Cyclopentadienyl-ruthenium and -osmium Chemistry. Part 18.† Oxidative Addition and Nitrosylation Reactions: Crystal Structure of $[Os(NO)(PMe_3)_2(\eta\text{-}C_5H_5)][PF_6]_2$ ‡

By **Michael I. Bruce,* I. Barry Tomkins,** and **Fook Sin Wong,** Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, South Australia 5001
Brian W. Skelton and **Allan H. White,*** Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, Western Australia 6009

Reaction of $[MX(PR_3)_2(\eta\text{-}C_5H_5)]$ (M = Ru, X = Cl; M = Os, X = Br; R = Me or Ph) with HPF_6 gives the metal(IV) complexes $[MH(X)(PR_3)_2(\eta\text{-}C_5H_5)][PF_6]$, and with Cl_2–$[NH_4][PF_6]$ gives $[RuCl_2(PMe_3)_2(\eta\text{-}C_5H_5)][PF_6]$. Reaction with $[NO][PF_6]$ gives the dications $[M(NO)(PR_3)_2(\eta\text{-}C_5H_5)]^{2+}$, which have unusually high ν(NO) frequencies (1 850—1 875 cm^{-1}). The crystal structure of $[Os(NO)(PMe_3)_2(\eta\text{-}C_5H_5)][PF_6]_2$ has been determined by single-crystal *X*-ray methods at 295 K and refined by least squares to a residual of 0.044 for 2 038 'observed' reflections. Crystals are orthorhombic, space group *Pbca*, with *a* = 21.680(6), *b* = 16.606(4), *c* = 12.772(5) Å, and *Z* = 8. The Os–N–O system is linear, Os–N 1.75(1), N–O 1.17(2) Å being indicative of the $Os{=}N^+{=}O$ moiety; Os–P lengths are 2.367(4) and 2.364(4) Å and Os–C 2.23(2)—2.29(2) Å.

MANY low-valent transition-metal complexes oxidatively add small molecules, such as Cl_2, HBr, MeI, *etc.* For these reactions to proceed, there must be non-bonding electron density on the transition metal, and two vacant or potentially vacant co-ordination sites. The oxidation states of the metal in reactant complex and product are separated by two units. Well known examples are d^8 complexes such as $[RhCl(PPh_3)_3]$ and $[IrCl(CO)(PPh_3)_2]$, and the d^{10} complex $[Pt(PPh_3)_4]$. Less common are reactions involving d^6 complexes, such as those of ruthenium(II) or osmium(II).

In a recent study of the oligomerisation of 1-alkynes with alkylruthenium complexes, we suggested the intermediacy of ruthenium(IV) complexes formed by oxidative addition of the alkyne to the metal centre.[1] However, no ruthenium(IV) complexes containing tertiary phosphines have been reported, apart from the hydrides $[RuH_4(PR_3)_3]$,[2] although deuteriation reactions proceeding *via* cyclometallated ruthenium(IV) intermediates have been proposed.[3] In contrast, addition of dichlorine to *mer*-$[OsCl_3(PR_3)_3]$ has given $[OsCl_4(PR_3)_2]$, and both tetra- and hexa-hydrido-osmium complexes are known.[4] Organometallic derivatives of ruthenium(IV) and osmium(IV) are also rare, and are restricted to $[RuCl_2(C_{12}H_{18})]$, obtained from butadiene and ruthenium trichloride,[5] halogen-oxidation products of metallocenes, such as $[RuI(\eta\text{-}C_5H_5)_2]^+$,[6,7] and the complex $[RuBr_3(CO)(\eta\text{-}C_5Me_4Et)]$, obtained by addition of bromine to $[\{Ru(CO)_2(\eta\text{-}C_5Me_4Et)\}_2]$.[8]

Our studies of the chemistry of $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$ and related complexes have revealed their unusual reactivity which results from the presence of the electron-rich metal atom. One feature which would be expected is the increased stability of higher oxidation states, which should be enhanced by replacement of PPh_3 by more basic tertiary phosphines, such as PMe_3. In addition, the greater stability of osmium(IV) over ruthenium(IV) suggested that we might find isolable organometallic complexes in oxidation reactions of suitable osmium(II) complexes. A preliminary communication of some of this work has appeared.[9]

RESULTS AND DISCUSSION

The syntheses of $[MX(PR_3)_2(\eta\text{-}C_5H_5)]$ (M = Ru, X = Cl, R = Me or Ph; M = Os, X = Br, R = Ph) have been described previously.[10,11] A direct exchange reaction of PMe_3 with $[OsBr(PPh_3)_2(\eta\text{-}C_5H_5)]$ in light petroleum (b.p. 100—120 °C) at 150 °C afforded two products, yellow $[OsBr(PMe_3)_2(\eta\text{-}C_5H_5)]$ (1), and white $[Os(PMe_3)_3(\eta\text{-}C_5H_5)]Br$ (2). The former is obtained by replacement of PPh_3 by the more nucleophilic PMe_3; further reaction results in replacement of bromide to give the cationic complex (2). Both complexes were identified by elemental analysis and spectroscopic data reported in the Experimental section. They are stable in air both in solution and as solids; as expected, complex (2) dissolves only in the more polar solvents.

No isolable products were obtained by addition of halogens to the PPh_3 complexes. However, $[RuCl(PMe_3)_2(\eta\text{-}C_5H_5)]$ reacts with dichlorine in the presence of $[NH_4][PF_6]$ to give $[RuCl_2(PMe_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (3) as an orange crystalline solid. The formulation of this complex follows from the analytical results, and the ^1H n.m.r. spectrum, which contains a characteristic signal for the PMe_3 ligands at δ 2.03, while the C_5H_5 resonance is at the unusually low-field position of δ 6.13.

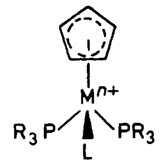
Reactions between $[RuCl(PMe_3)_2(\eta\text{-}C_5H_5)]$ or $[OsBr(PR_3)_2(\eta\text{-}C_5H_5)]$ (R = Me or Ph) and HPF_6 or HBF_4 have given the hydrido-cations $[RuH(Cl)(PMe_3)_2(\eta\text{-}C_5H_5)]^+$ (4) and $[OsH(Br)(PR_3)_2(\eta\text{-}C_5H_5)]^+$ [R = Me (5) or Ph(6)] respectively. A weak ν(RuH) absorption was found at 2 036 cm^{-1} in the i.r. spectrum of (4). These complexes are also characterised by high-field ^1H n.m.r. resonances at δ −9.7 (4), −14.9 (5), and −12.5 (6), confirming the presence of the metal-bonding hydrogen. We have no explanation for the large difference in

---

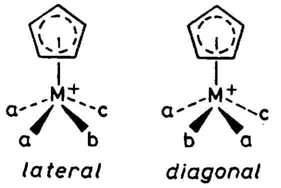
† Part 17 is ref. 9.

‡ (η-Cyclopentadienyl)nitrosylbis(trimethylphosphine)osmium bis(hexafluorophosphate).

chemical-shift values at present, but similar differences between ruthenium and osmium have been noted before, *e.g.* for $[MH(PR_3)_2(\eta\text{-}C_5H_5)]$. The triplet structure of these resonances arises from coupling to the ^{31}P nuclei, and indicates that both phosphorus atoms are equivalent, as expected for the *diagonal* isomer (a), but not for the *lateral* isomer (b).* The apparent triplet found for the PMe_3 protons also supports structure (a); spectra of complexes in which two PMe_3 ligands are not mutually *trans* show sharp doublets with some central fine structure, but the latter has a low relative intensity compared with the analogous resonances of *trans* $(PMe_3)_2$ complexes. In the case of (6), steric arguments also favour the formation of the *diagonal* isomer, that is the most stable isomer in which the bulky PPh_3 ligands would be as far apart as possible. At present, we cannot rule out the possibility that (6) [and also (3)—(5)] are fluxional, at room temperature, which would also explain the equivalence of the PMe_3 groups. Solubility considerations have so far precluded any low-temperature n.m.r. studies. Crystals of quality satisfactory for *X*-ray studies have not yet been obtained.



	M	*n*	R	L
(1)	Os	0	Me	Br
(2)	Os	1	Me	PMe_3
(7)	Ru	2	Me	NO
(8)	Os	2	Me	NO
(9)	Os	2	Ph	NO



	M	a	b	c
(3)	Ru	PMe_3	Cl	Cl *
(4)	Ru	PMe_3	H	Cl
(5)	Os	PMe_3	H	Br
(6)	Os	PPh_3	H	Br

* Isomers not possible

We have also treated the ruthenium(II) and osmium(II) complexes with $[NO][PF_6]$. The product from $[RuCl(PMe_3)_2(\eta\text{-}C_5H_5)]$ is a yellow solid, $[Ru(NO)(PMe_3)_2(\eta\text{-}C_5H_5)][PF_6]_2$ (7), characterised by a ν(NO) band at 1 875 cm^{-1}. The corresponding PPh_3 complex was too unstable to isolate, but had similar spectral properties, including ν(NO) at 1 850 cm^{-1}. The osmium complexes $[Os(NO)(PR_3)_2(\eta\text{-}C_5H_5)][PF_6]_2$ [R = Me (8) or Ph (9)] are also of limited stability, and the brown complex (9) decomposes slowly in the solid state, and retains solvent tenaciously. The nitrosyl complexes showed strong ν(NO) absorptions in the range 1 850—1 875 cm^{-1}, indicating a linear M–N–O arrangement (*i.e.* co-ordinated NO^+) in formally metal(II) complexes. After this work had been completed, the ruthenium complex (7) was described by others.[13]

The crystal structure of (8) has been determined by single-crystal *X*-ray diffraction methods (see Experimental section). The unit-cell contents (Figure 1) comprise $[Os(NO)(PMe_3)_2(\eta\text{-}C_5H_5)]^{2+}$ cations with $[PF_6]^-$ counter ions, confirming the stoicheiometry to be $[Os(NO)(PMe_3)_2(\eta\text{-}C_5H_5)][PF_6]_2$, one formula unit comprising the asymmetric unit of the crystal structure with no crystallographically imposed internal symmetry in any of the species. No abnormal features are observed in the anion geometries (Table 1) given due licence for the presence of high thermal motion in these species.

TABLE 1

Anion geometries. Presentation as for Table 2

(*a*) Anion A

	r_{P-F}	F(2)	F(3)	F(4)	F(5)	F(6)
F(1)	1.57(1)	89.2(7)	90.0(7)	89.8(7)	89.2(8)	177.9(9)
F(2)	1.57(1)		91.1(7)	88.9(6)	178.0(7)	92.9(8)
F(3)	1.56(1)			179.7(22)	90.1(8)	89.9(8)
F(4)	1.57(1)				89.9(7)	90.4(8)
F(5)	1.55(1)					88.7(9)
F(6)	1.55(2)					

(*b*) Anion B

	r_{P-F}	F(2)	F(3)	F(4)	F(5)	F(6)
F(1)	1.49(2)	83.9(9)	175.7(12)	97.4(13)	84.1(13)	91.7(8)
F(2)	1.57(1)		94.2(10)	86.3(11)	92.5(12)	174.3(11)
F(3)	1.52(2)			86.4(11)	92.0(11)	90.3(9)
F(4)	1.50(2)				178.0(12)	90.7(10)
F(5)	1.49(2)					90.6(11)
F(6)	1.52(1)					

The cation displays a pseudo-six-co-ordinate octahedral symmetry, with the η-C_5H_5 group occupying three co-ordination sites, and the NO and tertiary phosphine ligands the other three (Figure 2). Angles between the latter ligands are close to 90° (Table 2). The ligand array about the osmium has pseudo-symmetry very close to *m*: the Os–P distances [2.367(4), 2.364(4) Å] do not differ significantly, nor do angles P(1,2)–Os–C(0) [C(0) is the pseudo-atom at the centre of gravity of the C_5 ring], which are 118.9(1) and 118.8(1)°. There are no reports

TABLE 2

Osmium environment (selected). r_{Os-L}(Å) is the metal–ligand distance. The other entries in the matrix are the angles (°) subtended by the relevant entries at the head of the row/column

	r_{Os-L}	N	P(1)	P(2)
N	1.747(11)			
P(1)	2.367(4)	91.2(4)		
P(2)	2.364(4)	94.0(4)	94.7(1)	
C(1)	2.26(2)	111.4(5)	100.7(4)	149.8(4)
C(2)	2.29(2)	145.3(6)	88.3(4)	120.7(4)
C(3)	2.23(2)	157.0(6)	111.1(5)	90.0(5)
C(4)	2.23(2)	120.8(6)	146.4(5)	93.3(5)
C(5)	2.26(2)	98.8(6)	135.8(4)	127.0(4)
C(0)	1.92(–)	130.8(–)	118.9(1)	118.8(1)

---

* The terms *diagonal* and *lateral* have been introduced to distinguish the two isomers of square-pyramidal $[Ma_2bc(\eta\text{-}C_5H_5)]$ complexes in which the ligands a are mutually *trans* or *cis* respectively, in the square base.[12]

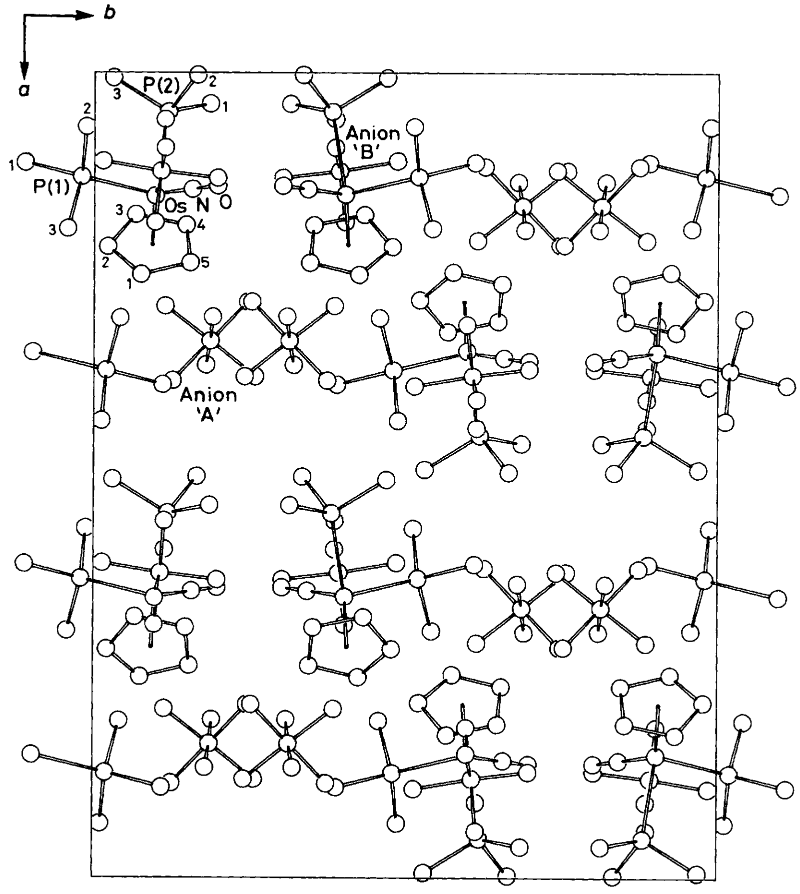


FIGURE 1 Unit-cell contents of $[Os(NO)(PMe_3)_2(\eta\text{-}C_5H_5)][PF_6]_2$ projected down *c*

of Os–PMe_3 distances in the literature; a few well defined six-co-ordinate complexes of osmium(II), containing mutually *trans* PPh_3 ligands, have been studied. In these, Os–P bonds of 2.39, 2.40(2) Å {in $[OsCl_2(HgCl)(NO)(PPh_3)_2]$ [14]}, 2.459(3) Å {in $[OsCl_2(CO)(NO)(PPh_3)_2]^+$ [15]}, and 2.444(2), 2.424(2) Å {in $[OsCl_2(CO)(HNO)(PPh_3)_2]$ [15]} have been reported. A comparative study [11] of $[RuCl(PMe_3)_2(\eta\text{-}C_5H_5)]$ and $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$ has given Ru–P bonds of 2.273(5)—2.280(6) Å and 2.335(1), 2.337(1) Å respectively, suggesting that PMe_3 binds more strongly to ruthenium (discounting possible steric effects) in pseudo-six-co-ordinate environments, with an Ru–P distance shorter by *ca.* 0.06 Å. Extension to osmium would suggest a value for Os–P in the range 2.33—2.40 Å, as found. It is also interesting to note that, for the two pairs of analogous complexes that have been studied for Ru and Os, namely $[M(NO)_2(PPh_3)_2]$ [16,17] and $[MH(nap)(dmpe)_2]$ [nap = 1-naphthyl, dmpe = 1,2-bis(dimethylphosphino)ethane],[18] the structures and bond distances are virtually identical, *e.g.* M–P 2.337(2), 2.353(2) Å (Ru), 2.324(2), 2.340(2) Å (Os) and 2.280(3), 2.301(3), 2.303(3), 2.333(3) Å (Ru), 2.285(5), 2.297(5), 2.301(5), 2.325(6) Å (Os) respectively.

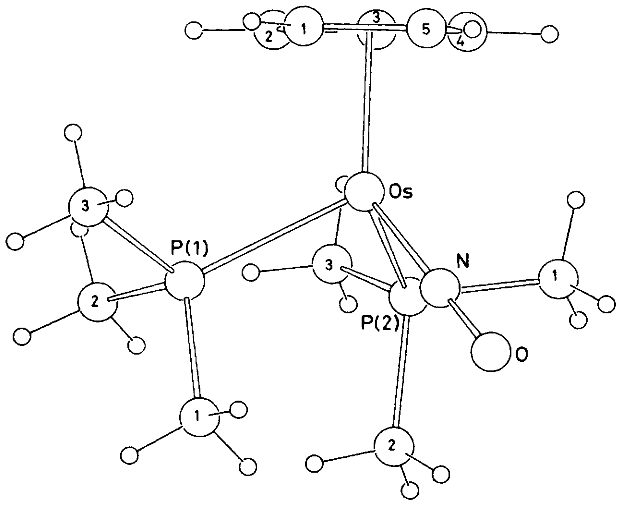


FIGURE 2 A single $[Os(NO)(PMe_3)_2(\eta\text{-}C_5H_5)]^{2+}$ cation showing atom labelling

The literature on well defined mononuclear Os–N–O geometries is likewise sparse: four-co-ordinate $[Os(NO)_2(PPh_3)_2]$ contains linear OsNO groups, with Os–N 1.771(6), 1.776(7) Å;[17] five-co-ordinate (tetragonal pyramidal) $[Os(OH)(NO)_2(PPh_3)_2][PF_6]$ contains both linear OsNO [Os–N 1.63(1) Å] and bent OsNO [Os–N 1.86(1) Å];[19] in six-co-ordinate $[OsCl_2(HgCl)(NO)(PPh_3)_2]$, Os–NO (linear) is 1.79(4) Å.[14] In the present complex, the linear Os–N–O grouping [179.8(15)°] has

Os–N 1.747(11) Å and N–O 1.17(2) Å, all parameters being indicative of an $Os{=}N^+{=}O$ system, which is also consistent with the high ν(NO) frequency (1 856 cm^{-1})

The present study appears to be the first determination of the $Os–C_5H_5$ geometry. The Os–C distances range between 2.23(2) and 2.29(2) Å (mean value, 2.25 Å). An early account used powder diffraction data to determine Os–C distances in osmocene: a value of 2.22 Å was reported.[20]

The above reactions confirm our expectations of forming isolable organo-ruthenium(IV) and -osmium(IV) complexes, and illustrate the increased stability when a more basic phosphine (PMe_3) replaces PPh_3. The increasing tendency of third-row metals, compared with their second-row congeners, to undergo oxidative-addition reactions is also nicely illustrated by the reactions of the PPh_3 complexes (Os more stable than Ru).

As found for the ruthenium series, replacement of PPh_3 in $[OsBr(PPh_3)_2(\eta\text{-}C_5H_5)]$ by PMe_3 occurs readily; the tendency to form cationic complexes by replacement of bromide by two-electron donor ligands is very great, and excess of PMe_3 readily adds to form $[Os(PMe_3)_3(\eta\text{-}C_5H_5)]Br$. The halide in the ruthenium and osmium complexes can also be replaced by NO^+, leading to the formation of the dications $[M(NO)(PR_3)_2(\eta\text{-}C_5H_5)]^{2+}$, isolated as their hexafluorophosphate salts.

The formation of these ruthenium(IV) and osmium(IV) cations further supports our contention that hydrido-ruthenium(IV) intermediates could be formed in the alkyne-oligomerisation reactions mentioned above; their inherent instability could lead to the rapid formation of the observed products by intramolecular reductive eliminations postulated.

The C_5H_5 resonances occur at unusually low field in these complexes, as a result of the relatively low electron density on the metal, as can be seen from the series of complexes $[RuCl(PMe_3)_2(\eta\text{-}C_5H_5)]$, $[Ru(NCMe)(PMe_3)_2(\eta\text{-}C_5H_5)]^+$, $[RuCl_2(PMe_3)_2(\eta\text{-}C_5H_5)]^+$, and $[Ru(NO)(PMe_3)_2(\eta\text{-}C_5H_5)]^{2+}$, in which the C_5H_5 protons resonate at δ 4.44, 4.64, 6.13, and 6.72 respectively.

EXPERIMENTAL

Spectra were recorded on Perkin-Elmer 457 and Jasco IRA2 double-grating (i.r.) and Varian Associates T60 (^1H n.m.r., at 60 MHz) or Bruker WP80 (^1H n.m.r., at 80 MHz) instruments. Solvents were dried and distilled before use. All reactions were carried out under a nitrogen atmosphere. Analyses were by the Australian Microanalytical Service (Melbourne), Pascher (Bonn), or the Canadian Microanalytical Service (Vancouver).

Literature methods were used to prepare $[RuCl(PR_3)_2(\eta\text{-}C_5H_5)]$ (R = Me or Ph) and $[OsBr(PPh_3)_2(\eta\text{-}C_5H_5)]$;[10,11] $HBF_4{\cdot}OMe_2$ and $[NO][PF_6]$ were obtained from Cationics Inc., Cleveland, Ohio.

Preparation of $[OsBr(PMe_3)_n(\eta\text{-}C_5H_5)]$ (*n* = 2 *or* 3).—Trimethylphosphine (190 mg, 2.53 mmol) was condensed on to $[OsBr(PPh_3)_2(\eta\text{-}C_5H_5)]$ (570 mg, 0.66 mmol) in light petroleum (b.p. 100—120 °C) (20 cm^3), and the mixture was heated in a sealed Carius tube (150 °C). After 15 h the contents of the tube consisted of a white precipitate and a yellow supernatant solution. The white *solid* obtained by filtration was washed with light petroleum to give pure $[Os(PMe_3)_3(\eta\text{-}C_5H_5)]Br$ (2) (150 mg, 41%), decomp. >140 °C (Found: C, 30.2; H, 5.3. $C_{14}H_{32}BrOsP_3$ requires C, 29.8; H, 5.7%). N.m.r. ($CDCl_3$): ^1H, δ 1.75 [t, *J*(HP) 9.0 Hz, 27 H, PMe_3] and 5.07 (s, 5 H, C_5H_5); ^{13}C, δ 25.6 [q, *J*(CP) 12.2 Hz, PMe_3] and 80.0 (s, C_5H_5). The filtrate afforded yellow *crystals* of $[OsBr(PMe_3)_2(\eta\text{-}C_5H_5)]$ (1) (110 mg, 34.9%), m.p. 130 °C (Found: C, 27.6; H, 4.6. $C_{11}H_{23}BrOsP_2$ requires C, 27.1; H, 4.7%). N.m.r. ($CDCl_3$): ^1H, δ 1.67 [t, *J*(HP) 8.5 Hz,* 18 H, PMe_3]; and 4.57 (s, 5 H, C_5H_5); ^{13}C, δ 23.4 [t, *J*(CP) 17.1 Hz, PMe_3] and 72.3 (s, C_5H_5).

Reaction between $[RuCl(PMe_3)_2(\eta\text{-}C_5H_5)]$ *and* Cl_2.—Dichlorine (12 mg, 0.18 mmol) in CCl_4 (2 cm^3) was added to $[RuCl(PMe_3)_2(\eta\text{-}C_5H_5)]$ (60 mg, 0.17 mmol) and $[NH_4][PF_6]$ (30 mg, 0.2 mmol) in dichloromethane (6 cm^3), to give an orange precipitate and red-brown supernatant solution. Evaporation, dissolution of the residue in methanol (2 cm^3), and addition of more $[NH_4][PF_6]$ gave orange $[RuCl_2(PMe_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (3) (70 mg, 75.6%), which was filtered off and washed with diethyl ether. The complex decomposes in the range 140—170 °C (Found: C, 24.6; H, 4.3. $C_{11}H_{23}F_6P_3Ru$ requires C, 24.7; H, 4.3%). Infrared (Nujol): ν(PF) 840vs(br) cm^{-1}. N.m.r.: ^1H, δ ([$^2H_6$]acetone) 2.03 [t, *J*(HP) 4.2 Hz, 18 H, PMe_3] and 6.13 (s, 5 H, C_5H_5); and ^{13}C, δ[$(CD_3)_2SO$] 15.2 [t, *J*(CP) 20.8 Hz, PMe_3] and 94.7 (s, C_5H_5).

Protonation Reactions.—(*a*) $[RuCl(PMe_3)_2(\eta\text{-}C_5H_5)]$. Addition of $HPF_6{\cdot}Et_2O$ (60 mg, 0.25 mmol) to a solution of $[RuCl(PMe_3)_2(\eta\text{-}C_5H_5)]$ (60 mg, 0.17 mmol) in dichloromethane (1 cm^3) gave a precipitate of fine yellow *needles*, which were filtered off, washed with CH_2Cl_2 and light petroleum, to give pure $[RuH(Cl)(PMe_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (4) (50 mg, 62.5%), m.p. 168 °C (Found: C, 26.9; H, 4.7. $C_{11}H_{24}ClF_6P_3Ru$ requires C, 26.5; H, 4.8%). Infrared (Nujol): ν(RuH) 2 036vw, ν(PF) 830vs(br) cm^{-1}. N.m.r.: ^1H, δ[$(CD_3)_2SO$] 1.58 [t, *J*(HP) 9.8 Hz, 18 H, PMe_3] and 5.11 (s, 5 H, C_5H_5); δ(CD_2Cl_2) −9.7 [t, *J*(HP) 34 Hz, 1 H, RuH]; ^{13}C, δ[$(CD_3)_2SO$] 21.74 [t, *J*(CP) 17.7 Hz, PMe_3] and 84.4 (s, C_5H_5).

(*b*) $[OsBr(PMe_3)_2(\eta\text{-}C_5H_5)]$. Addition of $HPF_6{\cdot}Et_2O$ (60 mg, 0.25 mmol) to a solution of $[OsBr(PMe_3)_2(\eta\text{-}C_5H_5)]$ (60 mg, 0.11 mmol) in dichloromethane (5 cm^3) immediately gave a suspension of fine yellow needles. Filtration, washing with CH_2Cl_2 and light petroleum, and drying gave the pure *complex*, $[OsH(Br)(PMe_3)_2(\eta\text{-}C_5H_5)][PF_6]$ (5) (60 mg, 85%), m.p. 200 °C (Found: C, 20.85; H, 3.75. $C_{11}H_{24}BrF_6OsP_3$ requires C, 20.85; H, 3.8%). Infrared (Nujol): ν(OsH) not observed; ν(PF) 831vs(br) cm^{-1}. ^1H N.m.r.: δ([$^2H_6$]acetone) 1.98 [t, *J*(HP) 5 Hz, 18 H, PMe_3] and 5.97 (s, 5 H, C_5H_5); δ(CD_2Cl_2) −14.9 [t, *J*(HP) 36.8 Hz, 1 H, OsH].

(*c*) $[OsBr(PPh_3)_2(\eta\text{-}C_5H_5)]$. A dark red solution was obtained on addition of $HBF_4{\cdot}Me_2O$ (25 mg, 0.19 mmol) to a solution of $[OsBr(PPh_3)_2(\eta\text{-}C_5H_5)]$ (86 mg, 0.1 mmol) in dichloromethane (10 cm^3). Addition of excess of diethyl ether precipitated a red oil, which was crystallised with difficulty by repeated extractions with benzene, dichloromethane, and reprecipitation by diethyl ether. Finally

---

* The *J*(HP) 'coupling' recorded for the PMe_3 complexes is the separation of the two outer lines of the apparent doublet or triplet normally found for these derivatives, and is a measure of $|J_{AX} + J_{A'X}|$ in the $X_9AA'X'_9$ spin system.

there were obtained dark red-brown crystals of [OsH(Br)-$(PPh_3)_2(\eta\text{-}C_5H_5)$][$BF_4$] (6) (52 mg, 55%), decomp. >125 °C (Found: C, 51.2; H, 4.0; P, 6.8. $C_{41}H_{36}BBrF_4OsP_2$ requires C, 52.0; H, 3.8; P, 6.6%). ^{1}H N.m.r. ($CDCl_3$): δ 7.4 (m, 30 H, PPh_3), 5.4 (s, 5 H, C_5H_5), and −12.48 [t, *J*(HP) 34 Hz, 1 H, OsH].

Reactions of [NO][PF_6].—(*a*) *With* [RuCl$(PMe_3)_2(\eta\text{-}C_5H_5)$]. Addition of [NO][$PF_6$] (30 mg, 0.18 mmol) to [RuCl$(PMe_3)_2(\eta\text{-}C_5H_5)$] (60 mg, 0.17 mmol) in dichloromethane (5 cm^3) afforded a yellow *precipitate* which was filtered off and washed with methanol to give pure [Ru(NO)-$(PMe_3)_2(\eta\text{-}C_5H_5)$][$PF_6$]$_2$ (7) (60 mg, 66%), m.p. 260 °C (Found: C, 20.9; H, 3.4; N, 2.0; O, 3.0. $C_{11}H_{23}F_{12}NOP_4Ru$ requires C, 20.7, H, 3.6, N, 2.4, O, 2.5%). Infrared (Nujol): ν(NO) 1 875s, ν(PF) 830vs(br) cm^{-1}. ^{1}H N.m.r. [$(CD_3)_2CO$]: δ 2.30 [t, *J*(HP) 13.2 Hz, 18 H, PMe_3] and 6.72 (s, 5 H, C_5H_5) {lit.[13] values: m.p. 245 °C (decomp.); ν(NO) 1 875 cm^{-1}; ^{1}H n.m.r. [$(CD_3)_2SO$] δ 2.02 (m) and 6.50 (s)}.

(*b*) *With* [RuCl$(PPh_3)_2(\eta\text{-}C_5H_5)$]. A slight excess of [NO][PF_6] (22 mg, 0.13 mmol) was added to a solution of [RuCl$(PPh_3)_2(\eta\text{-}C_5H_5)$] (73 mg, 0.1 mmol) in dichloromethane (10 cm^3). An immediate colour change from yellow to red occurred. The solution was filtered into excess of diethyl ether, and the buff-coloured precipitate was collected, washed with diethyl ether, and dried *in vacuo* (63 mg, 70%). The complex is unstable in the solid state and was not analysed. It had similar spectral properties to the osmium compound (see below), and was probably [Ru(NO)$(PPh_3)_2(\eta\text{-}C_5H_5)$][$PF_6$]$_2$. Infrared: ν(NO) 1 850 cm^{-1}. ^{1}H N.m.r. ($CDCl_3$): δ 7.36 (m, 30 H, PPh_3) and 6.07 (s, 5 H, C_5H_5).

TABLE 3

Non-hydrogen atom co-ordinates

Atom	*x*	*y*	*z*
Os	0.151 47(3)	0.097 56(3)	0.230 87(4)
(*a*) Nitrosyl ligand			
N	0.144 9(5)	0.157 5(6)	0.342 8(8)
O	0.140 6(6)	0.197 9(7)	0.417 7(9)
(*b*) Cyclopentadienyl ligand			
C(1)	0.251 4(7)	0.075 4(9)	0.188 7(12)
C(2)	0.216 9(8)	0.022 0(9)	0.130 3(13)
C(3)	0.176 8(8)	0.066 9(11)	0.066 2(12)
C(4)	0.190 0(8)	0.147 8(10)	0.082 5(13)
C(5)	0.236 9(8)	0.154 2(9)	0.160 8(14)
' C(0) '	0.214 4(–)	0.093 2(–)	0.125 7(–)
(*c*) Phosphine ligand 1			
P(1)	0.129 5(2)	−0.019 9(2)	0.328 9(3)
C(11)	0.111 9(11)	−0.110 4(9)	0.259 1(14)
C(12)	0.067 2(8)	−0.012 5(10)	0.420 6(12)
C(13)	0.194 3(8)	−0.042 1(11)	0.411 0(13)
(*d*) Phosphine ligand 2			
P(2)	0.048 2(2)	0.118 8(2)	0.178 5(3)
C(21)	0.038 4(8)	0.185 8(10)	0.068 7(14)
C(22)	0.002 6(8)	0.165 4(12)	0.279 3(14)
C(23)	0.006 3(9)	0.030 7(10)	0.138 1(16)
(*e*) Anion A			
P(A)	0.334 2(2)	0.186 7(3)	0.455 8(4)
F(A1)	0.290 8(7)	0.114 4(7)	0.428 1(11)
F(A2)	0.304 1(6)	0.190 4(7)	0.567 5(9)
F(A3)	0.285 3(6)	0.246 6(8)	0.411 8(11)
F(A4)	0.383 1(6)	0.126 2(7)	0.499 8(8)
F(A5)	0.363 8(7)	0.179 8(9)	0.345 6(9)
F(A6)	0.378 1(7)	0.258 2(8)	0.479 2(13)
(*f*) Anion B			
P(B)	0.122 4(3)	0.392 9(3)	0.218 8(4)
F(B1)	0.057 7(7)	0.386 4(8)	0.179 8(21)
F(B2)	0.110 1(9)	0.485 8(8)	0.213 0(17)
F(B3)	0.186 2(9)	0.402 2(10)	0.265 9(15)
F(B4)	0.153 2(9)	0.401 9(12)	0.114 2(13)
F(B5)	0.093 3(10)	0.386 2(13)	0.324 1(14)
F(B6)	0.130 9(7)	0.302 3(6)	0.214 3(15)

(*c*) *With* [OsBr$(PMe_3)_2(\eta\text{-}C_5H_5)$]. The reaction between [OsBr$(PMe_3)_2(\eta\text{-}C_5H_5)$] (50 mg, 0.1 mmol) and [NO][PF_6] (30 mg, 0.17 mmol) in dichloromethane (5 cm^3) afforded a yellow precipitate, which was washed with MeOH and light petroleum to give pure [Os(NO)$(PMe_3)_2(\eta\text{-}C_5H_5)$][$PF_6$]$_2$ (8) (40 mg, 60%), m.p. 300 °C (Found: C, 18.2; H, 3.1; N, 2.1. $C_{11}H_{23}F_{12}NOOsP_4$ requires C, 18.2; H, 3.2; N, 1.9%). Infrared (Nujol): ν(NO) 1 856s, ν(PF) 836vs(br) cm^{-1}. ^{1}H N.m.r. ([$^2H_6$]acetone): δ 2.40 [t, *J*(HP) 14 Hz, 18 H, PMe_3] and 6.82 (s, 5 H, C_5H_5).

(*d*) *With* [OsBr$(PPh_3)_2(\eta\text{-}C_5H_5)$]. A reaction between [OsBr$(PPh_3)_2(\eta\text{-}C_5H_5)$] (86 mg, 0.1 mmol) and [NO][PF_6] (22 mg, 0.13 mmol) in dichloromethane (10 cm^3) afforded a precipitate of [Os(NO)$(PPh_3)_2(\eta\text{-}C_5H_5)$][$PF_6$]$_2$ (9) (81 mg, 78%), m.p. >115 °C (decomp.), on addition of excess of diethyl ether to the solution. Analyses indicated that slow decomposition occurred in the solid state, and prolonged evacuation did not remove all the diethyl ether adsorbed on the solid (n.m.r.) (Found: C, 43.2; H, 3.2; N, 1.4; P, 9.1. $C_{41}H_{35}BrF_{12}NOOsP_4$ requires C, 44.8; H, 3.2; N, 1.3; P, 11.3%). Infrared (Nujol): ν(NO) 1 850 cm^{-1}. ^{1}H N.m.r. ($CDCl_3$): δ 7.5 (m, 30 H, PPh_3) and 6.33 (s, 5 H, C_5H_5).

Crystallography.—*Crystal data.* $C_{11}H_{23}F_{12}NOOsP_2$, $M = 665.4$, Orthorhombic, space group *Pbca* (D_{2h}^{15}, no. 61), $a = 21.680(6)$, $b = 16.606(4)$, $c = 12.772(5)$ Å, $U = 4\,598(2)$ Å^3, $D_m = 2.08(1)$, $Z = 8$, $D_c = 2.10$ g cm^{-3}, $F(000) = 2\,544$, monochromatic Mo-K_α radiation ($\lambda = 0.7106_9$ Å), $\mu_{Mo} = 56$ cm^{-1}, specimen size *ca.* 0.01 × 0.22 × 0.35 mm, $T = 295$ K.

Structure determination. A unique data set was measured within the limit $2\theta = 50°$ using a Syntex $P\bar{1}$ four-circle diffractometer in conventional θ—2θ scan mode, yielding

TABLE 4

Ligand geometries (non-hydrogen atoms); distances (Å), angles (°)

(*a*) Nitrosyl	
N–O	1.17(2)
Os–N–O	179.8(15)
(*b*) Cyclopentadienyl	
C(1)–C(2)	1.38(2)
C(2)–C(3)	1.41(2)
C(3)–C(4)	1.39(2)
C(4)–C(5)	1.43(2)
C(5)–C(1)	1.39(2)
C(5)–C(1)–C(2)	110(1)
C(1)–C(2)–C(3)	108(1)
C(2)–C(3)–C(4)	107(1)
C(3)–C(4)–C(5)	109(1)
C(4)–C(5)–C(1)	106(1)
(*c*) Phosphine ligands; *n* = 1,2 respectively	
P(*n*)–C(*n*1)	1.79(2), 1.80(2)
P(*n*)–C(*n*2)	1.79(2), 1.80(2)
P(*n*)–C(*n*3)	1.79(2), 1.80(2)
Os–P(*n*)–C(*n*1)	118.1(6), 115.0(6)
Os–P(*n*)–C(*n*2)	116.1(6), 112.4(6)
Os–P(*n*)–C(*n*3)	108.7(6), 116.0(6)
C(*n*1)–P(*n*)–C(*n*2)	102.9(9), 103.1(8)
C(*n*1)–P(*n*)–C(*n*3)	106.7(9), 102.7(9)
C(*n*2)–P(*n*)–C(*n*3)	102.9(8), 106.2(9)

3 707 independent reflections, 2 038 of these with $I > 3\sigma(I)$ being considered ' observed ' and used in the structure solution and refinement after absorption correction. Refinement was by (basically) 9×9 block-diagonal least squares; parameters of each of the anions, however, were refined jointly as two blocks only. Anisotropic thermal parameters were used for the non-hydrogen atoms. Hydrogen-atom positional parameters were estimated and constrained, while U_{H} was set at 1.25 U_{ii} (parent C). Residuals at convergence were (R,R') 0.044, 0.051, reflection weights being set at $[\sigma^2(F_o) + 0.0005(F_o)^2]^{-1}$. Neutral-atom scattering factors were used, those for the non-hydrogen atoms being corrected for anomalous dispersion (f',f'').[21] Computation was carried out using the ' X-RAY '76 ' program system [22] implemented by S. R. Hall on a Perkin-Elmer 8/32 computer. Material deposited as Supplementary Publication No. SUP 23211 (14 pp.) * comprises structure factors, thermal parameters, and hydrogen-atom parameters. Non-hydrogen atom co-ordinates are given in Table 3, ligand geometries in Table 4.

Atom numbering is shown in Figure 2; hydrogen-atom numbering follows that of the parent carbon, distinguished where necessary by suffixes a, b, and c.

We thank the Australian Research Grants Committee for grants in support of this work.

---

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

[1/1214 *Received, 3rd August*, 1981]

REFERENCES

[1] M. I. Bruce, R. C. F. Gardner, J. A. K. Howard, F. G. A. Stone, M. Welling, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1977, 621.

[2] W. H. Knoth, *J. Am. Chem. Soc.*, 1972, **94**, 104.

[3] T. Ito, S. Kitazume, A. Yamamoto, and S. Ikeda, *J. Am. Chem. Soc.*, 1970, **92**, 3011.

[4] P. G. Douglas and B. L. Shaw, *J. Chem. Soc. A*, 1970, 334.

[5] J. K. Nicholson and B. L. Shaw, *J. Chem. Soc. A*, 1966, 807; J. E. Lydon and M. R. Truter, *ibid.*, 1968, 362.

[6] E. O. Fischer and H. Grubert, *Chem. Ber.*, 1959, **92**, 2302.

[7] Y. S. Sohn, A. W. Schlueter, D. N. Hendrickson, and H. B. Gray, *Inorg. Chem.*, 1974, **13**, 301.

[8] I. W. Nowell, K. Tabatabaian, and C. White, *J. Chem. Soc., Chem. Commun.*, 1979, 547.

[9] M. I. Bruce and F. S. Wong, *J. Organomet. Chem.*, 1981, **210**, C5.

[10] M. I. Bruce and N. J. Windsor, *Aust. J. Chem.*, 1977, **30**, 1601.

[11] M. I. Bruce, F. S. Wong, B. W. Skelton, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1981, 1398.

[12] R. B. King, R. H. Reimann, and D. L. Darensbourg, *J. Organomet. Chem.*, 1975, **93**, C23.

[13] P. M. Treichel and D. A. Komar, *Synth. React. Inorg. Metal-Org. Chem.*, 1980, **10**, 205.

[14] G. A. Bentley, K. R. Laing, W. R. Roper, and J. M. Waters, *Chem. Commun.*, 1970, 998.

[15] R. D. Wilson and J. A. Ibers, *Inorg. Chem.*, 1979, **18**, 336.

[16] A. P. Gaughan, B. J. Corden, R. Eisenberg, and J. A. Ibers, *Inorg. Chem.*, 1974, **13**, 786.

[17] B. L. Haymore and J. A. Ibers, *Inorg. Chem.*, 1975, **14**, 2610.

[18] U. A. Gregory, S. D. Ibekwe, B. T. Kilbourn, and D. R. Russell, *J. Chem. Soc. A*, 1971, 1118.

[19] G. R. Clark, J. M. Waters, and K. R. Whittle, *J. Chem. Soc., Dalton Trans.*, 1975, 463.

[20] F. Jellinek, *Z. Naturforsch., Teil B*, 1959, **14**, 737.

[21] D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 1968, **24**, 321; D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.

[22] ' The X-RAY System; Version of March 1976,' Technical Report TR-446, ed. J. M. Stewart, Computer Science Center, University of Maryland, Maryland, U.S.A.