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Transition-metal Complexes containing Phosphorus Ligands. Part VI.[1] Convenient Synthesis of Some Tertiary Phosphine (and Arsine) Nitrosyl Halide Derivatives of Ruthenium and Osmium

By **S. D. Robinson** * and **M. F. Uttley**, Department of Chemistry, King's College, Strand, London WC2R 2LS

A selection of ruthenium and osmium nitrosyl halide complexes, $MX_3(NO)(AR_3)_2$ [M = Ru, Os; X = Cl, Br; A = P, R = alkyl, aryl, or mixed alkyl aryl; A = As, R = phenyl] have been prepared by a convenient single-stage synthesis involving addition of ruthenium or osmium halides and *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide or pentyl nitrite to a solution of the appropriate tertiary phosphine or arsine in a boiling alcoholic solvent. Attempts to prepare the tri-iodo-derivatives, $MI_3(NO)(AR_3)_2$, by this technique using ruthenium or osmium chlorides in the presence of a large excess of lithium iodide gave the required products, the corresponding chlorodi-iodo-derivatives or a mixture of complexes, depending on the nature of the neutral ligands present. A mechanism for the nitrosyl formation, involving ruthenium(IV) and osmium(IV) monohydrides, $MX_3H(AR_3)_2$, as intermediates is discussed, and an explanation for the formation of the mixed chlorodi-iodo derivatives is advanced. E.s.r. and i.r. spectroscopic evidence for the formation of a paramagnetic nitrosyl, tentatively formulated $RuCl_2(NO)(PPh_3)_2$, as a minor product in the synthesis of $RuCl_3(NO)(PPh_3)_2$ is reported.

IN a recent publication[2] we disclosed a convenient single stage synthesis of the triphenylphosphine nitrosyl chloride complexes $M'Cl_2(NO)(PPh_3)_2$ [M' = Rh, Ir] and $MCl_3(NO)(PPh_3)_2$ [M = Ru, Os] based on the use of *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide (hereafter referred to as mnts) or pentyl nitrite as sources of nitrosyl ligands. The present paper describes the application of this technique of synthesis to the preparation of a wide range of ruthenium and osmium nitrosyl halide complexes, $MX_3(NO)(AR_3)_2$, containing a variety of alkyl, aryl, and alkylaryl phosphines or triphenylarsine as neutral ligands. Spectroscopic evidence for the formation of a paramagnetic nitrosyl derivative, tentatively formulated as $RuCl_2(NO)(PPh_3)_2$, in trace amounts is also presented. Similar syntheses of related rhodium and iridium nitrosyl halide derivatives, $M'X_2(NO)(AR_3)_2$, have been reported in a previous paper.[3]

Although the remarkable affinity of ruthenium for nitrosyl ligands has been known for many years[4] the first nitrosyl derivatives of the type, $RuX_3(NO)(AR_3)_2$, have only recently been reported. The synthesis originally employed[5] for the chloro-derivatives involves reaction of preformed hydrated $[RuCl_3(NO)]_n$ or $Na_2[RuCl_5(NO)]$ with the appropriate tertiary phosphine or arsine ligand in an alcoholic solvent, and this method has subsequently been extensively employed.[6,7] The corresponding bromo- and iodo-complexes were prepared by metathetical exchange.[6] More recently reactions of the complexes $RuX(NO)(CO)(PPh_3)_2$[8] and $RuX(NO)(PPh_3)_2$[9] with halogens Y_2 have been used to synthesise the products $RuXY_2(NO)(PPh_3)_2$ (X = Cl; Y = Cl, Br, I; X = Br, Y = Br).

Osmium nitrosyl halide complexes, $OsX_3(NO)(APh_3)_2$ [X = Cl, Br, I] have been prepared by reaction of the appropriate osmium salt M_2OsX_6, and neutral ligand with nitric oxide in 2-methoxyethanol (A = P, As), or by treatment of the preformed complexes, $OsX_3(SbPh_3)_3$ with nitric oxide in benzene (A = Sb).[10,11]

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[3] S. D. Robinson and M. F. Uttley, *J. Chem. Soc.* (*A*), 1971, 1254.

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Other, related osmium nitrosyls recently characterised include $\mathrm{OsCl_2(OH)(NO)(PPh_3)_2}$, $\mathrm{OsCl(CO_3)(NO)(PPh_3)_2}$,[12] $\mathrm{[OsCl(NO_2)(NO)(PMe_2Ph)_3]^+}$, $\mathrm{OsCl_2(NO_2)(NO)(PMe_2Ph)_2}$,[13] $\mathrm{OsCl_2(NHOH)(NO)(PPh_3)_2}$ [14] and $\mathrm{OsCl_2(HgCl)(NO)(PPh_3)_2}$.[15]

Preparation of Ruthenium and Osmium Nitrosyl Chloride and Bromide Complexes $\mathrm{MX_3(NO)(AR_3)_2}$.—The method of synthesis employed in the present work offers substantial advantages over those previously published since it involves a single step reaction only, and eliminates the use of nitric oxide [11] or preformed nitrosyl halide complexes.[5,6,7a] The technique appears to be capable of application to the synthesis of nitrosyl chloride or bromide complexes containing a wide variety of tertiary phosphine or arsine ligands.

Melting point, i.r., analytical, and molecular weight data for some halogenonitrosyl complexes of ruthenium and osmium

Complex	X	R	M.p.	ν(NO) [a]	Found				Required			
					C	H	N	*M*	C	H	N	*M*
$\mathrm{RuX_3(NO)(PR_3)_2}$	Cl	Ph	290	1876	56·2	4·1	1·8		56·8	4·0	1·85	
	Cl [b]	Ph		1876			2·05				1·85	
	Br	Ph	274—276	1871	48·7	4·0	1·4		48·3	3·4	1·65	
	Br [b]	Ph		1871			1·45				1·65	
	I, Cl [c]	Ph	285—288	1865	45·4	3·25	1·55	870	45·75	3·15	1·5	944
	Cl	p-$\mathrm{C_6H_4Me}$	272—275	1834	59·85	5·1	1·45	815	59·6	4·95	1·65	846
	Br	p-$\mathrm{C_6H_4Me}$	278—279	1864	51·7	4·4	1·35	1015	51·5	4·3	1·45	979
	Cl	p-$\mathrm{C_6H_4OMe}$	205—208	1853	53·8	4·4	1·7	901	53·55	4·5	1·5	941
	Cl	p-$\mathrm{C_6H_4Cl}$	247—250	1845	44·8	2·35	1·35	1021	44·65	2·5	1·45	970
	Br	p-$\mathrm{C_6H_4Cl}$	267—269	1878	39·4	2·0	1·1	1195	39·25	2·2	1·3	1103
	I, Cl [c]	p-$\mathrm{C_6H_4Cl}$	299—300	1871	36·85	2·35	1·3	1163	37·55	2·1	1·2	1150
	Br	p-$\mathrm{C_6H_4F}$	(190—207) [d]	1874	43·35	2·6	1·65		43·1	2·4	1·4	
	Cl	Et	(125—130)	1829	31·0	6·2	2·8		30·4	6·4	2·9	
	Br	Et	118—121	1835	24·4	5·15		610	23·75	5·0		607
	Cl	$\mathrm{Pr^i}$	178	1840	39·0	7·5	3·2	548	38·75	7·6	2·5	557
	Br	$\mathrm{Pr^i}$		1826, 1857	31·45	6·0		670	31·25	6·1		691
	Cl	$\mathrm{Bu^n}$	76—77	1835	45·35	8·55	2·3	726	44·9	8·5	2·2	642
	Br	$\mathrm{Bu^n}$	(95—100)	1834	37·75	7·2	1·8		37·15	7·05	1·8	
$\mathrm{RuX_3(NO)(PR_2R')_2}$	Br	Ph,Me	210—215	1867	40·3	3·55	1·95		40·5	3·4	1·8	
$\mathrm{RuX_3(NO)(AsR_3)_2}$	Cl	Ph	293—295	1874	51·1	3·75	1·45		50·85	3·55	1·65	
	Br	Ph	310—312	1869	43·75	3·25	1·4		43·95	3·05	1·4	
	I	Ph	300—302	1856	38·35	2·5		1083	38·45	2·7		1124
$\mathrm{OsX_3(NO)(PR_3)_2}$	Cl	Ph	325—326	1850	51·2	3·7	1·7		50·85	3·55	1·65	
	Cl [b]	Ph		1850			1·8				1·65	
	Br	Ph	decomp. 300	1850	44·2	3·3			43·9	3·05		
	Cl	p-$\mathrm{C_6H_4Me}$	340—342	1805	54·1	4·9	1·6	933	53·6	5·15	1·5	934
	Cl	p-$\mathrm{C_6H_4Cl}$	295—297	1853	41·55	2·55	1·2	1129	40·85	2·3	1·3	1056
	Cl	$\mathrm{Bu^n}$	(72—76)	1811	39·85	7·65	1·75		39·4	7·45	1·9	
$\mathrm{OsX_3(NO)(AsR_3)_2}$	Cl	Ph	310—315	1845	45·8	3·5	1·35	986	46·05	3·25	1·5	938
	Br	Ph	328—330	1842	40·55	3·1	1·45		40·3	2·8	1·3	

[a] Nujol mulls. [b] Samples prepared using pentyl nitrite. [c] $\mathrm{RuClI_2(NO)(PPh_3)_2}$ found Cl, 3·95; I, 27·1; required Cl, 3·75; I, 26·85. $\mathrm{RuClI_2(NO)[P(C_6H_4Cl)_3]_2}$ found Cl, 21·3; I, 22·3; required Cl, 21·55; I, 22·05. [d] Melting points in parentheses determined in air; all other m.p.s under nitrogen. All m.p.s accompanied by decomposition.

The basic reaction employed in this work involves rapid, successive addition of alcoholic solutions of metal halide (ruthenium) or halide salt (osmium), and mnts or pentyl nitrite to a solution of the appropriate tertiary phosphine (or arsine) in a boiling alcoholic solvent. The mixture is boiled for a further 10—30 min, concentrated if necessary, then cooled to give the required complex which may be subsequently recrystallised as necessary. The ruthenium complexes are prepared in ethanol solution, however, syntheses of the corresponding osmium derivatives require more vigorous conditions and were performed in boiling 2-methoxyethanol. Poor yields, and difficulties experienced in isolating several of the products from alcoholic media, probably arise because of a tendency for salt formation to occur (see Ref. 7*b*); this aspect is currently being investigated.

In several syntheses the complexes, $\mathrm{MX_3(NO)(AR_3)_2}$, deposited were contaminated by small amounts (*ca.* 1—10%) of a second nitrosyl-containing species ν(NO) *ca.* 1750 $\mathrm{cm^{-1}}$, which was removed by recrystallisation from dichloromethane–methanol. In the case of $\mathrm{RuCl_3(NO)(PPh_3)_2}$ the presence of this impurity imparted a green colour to the product and was associated with the appearance of an e.s.r. pattern centred at 2·145 G. Fairy and Irving, in their original report [5] on the complexes, $\mathrm{RuX_3(NO)(PR_3)_2}$, noted the presence of a ' feeble paramagnetism ' in some of their products but did not record any extraneous ν(NO) bands. We tentatively formulate these minor products, which we have been unable to isolate, as the dihalides $\mathrm{MX_2(NO)(AR_3)_2}$. Some related di-iodo-derivatives have pre-

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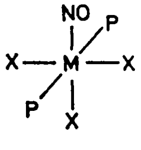
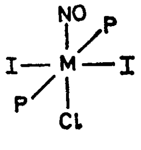
viously been reported but were found to be essentially diamagnetic and were therefore tentatively formulated as metal–metal bonded dimers.[16] It is also interesting to note that a recent synthesis of the related, diamagnetic rhodium nitrosyl dichloride, $RhCl_2(NO)(PPh_3)_2$, afforded traces of the paramagnetic trichloride $RhCl_3(NO)(PPh_3)_2$.[7a]

Structural and Physical Properties of the Products $MX_3(NO)(AR_3)_2$ (X = Cl, Br).—I.r.,[8,11] ^1H n.m.r.[8], and dipole moment data [6,11] have previously been cited in support of an octahedral structure (I) with *trans*-phosphine or arsine ligands for the ruthenium and osmium nitrosyl halide complexes, $MX_3(NO)(AR_3)_2$. The nitrosyl ligand has been assigned as formally NO^+ in these complexes, on the basis of i.r. data.[5,6] Values of $\nu(NO)$ reported in this work for the ruthenium and osmium complexes, $MX_3(NO)(AR_3)_2$, span the ranges 1829—1876 and 1811—1853 cm^{-1} respectively, and are in close agreement with values reported previously for similar complexes. Likewise, therefore, we assign our complexes as formal NO^+ derivatives of octahedral ruthenium(II) and osmium(II) with *trans*-phosphine or -arsine ligands [stereochemistry (I)]. A recent paper [7b] reports reactions of $RuCl_3(NO)$ with (APh_nMe_{3-n}) [A = P or As; n = 1 or 2] in alcoholic media leading to products of stoicheiometries $RuCl_3(NO)(APh_nMe_{3-n})_2$ and $[RuCl_2(NO)(APh_nMe_{3-n})_3]Cl$. N.m.r. (virtual coupling) data show that several of the former complexes may exist in two stereoisomeric forms; one with a *mer*-trihalide configuration (I, see above), the other with a *fac*-trihalide configuration. Related bromo- and iodo-derivatives are also reported. In view of these findings it is possible that some of our products, particularly those containing trialkylphosphines, may also possess the *fac*-trihalide stereochemistry. Molecular-weight data confirm that the complexes are monomeric in benzene solution.


(I)


(II)

Mechanism of Formation of Nitrosyl Halide Complexes $MX_3(NO)(AR_3)_2$.—The reactions of mnts [17] or pentyl nitrite [18,19] with preformed metal hydride complexes to yield nitrosyl derivatives have been known for many years. We suggest that in the syntheses under discussion the formation of nitrosyl complexes occurs by attack *in situ* on ruthenium(IV) or osmium(IV) hydride intermediates formed by reaction of the corresponding halides with the alcoholic solvent employed or with the excess of phosphine or arsine ligand present. Participation by hydridic species of this nature appears feasible since osmium(IV) hydrides, $OsHCl_3(PR_3)_2$ [20,21] and $OsH_2Cl_2(PR_3)_3$ [21] have recently been isolated and related tetrahydrides of ruthenium(IV), $RuH_4(PPh_3)_3$ [22] and osmium(IV), $OsH_4(PR_3)_3$ [23,24] are also known. The mechanism proposed above parallels the one suggested previously for the formation of the rhodium and iridium nitrosyls, $M'X_2(NO)(AR_3)_2$ under similar conditions.[3] If correct, this mechanism suggests that mnts has potential value as a trap for detecting formation of unstable hydridic intermediates.

Attempted Preparation of Ruthenium and Osmium Nitrosyl Tri-iodide Derivatives; Synthesis of Mixed Halide Products.—In the absence of suitable, soluble ruthenium or osmium iodo-species preparation of the iodo-nitrosyl derivatives, $MI_3(NO)(AR_3)_2$, by the single-stage procedure was attempted using ruthenium trichloride or sodium chloro-osmate respectively in the presence of a large excess of lithium or potassium iodide. The success of this approach appears to depend to some extent on the nature of the neutral ligands present. In several instances products analysing as chlorodi-iodo-complexes $MClI_2(NO)(AR_3)_2$ were deposited (see Table) while in others, mixtures of products were obtained. An analytically pure tri-iodo-derivative was isolated in only one instance.

It is well known that the nitrosyl ligand, like carbon monoxide, is strongly *trans*-directing [4,25] and prefers to co-ordinate *trans* to the ligand of weakest *trans*-influence in a given complex.[4] Therefore we assign to these chlorodi-iodo-derivatives the stereochemistry (II), since the *trans*-influence of chloride is less than that of iodide, and we suggest that in the presence of an excess of chloride and iodide the equilibrium between $MI_3(NO)(AR_3)_2$ and $MI_2Cl(NO)(AR_3)_2$ favours the latter complex in most instances. In the light of these observations it is interesting to note that Chatt and Shaw [6] apparently experienced no difficulty in converting the complexes $RuCl_3(NO)(AR_3)_2$ [AR_3 = PEt_2Ph, $AsEt_3$] to the corresponding tri-iodides by metathetical exchange. In contrast Fairy and Irving failed to achieve a similar conversion of $RuCl_3(NO)(PBu_3)_2$ to the tri-iodo analogue.[5]

EXPERIMENTAL

I.r. spectra were recorded using a Perkin-Elmer 457 grating spectrometer. Molecular weights were measured in benzene solution at 43·7° using a Perkin-Elmer–Hitachi

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[21] J. Chatt, D. P. Melville, and R. L. Richards, *J. Chem. Soc.* (*A*), 1971, 895.

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[23] P. G. Douglas and B. L. Shaw, *Chem. Comm.*, 1969, 624; *J. Chem. Soc.* (*A*), 1970, 334.

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[25] D. A. Snyder and D. L. Weaver, *Chem. Comm.*, 1969, 1425.

vapour pressure osmometer. M.p.s were recorded on a Kofler hot stage (in air) or on a Buchi melting point determination apparatus (under nitrogen). Analyses by Dr. Strauss, Oxford.

Tri-*p*-tolyl-, tri-*p*-anisyl-, tri-*p*-chlorophenyl-, methyldiphenyl- and triethyl-phosphines (Maybridge Chemical Co.), triphenyl-phosphine and -arsine (B.D.H.), tri-isopropyl- and tri-n-butyl-phosphines (Geigy) were used without further purification. Platinum metal salts were purchased from Johnson Matthey Ltd.

Analyses, m.p.s and molecular weights are given in the table.

Trichloronitrosylbis(triphenylphosphine)ruthenium.— Warm solutions of ruthenium trichloride (0·13 g) in ethanol (10 ml), and mnts (0·2 g) in ethanol (5 ml) were added successively to a boiling solution of triphenylphosphine (0·54 g) in ethanol (20 ml) and the mixture was heated under reflux for 10 min. After cooling, the precipitate was washed successively with ethanol, water, and methanol, and dried *in vacuo* as green crystals. These showed an extra i.r. band at 1744 cm^{-1} and an e.s.r. signal at 2·145 G attributed to the presence of a paramagnetic nitrosyl impurity. Recrystallisation from dichloromethane–methanol removed this impurity and the associated spectroscopic features, to afford the required product as *orange-brown platelets* (86%).

The following were similarly prepared: *trichloronitrosylbis(tri-*p*-tolylphosphine)ruthenium* as yellow microcrystals (57%); *trichloronitrosylbis(tri-*p*-anisylphosphine)ruthenium* as brown prisms (64%); *trichloronitrosylbis(tri-*p*-chlorophenylphosphine)ruthenium* as orange-brown platelets (60%); *trichloronitrosylbis(tri-isopropylphosphine)ruthenium*, obtained after evaporating the solution to small volume and cooling to 0 °C, as brown crystals (50%); *trichloronitrosylbis(triphenylarsine)ruthenium* as khaki microcrystals (43%).

The following were similarly prepared using ruthenium tribromide: ***tribromonitrosylbis(triphenylphosphine)ruthenium*** as brown microcrystals (80%); ***tribromonitrosylbis(tri-*p*-tolylphosphine)ruthenium*** as brown micro-crystals (45%); ***tribromonitrosylbis(tri-*p*-chlorophenylphosphine) ruthenium*** as orange brown microcrystals (89%); ***tribromonitrosylbis(tri-*p*-fluorophenylphosphine)ruthenium*** as orange microcrystals (19%); ***tribromonitrosylbis(tri-iso-propylphosphine)ruthenium***, obtained after evaporating the solution to small volume and cooling to 0 °C, as brown needles (38%); ***tribromonitrosylbis(triphenylarsine)ruthenium*** as light brown microcrystals (60%).

Trichloronitrosylbis(triethylphosphine)ruthenium.— Warm solutions of ruthenium trichloride (0·13 g) in ethanol (10 ml), and mnts (0·2 g) in ethanol (5 ml) were added successively to a boiling solution of triethylphosphine (0·24 g) in ethanol–water (10 ml, 1 : 1 v/v). The mixture was heated under reflux for 10 min, then concentrated to small volume when the required product separated as light brown prisms (25%).

Similarly prepared was *trichloronitrosylbis(tri-n-butylphosphine)ruthenium*, obtained after evaporation of the solution and dilution of the resultant oil with ethanol–water as light brown microcrystals (15%).

The following were similarly prepared using ruthenium tribromide: ***tribromonitrosylbis(methyldiphenylphosphine)-ruthenium*** recrystallised from dichloromethane–methanol as dark brown crystals (55%); ***tribromonitrosylbis(triethylphosphine)ruthenium*** as brown microcrystals (66%); ***tribromonitrosylbis(tri-n-butylphosphine)ruthenium*** recrystallised from dichloromethane–methanol as yellow-brown platelets (14%).

Chlorodi-iodonitrosylbis(triphenylphosphine)ruthenium.— Ruthenium trichloride (0·13 g) and potassium iodide (2·0 g) were boiled together in ethanol–water (25 ml, 4 : 1 v/v) for two minutes. To the boiling solution were added successively warm solutions of triphenylphosphine (0·52 g) in ethanol (10 ml), and mnts (0·2 g) in ethanol (5 ml). The mixture was heated under reflux for 20 min, cooled and the precipitate washed with ethanol, water, and methanol, then dried *in vacuo* and recrystallised from dichloromethane–methanol as *brown platelets* (95%).

Similarly prepared was *chlorodi-iodonitrosylbis(tri-*p*-chlorophenylphosphine)ruthenium* as brown needles (95%).

Tri-iodonitrosylbis(triphenylarsine)ruthenium.— Lithium iodide (2·0 g) in ethanol (10 ml) and ruthenium trichloride (0·13 g) in ethanol (10 ml) were refluxed together for 5 min. To the boiling solution were added successively warm solutions of triphenylarsine (0·6 g) in ethanol (20 ml) and mnts (0·2 g) in ethanol (5 ml). The mixture was heated under reflux for 15 min then, after cooling, the precipitate was washed successively with ethanol, water, and methanol, dried *in vacuo* and recrystallised from dichloromethane–methanol as *brown platelets* (84%).

Trichloronitrosylbis(triphenylphosphine)osmium.— Warm solutions of sodium chloro-osmate (0·19 g) in 2-methoxyethanol (10 ml) and mnts (0·2 g) in 2-methoxyethanol (5 ml) were added successively to a boiling solution of triphenylphosphine (0·36 g) in 2-methoxyethanol (10 ml). The mixture was heated under reflux for 30 min. Methanol (20 ml) was added and, after cooling, the precipitate was washed successively with ethanol, water, and methanol then dried *in vacuo* as *brown microcrystals* (91%).

The following were similarly prepared: *trichloronitrosylbis(tri-*p*-tolylphosphine)osmium* as salmon-pink microcrystals (64%); *trichloronitrosylbis(tri-*p*-chlorophenylphosphine)osmium* obtained from solution, upon careful dilution with water, as salmon-pink needles (56%); *trichloronitrosylbis(tri-n-butylphosphine)osmium*, obtained from solution upon evaporation to an oil and dilution with ethanol–water, as orange-brown crystals (31%); *trichloronitrosylbis(triphenylarsine)osmium* as brown microcrystals (64%).

The following were similarly prepared using ammonium bromo-osmate: ***tribromonitrosylbis(triphenylphosphine)-osmium*** as brown crystals (77%); ***tribromonitrosylbis(triphenylarsine)osmium*** as dark brown crystals (57%) from dichloromethane–methanol.

Trichloronitrosylbis(triphenylphosphine)ruthenium, Synthesis involving n-Pentyl Nitrite.—To a boiling solution of triphenylphosphine (0·54 g) in ethanol (20 ml) were added successively a warm solution of ruthenium trichloride (0·13 g) in ethanol (10 ml), and n-pentyl nitrite (2·0 ml). The mixture was heated under reflux for 5 min. After cooling, the precipitate was washed successively with ethanol, water, and methanol then dried *in vacuo* as green crystals showing an extra i.r. band at 1744 cm^{-1} attributed to a nitrosyl-containing impurity (see above). Recrystallisation from dichloromethane–methanol removed this impurity to yield the required product as *orange-brown platelets* (68%). *Tribromonitrosylbis(triphenylphosphine)-ruthenium* was similarly prepared, using ruthenium tribromide, as light brown microcrystals (22%).

Trichloronitrosylbis(triphenylphosphine)osmium, Synthesis *involving n-Pentyl Nitrite*.—Sodium chloro-osmate (0·19 g) in 2-methoxyethanol (10 ml), and n-pentyl nitrite (2 ml) were successively added to a boiling solution of triphenylphosphine (0·36 g) in 2-methoxyethanol (25 ml). The mixture was heated under reflux for 30 min, then diluted with methanol (20 ml). After cooling, the precipitate was washed successively with ethanol, water, and methanol, dried *in vacuo* and recrystallised from dichloromethane–methanol as *brown microcrystals* (70%).

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