(Y)(PMe_xPh)_{(3-x)})_3]$ {configuration (A) or (B); x = 1 or 2}, $|^2J(PH) + {}^4J(PH)|$ is less than $|^2J(PH)|$, therefore ${}^2J(PH)$ and ${}^4J(PH)$ have opposite signs. The spectrum of the phosphine ligands of the compound $[OsCl_2(CO)_2(PEt_3)_2]$ [configuration (C)] may be analysed in terms of the simple splitting pattern shown in the Figure. A 1:4:6:4:1 quintet arises from

TABLE 6

| Complexes of the | type | $[Os_2Cl_3(PR_3)_6][anion]$ |
|------------------|------|-----------------------------|

| | | | Molar | | Ana | lyses ¢ | | |
|---------------------|-------------------------------------|-----------|--|--------------------------|------------------------|------------------------|------------------------|------------|
| PR_3 | Anion | M.p. ª | Ω^{-1} cm ² mole ⁻¹ | С | H | Cl | Zn | v(Os-Cl) |
| PEtPh, | ZnCl _a , EtOH | 170 - 175 | 19.8 | 52.0(51.9) | 4.9(4.8) | 11.0(10.7) | $2 \cdot 8(3 \cdot 3)$ | 273m, 286m |
| PEtPh, | PF | 211 - 212 | 22.7 | $52 \cdot 9(52 \cdot 6)$ | $5 \cdot 1(4 \cdot 7)$ | 5.4(5.6) | . , | |
| PEtPh ₂ | BPĥ₄ | 170 - 171 | 14.1 | $62 \cdot 4(62 \cdot 0)$ | $5 \cdot 4(5 \cdot 3)$ | $5 \cdot 8(5 \cdot 1)$ | | 274m, 283m |
| PEt ₃ | ZnCl ₃ ,PEt ₃ | 181 - 183 | 18.1 | 34·2(34·0) | 7.6(7.1) | • • | | |
| PEt ₃ | PF. | 165 - 230 | 34.6 | 35.4(35.6) | 7.5(7.5) | | | |
| PMe ₂ Ph | ZnČl _s ,THF | 113—118 ª | $23 \cdot 9$ | 41.8(41.8) | $5 \cdot 4(5 \cdot 2)$ | | | 278s, br |
| PMe ₂ Ph | BPh_4 | 158-205 | 16.7 | 53·3(52·9) | 5.7(5.5) | | | |

" On a Köfler block, with decomposition. In nitrobenzene solution. Calculated values in parentheses. True m.p.

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the P-CH₃ resonance, typical of *trans*-PEt₃ groups with strong phosphorus-phosphorus coupling and a 1:2:4:6:6:6:4:2:1 pattern arises from the P-CH₂ resonance. The methylene pattern is symmetrical since there is a plane of symmetry through the P-CH₂ bond. Details of the resonances arising from the methyl groups of co-ordinated methyl cyanide and methyl isocyanide, which show large solvent shifts, are also given in Table 2.

The ³¹P n.m.r. spectra of some complexes are given in Table 5. Complexes of configuration (A) or (B) have two kinds of chemically inequivalent phosphorus atoms; it is, therefore, surprising that only one signal is seen for the spectra of the complexes of configuration (B). The ¹H n.m.r. spectra have shown that the phosphine



ligands are magnetically inequivalent, and possibly the two types of phosphorus atom in $[OsCl_2(Y)(PMe_2Ph)_3]$ [configuration (B); Y = CO or N₂] have the same chemical shift. Support for this argument comes from the spectra of $[OsX_2(Y)(PMe_2Ph)_3]$ [configuration (A); X = Cl or Br; Y = CO or RNC] where the ³¹P chemical shifts are similar and for $[OsCl_2(CO)(PMe_2Ph)_3]$ [configuration (A)] where the two signals overlap. Moreover, the signal of $[OsCl_2(N_2)(PMe_2Ph)_3]$ [configuration (B)] is broad and may be an unresolved doublet.

Far-i.r. Spectra.—Assignments of ν (Os-Cl) were made by comparison with the corresponding bromo-complexes (Table 4). In the spectra of complexes of configuration (A), only one (Os-Cl) stretching band was observed as discussed earlier. In those of the compounds $[OsCl_2(Y) (PMe_2Ph)_3$] {Y = CO, PhNC, MeNC, MeCN, PhCN, NH_2R [configuration (A)]} the values of v(Os-Cl) fall in the region 290-303 cm⁻¹. Since the only variation in the system is the nature of the ligand Y, and the large mass of the central atom will minimise coupling effects, the above variation of ν (Os-Cl) probably reflects the cis-influence of the ligand Y, in the decreasing order $NH_2R > PhCN > PhNC$, MeNC > MeCN > CO. Complexes of configuration (C), where Cl is trans to Cl, show the expected single (Os-Cl) band in the range 303-313 cm⁻¹.

Isomers (B) show two bands, and for the series of

complexes $[OsCl_2(Y)(PMe_2Ph)_3]$ {configuration (B); Y = CO, N₂, RNC, PhNC} we assume (using the arguments above) that the mean (Table 4) of these two frequencies represents the variation in (Os-Cl) force constant induced by the change of ligand Y, *trans* to one of the chlorides. This gives the *trans*-influence order PhNC, MeNC > CO > N₂ which appears to parallel the σ -donor ability of these ligands.

The isomers (D), where chloride is *trans* to CO, give two ν (Os-Cl) values, which lie within the range 277- 305 cm^{-1} . Thus the v(Os-Cl) values fall into the ranges: 290-313 cm⁻¹ for Cl trans to Cl and 277-305 cm⁻¹ for Cl trans to carbon monoxide and related ligands. For carbonyl and dinitrogen complexes of configuration (B). the higher frequency band falls in the range 286-307 cm⁻¹, *i.e.* within the range for chloride *trans* to carbon monoxide. Thus it seems likely that the lower frequency band, although due to a coupled vibration, will correspond mainly to v(Os-Cl) for chloride trans to phosphorus and this range is 248-272 cm⁻¹. These three ranges of frequency closely parallel those found by Lupin and Shaw¹² for the analogous complexes of ruthenium(II), corresponding $\nu(Os-Cl)$ values being close to, or lower than, v(Ru-Cl) values, as expected from the mass effect.

Some Reactions of the Osmium(II) Complexes.—(a) Reaction with dichlorine. This reaction was investigated for the series of complexes [OsCl₂(Y)(PMe₂Ph)₃] {configuration (A) or (B); Y = CO, MeNC, PhNC, MeCN or PhCN}. Usually inseparable mixtures of products or intractable oils were obtained, which showed increased values of $v(A \equiv B)(A \equiv B = C \equiv O, \text{ or } N \equiv C)$, corresponding to oxidation of the central metal. Possibly mixtures result because some phosphine ligand could be lost from the metal, initially as R₃PCl₂, but from reaction of [OsCl₂(PMe₂Ph)₃(MeNC)] [configuration (A)] a crystalline, green, paramagnetic salt [OsCl₂(PMe₂Ph)₃(MeNC)]Cl, was isolated in low yield. Although the above products could not be purified except in the one case, it is highly likely that the ligands (Y) are still bound to the central metal atom; whereas dinitrogen, which requires for its binding a critical balance of σ -acceptor and π -donor functions of the metal, is quantitatively lost when the metal is oxidised.¹

(b) Displacement reactions. Although dinitrogen is fairly easily lost from the complex $[OsCl_2(N_2)(PMe_2Ph)_3]$ by oxidation, it is not readily displaced by two-electron donors such as 1,2-bis(diphenylphosphino)ethane.¹ Similarly carbon monoxide, methyl cyanide, methyl isocyanide and phenyl isocyanide only displace dinitrogen very slowly from the above dinitrogen complex as illustrated in equation (1).

$$\begin{array}{c} [\mathrm{OsCl}_{2}(\mathrm{N}_{2})(\mathrm{PMe}_{2}\mathrm{Ph})_{3}] \xrightarrow[\mathrm{toluene}\ (72\mathrm{h.})]{} \\ (\mathrm{B}) \end{array} \\ [\mathrm{OsCl}_{2}(\mathrm{CO})(\mathrm{PMe}_{2}\mathrm{Ph})_{3}] + [\mathrm{OsCl}_{2}(\mathrm{N}_{2})(\mathrm{PMe}_{2}\mathrm{Ph})_{3}] \quad (1) \\ (\mathrm{B})\ 75\% \qquad (\mathrm{B})\ 25\% \end{array}$$

¹² M. S. Lupin and B. L. Shaw, J. Chem. Soc. (A), 1968, 741.

As expected, carbon monoxide bound to a potential dinitrogen-binding site is very difficult to displace, *e.g.* the carbon monoxide in $[OsCl_2(CO)(PMe_2Ph)_3]$ [configuration (B)] is not replaced by a tertiary phosphine.

One molar equivalent of carbon monoxide is displaced by tertiary phosphine from $[OsCl_2(CO)_2(PPhPr_2)_2]$ {configuration (C)} to give the stable monocarbonyl of configuration (B) as illustrated in equation (2).

$$\begin{bmatrix} OsCl_2(CO)_2(PPhPr_2)_2 \end{bmatrix} + PPhPr_2 \xrightarrow{\text{toluene}}_{14h.} \\ (C) \\ \begin{bmatrix} OsCl_2(CO)(PPhPr_2)_3 \end{bmatrix} (B) + CO \quad (2) \\ (B) \end{bmatrix}$$

All the carbon monoxide was displaced from $[OsCl_2(CO)_2(PEtPh_2)_2]$ [configuration (C)] when it was heated in a mixture of pyridine and hydroiodic acid for one week. Methyl isocyanide was not completely displaced from $[OsCl_2(MeNC)_2(PEt_3)_2]$ [configuration (C)] when it was heated with triethyl phosphine for 8 h; partial substitution gave some $[OsCl_2(MeNC)(PEt_3)_3]$ [configuration (B)]. In contrast to the above reactions, the methyl cyanide in $[OsCl_2(PMe_2Ph)_3(MeCN)]$ [configuration (A)] is easily displaced by carbon monoxide, at room temperature, to give $[OsCl_2(CO)(PMe_2Ph)_3]$ [configuration (A)].

EXPERIMENTAL

All manipulations involving air-sensitive materials, such as tertiary phosphines, were carried out using Schlenk, or standard high-vacuum techniques. Solvents were degassed before use and tetrahydrofuran was distilled from sodium diphenylketyl into reaction vessels under dinitrogen or argon. The compounds $[OsX_3(PR_3)_3]$ (X = Cl or Br; PR₃ = tertiary phosphine or AsMe₂Ph) were prepared by established methods.¹³

M.p.s were measured on a Kofler hot stage and molecular weights were determined with an Hitachi-Perkin-Elmer 115 osmometer. A Faraday balance was used for magnetic measurements and a Portland electronics conductivity bridge was used for conductance measurements at *ca.* 20°.

The i.r. spectra were measured on the R.I.I.C. Fourier spectrophotometer F.S. 620, and Grub-Parsons D.M.4 and Unicam S.P. 1200 instruments. The ¹H n.m.r. spectra were measured using Varian A 60 or H.A. 100 instruments and ³¹P n.m.r. on a Perkin-Elmer R 10 instrument. An A.E.I. M.S. 10 instrument was used for mass-spectral measurements. Reactions under gas pressure were run in 100 cm³ glass flasks, placed inside a Baskerville rocking autoclave.

Microanalyses were by Mr. A. G. Olney of Sussex University.

Preparation of Osmium(II) Complexes

Methods are general and typical examples are given here. Analytical data *etc.*, for the compounds prepared by these methods are given in Table 1.

(a) Complexes of Configuration (A) (Y = CO, RNC, RCN). Dichlorotris(dimethylphenylphosphine)methyl isocyanideosmium(II), [OsCl₂(PMe₂Ph)₃MeNC] [Configuration (A)]. mer-[OsCl₃(PMe₂Ph)₃] (1.42 g), methyl isocyanide (1.4 cm³), 85%). (b) Complexes of Configuration (B) (Y = CO, RNC).— These complexes may be obtained by isomerization of complexes of configuration (A). Thus dibromocarbonyltris-(dimethylphenylphosphine)osmium(II), $[OsBr_2(CO)(PMe_2Ph)_3]$ {configuration (B)} was formed when $[OsBr_2(CO)(PMe_2Ph)_3]$ {configuration (A)} (0.15 g) was heated under reflux in ethanol for six days; the solution was cooled and white plates separated which were filtered off and recrystallised from ethanol as white prisms (0.12 g, 80%).

Alternatively, complexes of configuration (C) may be converted into those of configuration (B) by a reaction with tertiary phosphine. As an example dichlorocarbonyltris-(phenyl-di-n-propylphosphine)osmium(II), [OsCl₂(CO)-(PPhPrⁿ₂)₃] [configuration (B)] was formed when [OsCl₂-(CO)₂(PPhPrⁿ₂)₂] [configuration (C)] (0.17 g) was heated under reflux in toluene (30 cm³) with PPhPrⁿ₂ (1.5 g) for 14 h. The solvent was removed and the residue gave white prisms (0.1 g, 59%) from methanol.

(c) Complexes of Configuration (C) (Y = CO, MeNC).— These complexes may also be obtained by method (a). Thus dichlorodicarbonylbis(triethylphosphine)osmium(II), $[OsCl_2(CO)_2(PEt_3)_2]$ [configuration (C)] was formed when mer- $[OsCl_3(PEt_3)_3]$ (1.56 g) and an excess of amalgamated zinc (11 g) were heated together under reflux in THF (25 cm³) with passage of carbon monoxide through the solution until it was yellow (0.25 h). The solution was filtered, solvent removed and the residue recrystallised from methanol as yellow prisms (0.53 g, 40%).

Dichlorodicarbonylbis(dimethylphenylarsine)osmium(II), $[OsCl_2(CO)_2(AsMe_2Ph)_2]$ [Configuration (C)].—This complex was prepared by the above method in low yield (2%), and a better yield (41%) was obtained by reduction of mer- $[OsCl_3(AsMe_2Ph)_3]$ (0.68 g) in THF (10 cm³) with amalgamated zinc (5 g) under carbon monoxide (14,200 kN m⁻²) at 93° for one day. Recrystallisation of the yellow product obtained after removal of solvent, gave yellow prisms from ethanol.

An osmium(iv) complex could also be used as starting material for the preparation of dibromodicarbonylbis(ethyldiphenylphosphine)osmium(ii), $[OsBr_2(CO)_2(PEtPh_2)_2]$ [configuration (C)]. Thus a solution of trans- $[OsBr_4(PEtPh_2)_2]$ (0.57 g) in THF (25 cm³) with a stream of carbon monoxide passing through it, was heated with amalgamated zinc (5 g) under reflux (1.5 h); the zinc and solvent were removed from the yellow solution and the residue gave yellow prisms (0.30 g, 58%) from THF-methanol.

(d) Complexes of Configuration (D) (Y = CO).—These complexes were obtained by the thermal isomerization of complexes of configuration (C). Thus dichlorodicarbonylbis-(triethylphosphine)osmium(II), $[OsCl_2(CO)_2(PEt_3)_2]$ [configuration (D)] was formed when yellow $[OsCl_2(CO)_2(PEt_3)_2]$ [configuration (C)] (0.25 g) was heated in toluene (7 cm³) under reflux until a colourless solution formed (3.5 h); removal of solvent and recrystallisation of the white residue from methanol gave white plates (0.15 g, 60%).

Preparation of fac-Dichlorotris(dimethylphenylphosphine)methyl isocyanideosmium(II), fac-[OsCl₂(PMe₂Ph)₃(MeNC)].--[OsCl₂(PMe₂Ph)₃(MeNC)] [Configuration (A)] (0.50 g) was

¹³ J. Chatt, G. J. Leigh, D. M. P. Mingos, and R. J. Paske, *J. Chem. Soc.* (A), 1968, 2636. kept in benzene solution for 11 days until the solution was dark green; the very pale green *crystals* which had formed were filtered off, washed twice with benzene, and dried (0.31 g, 62%). The green crystals melted at 128° and above this temperature the white isomer of configuration (B) formed (identified by its m.p. and i.r. spectrum).

Reactions of Nitrogen Oxide

Chloro(nitro)(nitrosyl)tris(dimethylphenylphosphine)-(a) osmium(II) tetraphenylboron, $[OsCl(NO_2)(NO)(PMe_2Ph)_3]$ -BPh4.-mer-[OsCl3(PMe2Ph)3] (0.90 g) and amalgamated zinc (5 g) were heated under reflux in THF (20 cm³) with passage of nitrogen oxide through the solution. After 1.5 h an orange solution was obtained which was filtered and evaporated to dryness to give a yellow oil. The oil was heated under reflux in THF (15 cm³) with Na[BPh₄] (1 g) and amalgamated zinc (6 g) for 0.5 h and after filtration, the solvent was removed to give a brown oil; this gave a yellow residue with ethanol and hence yellow prisms (0.09 g, 9%) from acetone-methanol. The molar conductivity of the complex in nitrobenzene solution was 19.1 ohm⁻¹ cm² mol⁻¹ (4×10^{-4} M-solution). The NO₂ (wagging) band 9 occurred at 605 cm⁻¹.

(b) Dichloro(nitro)(nitrosyl)tris(dimethylphenylphosphine)-osmium(II), [OsCl₂(NO₂)(NO)(PMe₂Ph)₂].—mer-[OsCl₃-(PMe₂Ph)₃] (0.50 g) and amalgamated zinc (3 g) were heated under reflux in THF (15 cm³) with passage of nitrogen oxide through the solution for 0.5 h. The yellow solution was filtered, evaporated to dryness, and the residue gave pale orange prisms from aqueous methanol (0.08 g, 15%). The NO₂ (wagging) band ⁹ occurred at 583 cm⁻¹.

trans-Dichlorotetrakis(dimethylphenylphosphine)osmium-(II), trans- $[OsCl_2(PMe_2Ph)_4]$.—This complex was prepared from mer- $[OsCl_3(PMe_2Ph)_3]$ (0.49 g), PMe_2Ph (1.2 g), and amalgamated zinc (3 g) in THF (20 cm³) solution at reflux for 0.7 h. The yellow solution obtained was filtered and evaporated to dryness; recrystallisation of the residue from aqueous THF followed by a recrystallisation from ethanol gave yellow prisms (0.19 g, 42%), whose n.m.r. spectrum in deuteriochloroform showed a broad singlet at τ 8.47 for the PMe groups.

The Preparation of Complexes of the Type $[OsCl_3(PR_3)_6]$ -[anion].—If argon was used instead of ligand Y in the above preparations, reduction of mer- $[OsCl_3(PR_3)_3]$ complexes gave compounds of the formula $[Os_2Cl_3(PR_3)_6][ZnCl_3(solvent)]$, which readily gave complexes of the type $[Os_2Cl_3(PR_3)_6]X$ $(X = Cl, PF_6 \text{ or } BPh_4)$ by metathesis. The analytical details *etc.*, for these yellow, diamagnetic complexes are given in Table 6.

Reactions of Osmium(II) Complexes

Dichlorotris(dimethylphenylphosphine)methyl isocyanideosmium(III)chloride, $[OsCl_2(PMe_2Ph)_3(MeNC)]Cl.$ —A stream of dichlorine was passed through a solution of $[OsCl_2-(PMe_2Ph)_3(MeNC)]$ [Configuration (A)] (0.47 g) in chloroform (10 cm³) for 0.1 h. The resulting purple solution was taken o dryness in vacuo and the green oil obtained, after olidification with ether, gave fibrous green needles from

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water (0.13 g, 27%; $\mu_{eff} = 1.73$ B.M.; molar conductivity = 24.3 ohm⁻¹ cm² mol⁻¹ in nitrobenzene solution). The Reaction of Methyl Isocyanide with [OsCl₂(N₂)-(PMe₂Ph)₃] [Configuration (B)].—Methyl isocyanide (2 cm³) and toluene (5 cm³) were distilled in vacuo onto [OsCl₂(N₂)-(PMe₂Ph)₃] (0.055 g, 7.9×10^{-5} moles). The solution was heated at 70° for three days; during this time dinitrogen (2.6 × 10⁻⁵ moles, 33%) was evolved. Complete displacement of dinitrogen was achieved after 1 week. No solid complex could be isolated from the brown, oily reaction product. Similar reactions using phenyl isocyanide and methyl cyanide gave slow dinitrogen evolution and intractable products.

Reaction of Carbon Monoxide with $[OsCl_2(N_2)(PMe_2Ph)_3]$, [Configuration (B)].—A solution of $[OsCl_2(N_2)(PMe_2Ph)_3]$ (0.053 g) in toluene (5 cm³) under carbon monoxide (101 kN m⁻²) was heated at 70° for 3 days; removal of the toluene and trituration of the residue with ethyl ether gave pink crystals, shown by their i.r. spectrum to be $[OsCl_2(CO)-(PMe_2Ph)_3]$ [configuration (B)] (75%) and unchanged $[OsCl_2(N_2)(PMe_2Ph)_3]$.

Reaction of Triethylphosphine with $[OsCl_2(MeNC)_2(PEt_3)_2]$, [Configuration (C)].—Yellow $[OsCl_2(MeNC)_2(PEt_3)_2]$ (0.1 g) was heated under reflux with triethyl phosphine (1.36 g) for 8 h. The solution was then evaporated to dryness *in* vacuo and the resulting yellow oil, on treatment with methanol, gave a pale yellow solid (0.08 g), which was shown to be a mixture of unchanged starting material and $[OsCl_2(MeNC)(PEt_3)_3]$ [configuration (B)] by i.r. and n.m.r. spectroscopy.

Reaction of Carbon Monoxide with $[OsCl_2(MeCN)-(PMe_2Ph)_3]$, [Configuration (A)].—A stream of carbon monoxide was passed through a solution of $[OsCl_2(MeCN)-(PMe_2Ph)_3]$ (0·1 g) in chloroform for 2 h; solvent was removed in a stream of carbon monoxide. Recrystallisation of the yellow residue from ethanol gave $[OsCl_2(CO)-(PMe_2Ph)_3]$ (0·08 g, 82%) which was identified by its i.r. and n.m.r. spectra.

Reaction of Hydriodic Acid-Pyridine with $[OsCl_2(CO)_2-(PEtPh_2)_2]$, $[Configuration (C)].--[OsCl_2(CO)_2(PEtPh_2)_2]$ (0.0569 g) and pyridine (5 cm³) were placed in one limb of an H tube, and the limb, which carried a break-seal, was sealed. Concentrated hydriodic acid solution (3 cm³, 44% solution) was placed in the other limb, both solutions were de-gassed, the vessel was sealed *in vacuo* and the reagents mixed. The sealed vessel was heated for one week at 70° giving a clear yellow solution; carbon monoxide (1.28 cm³, 98%) was obtained on opening the vessel via the break-seal.

Preparation of trans-tetrabromobis (ethyldiphenylphosphine)osmium(IV), $[OsBr_4(PEtPh_2)_2]$.—Osmium tetroxide (0.60 g), PEtPh₂ (2.2 g), and concentrated hydrobromic acid (2 cm³) were heated under reflux in ethanol (30 cm³). A purple precipitate separated, which gave purple prisms from toluene-ethanol (0.98 g, 44%), m.p. 190—210° (decomp.) (Found: C, 36.3; H, 3.3. C₂₈H₃₀Br₄OsP₂ requires C, 35.8; H, 3.3%).

We thank Mr. G. G. Mather for ³¹P n.m.r. measurements.

[0/1956 Received, November 16th, 1970]