Reactions of Complexes of Ruthenium and Osmium Halides with Ammonia, Amines, and Hydrazine

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Ammonia and primary amines (am) react with $[MX_3(PR_3)_3]$ (M = Ru or Os, X = Cl or Br, and PR_3 = tertiary phosphine) in ethanol at 20° to form M(II) complexes, *mer*-$[MX_2am(PR_3)_3]$, and acetaldehyde. Secondary and tertiary amines with $[MX_3(PMe_2Ph)_3]$ also cause reduction, but the product is an alcohol complex $[MX_2(C_2H_5OH)(PMe_2Ph)_3]$. The reduction may occur through a hydride complex intermediate because some hydrogen is produced in all the above reactions. The alcohol complexes are probably formed for steric reasons because the least sterically hindered secondary amine, piperidine, forms a piperidine complex.

When the alcohol contains a small amount of water di-n-alkylamines $(C_nH_{2n+1})_2NH$ are dealkylated to form the corresponding primary amine complexes $[MX_2\,am\,(PR_3)_3]$ (*cf.* similar decarbonylation of alcohol and aldehydes). The cleaved alkyl group generally appears as $C_{n-1}H_{2n}$ and all the lower n-alkanes down to methane, but from dimethylamine higher hydrocarbons are obtained and from diethylamine a little propane.

Hydrazine in limited amounts forms mononuclear complexes $[MCl_2(N_2H_4)(PMe_2Ph)_3]$ or more commonly hydrazine-bridged complexes $[M_2X_4(N_2H_4)_2(PR_3)_4]$. Nitrogen, hydrogen, and hydrazine hydrochloride are also produced. Under more vigorous reaction conditions $[Ru(NH_3)_5N_2]^{2+}$ is formed.

We have recently described the preparation [1] of the complexes $[MX_3(PR_3)_3]$ (M = Ru or Os, X = Cl or Br, and PR_3 = tertiary phosphine) which we intended to convert into neutral nitrido-complexes analogous to the rhenium compounds already known,[2] by reaction with hydrazine. However, the reaction with these complexes yielded a variety of products dependent upon reaction conditions, and it seemed more likely that a less vigorous reagent such as ammonia might yield nitrido-complexes. Thus the interactions of ammonia and, for comparison, of a variety of amines, as well as hydrazine, with the phosphine complexes were investigated, and here we record our findings.

Reactions of Ammonia and Primary Amines.—Upon shaking a mixture of the ruthenium or osmium halide complex, $[MX_3(PR_3)_3]$, and ammonia, or a primary amine in ethanol, a slow reaction occurs, yielding $[MX_2\,am\,(PR_3)_3]$ (where M = Ru or Os, am = ammonia or primary amine, X = Cl or Br, and PR_3 = tertiary phosphine). The reaction is unaffected by the presence of water in the ethanol. After the reaction amine hydrochloride or ammonium chloride was recovered to the extent of 80—95% of the chlorine removed from the metal. When the reactions are carried out *in vacuo*, about 0·05 equivalent of hydrogen is always found, accompanied by some acetaldehyde. We have no firm indication of the mechanism of this reaction, but since reduction in alkaline ethanol commonly leads to hydrides, and some hydrogen is evolved during the reaction, a hydrido-complex is a possible transient intermediate.

The products are diamagnetic, yellow or orange-yellow solids which are slightly air-sensitive, but in solution they are much more sensitive, and decompose rapidly in the absence of small amounts of ammonia or the appropriate amine. The analysis does not distinguish between an imido-formulation $[MX_2(NRH)(PR_3)_3]$ or an amine formulation $[MX_2(NRH_2)(PR_3)_3]$ but the diamagnetism confirms the latter. The complexes react with hydrochloric acid to re-form $[MX_3(PR_3)_3]$ together with ammonium chloride or amine hydrochloride (80—90%) and hydrogen. Dimethylphenylphosphine complexes were investigated most thoroughly because they give the most easily isolable products. Those from diethylphenylphosphine are much more soluble and difficult to crystallise. Only the alkylamines gave well defined products, the arylamines yielded intractable dark-coloured solids.

The infrared spectra of the products (Table 1) in the metal–halogen stretching region show only one band assignable to ν(M–Cl) by comparison with the corresponding bromides. This one band is consistent with a *trans*-arrangement of the halogen atoms. The ammine complexes show bands assignable to N–H vibrations which are very similar to those in the spectra of other ammines.[3]

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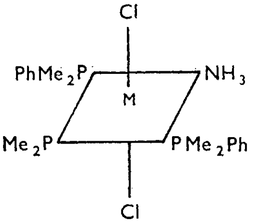
[1] J. Chatt, G. J. Leigh, D. M. P. Mingos, and R. J. Paske, *J. Chem. Soc.* (*A*), 1968, 2636.

[2] J. Chatt, J. D. Garforth, N. P. Johnson, and G. A. Rowe, *J. Chem. Soc.*, 1964, 1012.

[3] K. Nakamoto, 'The Infrared Spectra of Complex Molecules,' Wiley, New York and London, 1967.

The ^1H n.m.r. spectrum of dichloroamminetris(dimethylphenylphosphine)osmium(II) shows no signals assignable to protons on the nitrogen. However, the methyl protons appear as a triplet of intensity 2 centred at −1·56 p.p.m. with respect to tetramethylsilane and a doublet of intensity 1 centred at −1·86 p.p.m., consistent with a meridional (*mer*) arrangement of the phosphine ligands. The ruthenium analogue has a poorly resolved ^{31}P resonance spectrum consisting of a triplet of intensity 1 (112·3 p.p.m. with respect to triphenyl phosphite) and a doublet of intensity 2, *J* (*P*Ru*P*) 34 c./sec. (121·8 p.p.m. with respect to triphenyl phosphite) which also supports the *mer*-configuration. The dimethylphenylphosphine complexes thus have a configuration (I), and since all the complexes listed in Table 1 have similar long-wave infrared spectra, it is highly probable that they have the same configuration.



(I)

TABLE 1

Ammine and primary amine complexes of ruthenium and osmium

	M.p.	Colour	Analyses [a]					M [a]	Infrared spectrum [b] 360—200 cm.$^{-1}$
			C	H	N	Cl or Br	P		
$[RuCl_2(NH_3)(PMe_2Ph)_3]$ [c]	148—152°	Yellow	47·6(47·8)	6·0(6·0)	2·4(2·3)	12·2(11·8)	14·5(15·4)	653(603)	356m, 347w, 336w, 328w, 319w, *313*s, 231m
$[RuBr_2(NH_3)(PMe_2Ph)_3]$	171—174(d.)	Yellow-orange	41·8(41·6)	5·5(5·2)	2·1(2·0)	—	—	702(692)	352m, 345m, 334w, 317m, 237m
$[OsCl_2(NH_3)(PMe_2Ph)_3]$ [c]	121—125(d.)	Yellow	41·7(41·6)	5·4(5·2)	2·2(2·0)	10·9(10·3)	—	737(692)	354m, 333m, 318m, *291*s, 234m
$[OsBr_2(NH_3)(PMe_2Ph)_3]$	125—130(d.)	Yellow-orange	36·5(36·9)	4·7(4·6)	1·8(1·8)	—	—	789(781)	353m, 344w, 332w, 319m, 290m, 278w, 243w
$[RuCl_2(NH_2Me)(PMe_2Ph)_3]$ [c]	163—164	Yellow	48·1(48·6)	6·3(6·2)	2·4(2·3)	12·0(11·5)	15·4(15·1)	627(618)	352m,br, 324m, *305*s, 277w, 234m
$[RuBr_2(NH_2Me)(PMe_2Ph)_3]$ [c]	166—167	Yellow-orange	43·6(42·5)	5·9(5·4)	2·3(2·0)	—	—	700(706)	350m, 322w, 314m, 300w, 280w, 253m
$[OsCl_2(NH_2Me)(PMe_2Ph)_3]$ [c]	133—135(d.)	Yellow	41·9(42·5)	5·3(5·4)	2·2(2·0)	10·2(10·1)	—	683(706)	355m, 325w, 318m, *291*s, 279m, 240m
$[OsBr_2(NH_2Me)(PMe_2Ph)_3]$ [c]	132—136(d.)	Yellow-orange	38·4(37·7)	6·1(4·8)	1·6(1·8)	—	—	783(795)	352m, 332w, 317m, 289m, 278w, 242w
$[OsCl_2(NH_2Et)(PMe_2Ph)_3]$ [c]	154—156(d.)	Yellow	43·3(43·4)	5·2(5·5)	1·9(1·9)	9·3(9·8)	—	702(720)	—
$[OsCl_2(NH_2Pr^n)(PMe_2Ph)_3]$	128—132(d.)	Yellow	43·8(44·1)	5·6(5·7)	2·0(1·9)	8·5(9·7)	—	752(734)	—
$[OsCl_2(NH_2Pr^i)(PMe_2Ph)_3]$	108—112(d.)	Yellow	43·9(44·1)	5·7(5·7)	1·9(1·9)	8·8(9·7)	—	749(734)	—
$[RuCl_2(NH_2Bu^n)(PMe_2Ph)_3]$ [c]	161—163(d.)	Yellow	51·7(51·0)	7·1(6·7)	2·0(2·1)	11·1(10·8)	13·8(14·1)	679(659)	359m, 351m, 324w, *306*s, 265w, 238w
$[RuBr_2(NH_2Bu^n)(PMe_2Ph)_3]$ [c]	177—181(d.)	Yellow	45·5(44·9)	6·6(5·2)	2·5(1·9)	—	—	742(748)	355m, 333w, 323w, 311m, 304m, 265w, 243m
$[OsCl_2(NH_2Bu^n)(PMe_2Ph)_3]$ [c]	132—136(d.)	Yellow	44·9(44·9)	5·8(5·9)	1·9(1·9)	9·4(9·5)	—	757(748)	357s, 335w, 329w, 315m, *290*s, 250w
$[OsBr_2(NH_2Bu^n)(PMe_2Ph)_3]$ [c]	128—133(d.)	Yellow	40·2(40·1)	5·7(5·3)	1·7(1·7)	—	—	841(837)	355s, 334w, 327w, 314m, 278w, 262w
$[OsCl_2(NH_2Et)(PEt_2Ph)_3]$	107—111(d.)	Yellow	47·6(47·8)	6·5(6·5)	1·9(1·7)	9·2(8·8)	—	835(804)	—

All compounds are non-conductors in nitrobenzene solution.

[a] Required values in parentheses. [b] Frequencies in italics assigned to metal–chlorine stretch. [c] Diamagnetic in the solid state; other compounds were not investigated.

Reactions of Secondary and Tertiary Amines.—Secondary and tertiary amines of types NHR_2 and NR_3 (R = alkyl groups) react with $[MX_3(PMe_2Ph)_3]$ in ethanol under absolutely anhydrous conditions to yield $[MX_2(C_2H_5OH)(PMe_2Ph)_3]$. The presence of moisture does not affect the tertiary amine reactions, but the secondary amines give a different reaction, described below.

The ethanol products are relatively unstable, both in the solid and in solution, and easily form $[MX_2(PMe_2Ph)_3]$, which is green. Their infrared spectra show a sharp band at about 3500 cm.$^{-1}$ which is assignable to the O–H stretch of co-ordinated ethanol. The ethanol is replaced by methanol on recrystallisation from methanol, but the brown crystals of the methanol complex decompose even under nitrogen. The reaction of secondary amines with $[OsCl_3(PMe_2Ph)_3]$ in 2-methoxyethanol yields the corresponding 2-methoxyethanol complex mixed with $[(PMe_2Ph)_3OsCl_3Os(PMe_2Ph)_3]Cl$.[4]

The far-infrared spectra show a single ν(M–Cl) stretching frequency and the configuration (I), with alcohol in place of ammonia, again seems likely.

As with the reactions of primary amines and ammonia, acetaldehyde is produced when the alcohol complexes are formed, and amine hydrochlorides were isolated in 80—90% yields. Again, a hydride or, possibly, $[MX_2(PMe_2Ph)_3]$ could be intermediates. The overall reaction appears to be:

$$2[MX_3(PMe_2Ph)_3] + 3C_2H_5OH + 2NR_2H \longrightarrow$$
$$2[MX_2(C_2H_5OH)(PMe_2Ph)_3] + 2NR_2H_2X + CH_3CHO$$

We believe that steric factors control whether an amine or an alcohol complex is produced, because models show that these metal–tertiary-phosphine complexes are very crowded. The only secondary amine we were able to incorporate was piperidine, which requires less space than dialkyl- or trialkylamines.

It is of interest that when solutions of $[MX_3(PR_3)_3]$ in ethanol are made more strongly alkaline, for example, with potassium hydroxide in place of amine, carbonyl complexes are produced.[5] Carbonyl complexes are also produced under these conditions from $[(R_3P)_3RuCl_3Ru(R_3P)_3]Cl$.[5,6]

Reactions of Secondary Amines in the Presence of Water.—When undried 'absolute' alcohol is used as solvent for the reactions of *secondary* amines with $[RuCl_3(PMe_2Ph)_3]$ or $[OsCl_3(PMe_2Ph)_3]$ considerable decomposition takes place and a relatively low yield (30—50%) of the *primary* amine complex is obtained. The products were completely characterised for reactions of Me_2NH, Et_2NH, Pr^n_2NH, and Bu^n_2NH. The reactions of Pr^i_2NH, $(cyclo\text{-}C_6H_{11})_2NH$, and $(C_6H_{13}{}^n)_2NH$ were

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[4] J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 1961, 896.

[5] J. Chatt, B. L. Shaw, and A. E. Field, *J. Chem. Soc.*, 1964, 3466.

[6] R. H. Prince and K. A. Raspin, *Chem. Comm.*, 1966, 156.

only cursorily investigated but appear to follow a similar pattern; the products were identified by infrared spectroscopy.

It is difficult to envisage how these dealkylation reactions occur. The chloride lost by the metal was recovered (80—90%) as the *secondary* amine hydrochloride. No acetaldehyde could be detected by gas chromatography and the secondary amines were found not to react with the M^{II}–ethanol complexes described above. This suggests that the alcohol is not involved in the reduction of M^{III} to M^{II} and that the ethanol complexes are not intermediates. Cleavage of the displaced alkyl group also occurs, probably during the reduction, and the hydrocarbon fragments obtained are shown in Table 2. Hydrogen was also detected in greater amounts than in the reactions with primary amines.

Table 2 suggests that steric factors influence the reaction because (cyclo-C_6H_{11})$_2$NH is cleaved, whereas piperidine forms a piperidine complex. It also shows that the alkyl chain is cleaved mainly in two places, between nitrogen and C-1 and between C-1, and C-2. The reduction of transition-metal halides by amines is common.[7] The reactions are often heterogeneous, the products complex, and the mechanism is not understood. It may be that a metal hydride is involved in our system, because water is a necessary component, and is commonly a source of co-ordinated hydride.

The decarbonylation, *i.e.* dealkylation, of alcohols and aldehydes to produce hydrocarbons is now a well known reaction of transition metal complexes of tertiary phosphines, and the dealkylation of the secondary amines above is probably closely related to such reactions.

Reactions of Hydrazine.—The reactions of hydrazine have some similarity to those of ammonia; for example, the products are generally M^{II} compounds and the hydrazine is co-ordinated in the position vacated by the chloride. Hydrazine is, however, bidentate and there is a tendency for the complexes to become binuclear through bridging hydrazine molecules with the elimination of a molecule of the tertiary phosphine. Also, transition metal compounds often catalyse the disproportionation of hydrazine to nitrogen and ammonia, a reaction first observed in ruthenium chemistry by Goremykin.[8,9] This disproportionation occurs in the reaction of a large excess of hydrazine with [$RuCl_3(PR_3)_3$] and leads eventually to [$Ru(NH_3)_5N_2$]Cl_2.[10]

TABLE 2

Reactions of osmium and ruthenium complexes with secondary amines in the presence of water

Initial complex	Amine	Complex isolated	Proportions of volatile products
[$OsCl_3(PMe_2Ph)_3$]	Me_2NH	[$OsCl_2(MeNH_2)(PMe_2Ph)_3$]	$CH_4 \sim C_2H_6 \sim$ n-$C_3H_8 \sim$ n-C_4H_{10}
[$OsCl_3(PMe_2Ph)_3$]	Et_2NH	[$OsCl_2(EtNH_2)(PMe_2Ph)_3$]	$CH_4 \gg C_2H_6 \sim$ n-C_3H_8
[$OsCl_3(PMe_2Ph)_3$]	$Pr^n{}_2NH$	[$OsCl_2(Pr^nNH_2)(PMe_2Ph)_3$]	$C_2H_6 > CH_4 \sim$ n-C_3H_8
[$OsCl_3(PMe_2Ph)_3$]	$Pr^i{}_2NH$	[$OsCl_2(Pr^iNH_2)(PMe_2Ph)_3$] (in part)	$CH_4 \gg C_2H_6 \sim$ n-C_3H_8
[$OsCl_3(PMe_2Ph)_3$]	$Bu^n{}_2NH$	[$OsCl_2(Bu^nNH_2)(PMe_2Ph)_3$]	n-$C_3H_7 > CH_4 \sim C_2H_6 >$ n-C_4H_{10}
[$OsCl_3(PMe_2Ph)_3$]	(n-C_6H_{13})$_2$NH	[$OsCl_2$(n-$C_6H_{13}NH_2$)(PMe_2Ph)$_3$]	n-$C_5H_{12} > CH_4 \sim C_2H_6 \sim$ n-$C_3H_8 \sim$ n-C_4H_{10}
[$OsCl_3(PMe_2Ph)_3$]	(cyclo-C_6H_{11})$_2$NH	[$OsCl_2$(cyclo-$C_6H_{11}NH_2$)(PMe_2Ph)$_3$]	No volatile alkanes
[$OsCl_3(PMe_2Ph)_3$]	Piperidine	[$OsCl_2(C_5H_{10}NH_2)(PMe_2Ph)_3$]	—
[$RuCl_3(PMe_2Ph)_3$]	Me_2NH	[$RuCl_2(MeNH_2)(PMe_2Ph)_3$]	—
[$RuCl_3(PMe_2Ph)_3$]	$Bu^n{}_2NH$	[$RuCl_2(Bu^nNH_2)(PMe_2Ph)_3$]	—

TABLE 3

Mononuclear complexes of ruthenium and osmium with hydrazines

			Analyses [a]						
	M.p.	Colour	C	H	N	Cl or Br	P	*M* [a]	Infrared spectrum [b] 400—200 cm.$^{-1}$ /
[$RuCl_2(N_2H_4)(PMe_2Ph)_3$] [c]	146—150°(d.)	Orange	46·6(46·6)	6·7(6·0)	4·4(4·5)	11·5(11·5)	14·9(15·0)	577(618)	401s, 344w, *312*s, 232m
[$RuBr_2(N_2H_4)(PMe_2Ph)_3$]	166—169(d.)	Orange	41·9(40·7)	5·7(5·2)	3·8(4·0)	22·7(22·6)	—	Too insol.	400s, 350w, 280w, 231m
[$RuCl_2(NH_2NHPh)(PMe_2Ph)_3$]	156—159(d.)	Yellow-green	51·6(52·0)	6·0(5·9)	4·2(4·0)	—	13·5(13·4)	Too insol.	—
[$OsCl_2(N_2H_4)(PMe_2Ph)_3$]	122—126(d.)	Orange	40·7(40·7)	5·5(5·2)	3·8(4·0)	10·0(10·0)	—	586(707)	—
[$OsCl_2(NH_2NHPh)(PMe_2Ph)_3$]	146—149(d.)	Yellow	45·8(46·0)	5·4(5·2)	3·6(3·6)	8·9(9·1)	—	Too insol.	—

All compounds are non-conductors in nitrobenzene solution.

[a] Required values in parentheses. [b] Frequency in italics assigned to metal–chlorine stretch. [c] Diamagnetic in solid state; other compounds not tested.

TABLE 4

Binuclear complexes of ruthenium and osmium with hydrazine

			Analyses [a]						
	M.p.	Colour	C	H	N	Cl or Br	P	*M* [a]	Infrared spectrum [b] 400—200 cm.$^{-1}$
[{$RuCl_2(N_2H_4)(PMe_2Ph)_2$}$_2$] [c]	decomp. > 150°	Pale yellow	40·1(40·0)	6·2(5·4)	5·7(5·8)	14·9(14·8)	13·1(12·9)	Too insol.	*306*m, 264w, 239w
[{$RuBr_2(N_2H_4)(PMe_2Ph)_2$}$_2$]	221—223(d.)	Orange-yellow	34·4(33·7)	4·9(4·6)	5·0(4·9)	28·1(28·1)	—	Too insol.	377w, 365w, 348w, 264w, 227w, 211w
[{$RuCl_2(N_2H_4)(PEt_2Ph)_2$}$_2$]	183—186(d.)	Orange-yellow	44·6(44·8)	6·4(6·3)	5·3(5·8)	13·0(13·2)	11·3(11·6)	Too insol.	375m, *315*m, 266m, 254m, 226m
[{$RuBr_2(N_2H_4)(PEt_2Ph)_2$}$_2$] [c]	187—189(d.)	Orange-yellow	38·6(38·4)	5·6(5·4)	4·7(4·5)	—	—	Too insol.	375m, 314w, 304w, 265m, 254m, 224s
[{$RuCl_2(N_2H_4)(PBu^n{}_2Ph)_2$}$_2$]	143—146(d.)	Orange-yellow	51·6(51·9)	7·8(7·7)	4·4(4·3)	12·0(11·0)	10·1(9·6)	1241(1296)	395s, *315*s, 266m, 239s
[{$RuCl_2(N_2H_4)(PPh_3)_2$}$_2$]	174—177(d.)	Orange-yellow	58·8(59·3)	4·8(4·7)	3·8(3·8)	10·0(9·8)	8·1(8·5)	Too insol.	*318*s, 269m, 250m
[{$OsCl_2(N_2H_4)(PEt_2Ph)_2$}$_2$]	180—182(d.)	Yellow	38·2(38·4)	6·1(5·4)	4·3(4·5)	11·2(11·4)	—	Too insol.	—
[{$OsCl_2(N_2D_4)(PBu^n{}_2Ph)_2$}$_2$]	114—118(d.)	Pale yellow	46·9(45·5)	7·3(7·3)	3·7(3·8)	10·6(9·5)	—	1273(1482)	—

All compounds are non-conductors in nitrobenzene solution.

[a] Required value in parentheses. [b] Frequencies assigned to metal–chlorine stretch in italics. [c] Diamagnetic in solid state; other compounds not tested.

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[7] G. W. A. Fowles, *Progr. Inorg. Chem.*, 1964, **6**, 1.

[8] T. D. Artokratova and V. J. Goremykin, *Izvest. Akad. Nauk. S.S.S.R., Otdel. khim. Nauk*, 1947, 427.

[9] C. K. Prout and H. M. Powell, *J. Chem. Soc.*, 1962, 137.

[10] A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsalu, and C. V. Senoff, *J. Amer. Chem. Soc.*, 1967, **89**, 5595.

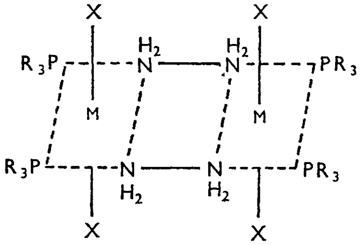
The mononuclear complexes, $[MCl_2(N_2H_4)(PMe_2Ph)_3]$, were obtained under mild conditions with a limited amount of hydrazine, and are listed in Table 3. They were either too insoluble for molecular-weight determination or else decomposed in solution. They are diamagnetic. The hydrazine was recovered from the complexes upon acid degradation to the extent of 75—95%. The infrared spectra again indicate *trans*-halogens and so configuration (I) is again probable. The spectra also have two or three strong bands in the 3350—3000 cm.$^{-1}$ region. The binuclear complexes (see below) generally have more complicated spectra in this region, which serves to differentiate them from the mononuclear and confirms that the function of the hydrazine is different in each.

The mononuclear complexes could be obtained only with dimethylphenylphosphine. Upon warming those of ruthenium in petroleum (b.p. 60—80°), they lost a molecule of the phosphine to form binuclear complexes. The complexes $[MX_3(PEt_2Ph)_3]$ formed the binuclear product directly with hydrazine (see Table 4). The osmium complexes $[OsX_3(PR_2Ph)_3]$ ($R = Pr^n$ or Bu^n) gave a variety of products, including complexes of molecular nitrogen, which will be described separately. The analysis does not distinguish between the possible formulations $[\{MX_2(N_2H_4)(PR_3)_2\}_n]$ (A) or $[MX_2(NH_3)_2(PR_3)_2]$ (B). However, 65—80% hydrazine was recovered by acid treatment, confirming (A). The complexes are generally too insoluble for molecular-weight determination but $[\{RuCl_2(N_2H_4)(PBu^n{}_2Ph)_2\}_2]$ is sufficiently soluble and is dimeric in benzene solution. They all have similar infrared spectra in the N–H stretching region, which indicates that all are probably dimeric. They are also non-electrolytes in nitrobenzene.

The metal atoms could be bridged by hydrazine or by halogen. However, phenylhydrazine does not form binuclear complexes, suggesting that hydrazine is the bridging group. The far-infrared spectra shown in Table 4 are consistent with two *trans*-halogen atoms co-ordinated to each metal atom.

It has been suggested [11] that the N–N stretching frequency provides the most satisfactory method of distinguishing between a unidentate and a bidentate hydrazine.[12] It occurs at 960—985 cm.$^{-1}$ in complexes of the First Transition Series containing bridging hydrazine and at a somewhat lower frequency if they contain unidentate hydrazine.[11] Unfortunately, we were unable to use this criterion, because bands also occur in this region of the spectrum in the spectra of the corresponding complexes $[MCl_3(PR_3)_3]$. The present evidence suggests (II) as the most likely structure.

The preparative reactions with hydrazine all produced nitrogen, hydrogen, and hydrazine hydrochloride, suggesting that hydrazine reduces M^{III} to M^{II}. Further reaction of the ruthenium hydrazine complexes with hydrazine hydrate yielded a mixture of unstable salts whose spectra had a sharp band characteristic of $[Ru(NH_3)_5N_2]^{2+}$ [10] irrespective of the phosphine involved. Ammonia was produced as well as the other by-products described.



(II)

Hydrazine with tertiary phosphine derivatives of rhenium in ethanol is readily degraded to yield nitrido-complexes [2] but with similar osmium and ruthenium compounds it forms hydrazine complexes, and in excess may react vigorously with disproportionation to ammonia and nitrogen, giving metal ammines and complexes of molecular nitrogen. These reactions are still being investigated, and will be reported later.

EXPERIMENTAL

Ruthenium trichloride and osmium tetroxide were kindly loaned by Johnson Matthey & Co. Ltd. Phosphines were generally synthesised by standard procedures, and other materials were obtained commercially.

Hydrazine was determined using *p*-dimethylaminobenzaldehyde.[13]

Molecular weights were measured osmometrically in benzene solution, and magnetic moments by a Faraday balance. The infrared spectra were obtained in the region 400—200 cm.$^{-1}$ using a Grubb-Parsons DM4 spectrometer. The ^1H and ^{31}P n.m.r. spectra were measured in dichloromethane solution on a Perkin-Elmer R10 spectrometer. Melting points are generally in the air. Analyses are shown in the Tables.

All manipulations were carried out in an atmosphere of pure, dry nitrogen. Reactions *in vacuo* were carried out in sealed tubes fitted with break-seals. After the reaction, volatiles and permanent gases were removed using a vacuum line.

Reactions of Ammonia and Primary Amines.—Dichloro(ammine)tris(dimethylphenylphosphine)ruthenium(II). A saturated solution of ammonia in dry ethanol (30 ml.) was added to trichlorotris(dimethylphenylphosphine)ruthenium(III) (1·65 g.) in a nitrogen-filled vessel fitted with two break-seals and a constriction for sealing. The mixture was degassed to remove as much nitrogen as possible and sealed. The suspension was shaken at room temperature for 1 week. The vessel was then opened and the non-condensable gas (28·9 ml. at 20°/6·02 cm.) removed and shown to be a mixture of nitrogen and hydrogen. The yellow solid was filtered off and recrystallised from ethanol, to which a small amount of dry ammonia had been added, to give the *product* (1·29 g., 81%), m.p. 148—152°. The compound was a non-conductor in nitrobenzene solution, and diamagnetic in the solid state. The filtrate from the preparation was evaporated dry, leaving a dark residue.

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[11] D. Nicholls, M. Rowley, and R. Swindells, *J. Chem. Soc.* (*A*), 1966, 950.

[12] L. Sacconi and A. Sabatini, *J. Inorg. Nuclear Chem.*, 1963, **25**, 1389.

[13] G. W. Watt and J. D. Chrisp, *Analyt. Chem.*, 1952, **24**, 2006.

Extraction with ether yielded ammonium chloride (0·13 g., 95%). The solvent was shown by gas–liquid chromatography to contain acetaldehyde. A somewhat lower yield of ruthenium(II) complex was obtained using 0·880 ammonia rather than dry ammonia gas.

Dibromo(*ammine*)*tris*(*dimethylphenylphosphine*)*ruthenium*(II). Tribromotris(dimethylphenylphosphine)ruthenium(III) (0·20 g.) was suspended in a solution of 0·880 ammonia (0·50 ml.) in ethanol (10 ml.) and the mixture heated under reflux for 10 min. Upon cooling the solution, an orange-yellow solid crystallised out and was recrystallised from ethanol–0·880 ammonia yielding the *product* (0·15 g., 82%), m.p. 171—174° (decomp.). The compound was a non-conductor in nitrobenzene solution.

The *osmium ammine compounds* were prepared by a method essentially similar to that described for the dibromo(ammine)ruthenium(II) complex in 40% yield (dichloride) and 80% yield (dibromide).

Dichloro(*methylamine*)*tris*(*dimethylphenylphosphine*)*ruthenium*(II). Trichlorotris(dimethylphenylphosphine(ruthenium(III) (0·40 g.) was suspended in a solution of methylamine (0·10 ml., 5 mol.) in dry ethanol (10 ml.) in a vessel of the type described for the ammonia reaction. The suspension was shaken at room temperature for 24 hr. and then worked up as described for the ammonia. The non-condensable gas (nitrogen and hydrogen) occupied 28·99 ml. at 1·132 cm. pressure at room temperature. The yellow solid was recrystallised from ethanol–methylamine giving the *product* (0·31 g., 78%), m.p. 163—164°. The compound was a non-conductor in nitrobenzene solution and diamagnetic in the solid state. Methylamine hydrochloride (93%) was recovered and acetaldehyde detected.

A similar preparation in the presence of 200 mol. of water gave a very similar yield of products.

An essentially similar preparation yielded the *dibromo-ruthenium* analogue (75% yield) and the *dichloro-* and *dibromo-ruthenium* compounds with n-butylamine (76% and 82% yields, respectively).

Dichloro(*methylamine*)*tris*(*dimethylphenylphosphine*)*osmium*(II). Trichlorotris(dimethylphenylphosphine)osmium(III) (0·40 g.) was suspended in a solution of methylamine (0·04 ml.) in ethanol (30 ml.) and the mixture shaken for 24 hr. at room temperature. The yellow *solid* (0·35 g., 87%) was filtered off and recrystallised from ethanol–methylamine, m.p. 133—135° (decomp.). The compound is a non-conductor in nitrobenzene solution and is diamagnetic in the solid state.

By the same method were synthesised *dichloro-osmium*(II) derivatives of ethylamine (90%), n-propylamine (75%), isopropylamine (50%), and n-butylamine (70%); *dichloro*(*ethylamine*)*tris*(*diethylphenylphosphine*)*osmium*(II) (90%); and *dibromo-osmium*(II) derivatives of metnylamine (70%) and n-butylamine (70%) with dimethylphenylphosphine.

Reactions of Anhydrous Secondary and Tertiary Amines.—*Dichloro*(*ethanol*)*tris*(*dimethylphenylphosphine*)*ruthenium*(II). Trichlorotris(dimethylphenylphosphine)ruthenium(III) (0·45 g.) was suspended in a solution of trimethylamine (0·20 ml.) and water (3·00 ml.) in ethanol (10 ml.) in the type of vessel used for the ammonia reactions. The mixture was allowed to react for 120 hr. The non-condensable gas (28·99 ml. at room temperature and 2·253 cm. pressure) was hydrogen. The yellow *solid* was filtered off, but could not be recrystallised owing to its rapid decomposition in common solvents. Similarly the molecular weight could not be determined. Yield 0·21 g. (47%), m.p. 102—105° (decomp.). Acetaldehyde, and trimethylamine hydrochloride (78%) were also obtained. The compound was diamagnetic in the solid state. The infrared spectrum showed a single band at 3540 cm.$^{-1}$ assignable to ν_{OH} of co-ordinated alcohol. The region below 400 cm.$^{-1}$ was complex: 401s, 360m, 329s, 282w, 230w plus a band (s) at 314 cm.$^{-1}$ assigned to ν_{Ru-Cl}.

The same complex was obtained using dry trimethylamine in anhydrous ethanol; triethylamine, ethanol, and water; tri-n-propylamine, ethanol, and water; dry tri-n-butylamine in anhydrous ethanol; and tri-n-butylamine, ethanol, and water. It was also obtained using anhydrous dimethylamine in dry ethanol and anhydrous di-n-butylamine in dry ethanol. The yields were always 50—60% and acetaldehyde was always a by-product.

An impure *dibromo-analogue* was made. This was diamagnetic. Its infrared spectrum had a band at 3540 cm.$^{-1}$ and below 400 cm.$^{-1}$ was as follows: 399s, 355m, 330m, 304w, 273w, 239w.

Dichloro(*ethanol*)*tris*(*dimethylphenylphosphine*)*osmium*(II). Trimethylamine (1·00 ml.) was added to a suspension of trichlorotris(dimethylphenylphosphine)osmium(III) (0·30 g.) in ethanol (30 ml.) in the usual reaction vessel. After 16 hr. the yellow *solid* was filtered off, dried and analysed. Yield 0·10 g. (33%), m.p. 94—98° (decomp.). The compound is a non-conductor in nitrobenzene solution, but it could not be recrystallised as it decomposed too quickly. The compound is diamagnetic in the solid state. I.r. spectrum: ν_{OH} at 3510 cm.$^{-1}$; 400s, 359m, 332m, 315w, 295s, 235w.

The same complex was obtained (36%) from dimethylamine in an anhydrous system.

Dichloro(*piperidine*)*tris*(*dimethylphenylphosphine*)*osmium*(II). Trichlorotris(dimethylphenylphosphine)osmium(III) (0·50 g.) was suspended in ethanol (20 ml.) and piperidine (1 ml.) added. The mixture was shaken at room temperature for 6 hr., during which time a green-yellow solid separated. This was recrystallised from ethanol–piperidine to yield the *product* (0·24 g., 50%), m.p. 161—164°. The complex is a non-conductor in nitrobenzene solution and is diamagnetic in the solid state.

Reactions of Secondary Amines in the Presence of Water.—In a typical reaction trichlorotris(dimethylphenylphosphine)osmium(III) was suspended in ethanol (20 ml.), dimethylamine (0·38 ml.) and water (0·67 ml.) contained in a nitrogen-filled Schlenk tube. The tube was closed with a serum cap and shaken at room temperature for 16 hr. The gas over the solution was sampled using a hypodermic syringe and the sample chromatographed. It was found to contain approximately equal quantities of methane, ethane, n-propane, and n-butane. The tube was then opened and the yellow product filtered off and washed with ethanol. Analysis, melting point, and infrared spectrum confirmed that the product was dichloro(methylamine)tris(dimethylphenylphosphine)osmium(II) (0·20 g., 40%).

The filtrate from the preparation was distilled *in vacuo* and the residue shown to contain dimethylamine hydrochloride. The distillate was ethanol.

The following reactions were carried out with $[OsCl_3(PMe_2Ph)_3]$ in the same fashion, and the product isolated was always the primary amine complex unless otherwise stated: diethylamine (55% yield of complex); di-n-propylamine (45% yield of complex); di-isopropylamine (product was a mixture of $[OsCl_2(Pr^iNH_2)(PMe_2Ph)_3]$ and $[OsCl_2(EtOH)(PMe_2Ph)_3]$ on the basis of its infrared spectrum); di-n-butylamine (30% yield of complex); di-n-hexylamine (30% yield of complex); di-cyclohexylamine (25% yield of $[OsCl_2(EtOH)(PMe_2Ph)_3]$). The gaseous products are detailed in Table 2. Acetaldehyde was probably also a product, but was not identified in every sample investigated. The chloride removed from the osmium was found as the secondary amine hydrochloride.

The reactions of $[RuCl_3(PMe_2Ph)_3]$ with Me_2NH and Bu^n_2NH were similarly investigated. The complex product was the primary amine derivative (37% and 30% respectively). The non-condensable product was hydrogen and the secondary amine hydrochloride was recovered from the residues.

Reactions of Hydrazines.—(a) *Mononuclear complexes. Dichloro(hydrazine)tris(dimethylphenylphosphine)osmium*(II). Hydrazine hydrate (1·0 ml.) was added to a suspension of trichlorotris(dimethylphenylphosphine)osmium(III) (0·40 g.) in ethanol (10 ml.) and the mixture was shaken at room temperature for 30 min. The yellow *solid* which formed was filtered off, washed with ethanol, and dried in vacuum (0·25 g., 63%), m.p. 122—126° (decomp.). The complex was a non-conductor in nitrobenzene solution. *Dichloro(hydrazine)tris(dimethylphenylphosphine)ruthenium*(II) (75%) and *dibromo(hydrazine)tris(dimethylphenylphosphine)ruthenium*(II))78%) were prepared similarly.

Dichloro(phenylhydrazine)tris(dimethylphenylphosphine)osmium(II). Trichlorotris(dimethylphenylphosphine)osmium(III) (0·50 g.) was suspended in a solution of phenylhydrazine (0·50 ml.) in ethanol (20 ml.) and the mixture was shaken at room temperature for 6 hr. The pale yellow *solid* was filtered off, washed with ethanol, and dried (0·40 g., 88%), m.p. 146—149° (decomp.). The compound was a non-conductor in nitrobenzene solution but too insoluble for molecular-weight determination. *Dichloro(phenylhydrazine)tris(dimethylphenylphosphine)ruthenium*(II) was similarly prepared (80%).

(b) *Binuclear complexes. Tetrachlorobis-(μ-hydrazine)-tetrakis(dimethylphenylphosphine)diruthenium*(II). Trichlorotris(dimethylphenylphosphine)ruthenium(III) (0·20 g.) was suspended in a solution of hydrazine hydrate (0·50 ml.) in ethanol (10 ml.) and the mixture heated under reflux for 5 min. The yellow solid was filtered off, washed with water and ethanol, and dried (0·14 g., 75%), m.p. 150—156° (decomp.). The compound was a non-conductor in nitrobenzene solution, diamagnetic in the solid state, but too insoluble for a molecular-weight determination. Hydrazine hydrochloride was recovered from the mother liquor.

Analogous *products* were obtained in a similar manner from tribromotris(dimethylphenylphosphine)ruthenium(III) (10 min. reaction time, 80% yield), trichlorotris(diethylphenylphosphine)osmium(III) (30 min., 95%), trichlorotris-(diethylphenylphosphine)ruthenium(III) (5 min., 80%), tribromotris(diethylphenylphosphine)ruthenium(III) (5 min., 90%), tribromotris(di-n-butylphenylphosphine)osmium(III) (5 min., 70%), trichlorotris(di-n-butylphenylphosphine)ruthenium(III) (10 min., 75%), and trichlorotris(triphenylphosphine)ruthenium(III) (60 min., 90%). It was not possible to recrystallise any of these compounds.

Tetrachlorobis-(μ-tetradeuterohydrazine)tetrakis(di-n-butylphenylphosphine)di-osmium(II) was prepared as above from trichlorotris(di-n-butylphenylphosphine)osmium(III) (0·04 g.) in methyl $[^2H]$alcohol (1·40 g.) and tetradeuteriohydrazine deuteriate (0·04 g.). The yield was 0·29 g. (95%).

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