Some Reactions of Dimethyl(1-naphthyl)phosphine with Ruthenium and Osmium Compounds †

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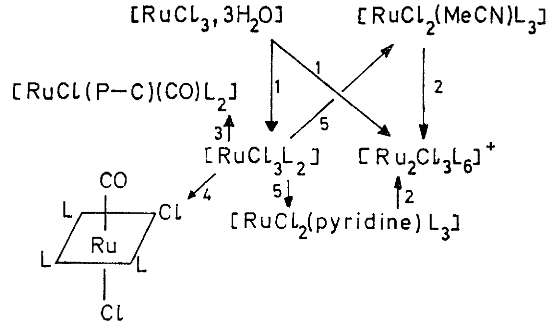
Hydrated ruthenium trichloride reacts with dimethyl(1-naphthyl)phosphine(L) to give mainly five-co-ordinate $[RuCl_2L_3]$ and a small amount of $[Ru_2Cl_3L_6]^+$, isolated as the salt with BPh_4^-. $[RuCl_2L_3]$ readily takes up carbon monoxide to give $[RuCl_2(CO)L_3]$ and also other ligands (Q) to give labile products $[RuCl_2QL_3]$ (Q = pyridine, 2-methylpyridine, 4-methylpyridine, acetonitrile, methyl isocyanide, or tetracyanoethylene). It shows no tendency to become internally metallated, however. Osmium tetroxide in the presence of concentrated hydrochloric acid and alcohols reacts with L to give maroon *mer*-$[OsCl_3L_3]$ in high yield, together with a small amount of the green internally metallated $[OsCl_2(P\text{–}C)L_2]$, P–C = $Me_2PC_{10}H_6^-$. $[OsBr_2(P\text{–}C)L_2]$ was also prepared. $[OsCl_2(P\text{–}C)L_2]$ reacts with boiling 2-methoxyethanol in the presence of sodium hydroxide to give $[Os(P\text{–}C)_2(CO)L]$ and with carbon monoxide in 2-methoxyethanol to give $[OsCl_2(CO)L_2]$.

We have shown that bulky tertiary phosphine ligands generate unusual chemistry,[1] *e.g.* low valency states, co-ordinatively unsaturated species, hydride formation, and metal–metal bond formation: and very commonly there is a tendency for the bulky tertiary phosphine ligand to be internally metallated.[1-3] We have also shown that dimethyl(1-naphthyl)phosphine(L) is often readily metallated in the 8- or *peri*-position in an octahedral complex but is much more resistant to metallation in a square planar complex, *e.g.* *mer*-$[IrCl_3L_3]$ is rapidly converted into $[IrCl_2(P\text{–}C)L_2]$ (125°, 2 min) but *cis*-$[PtCl_2L_2]$ is stable to prolonged heating {P–C ≡ 8-metallated dimethyl(1-naphthyl)phosphine}. We have now studied the nature of the products formed from dimethyl(1-naphthyl)phosphine and ruthenium or osmium halides.

Ruthenium Complexes.—For convenience the various reactions have been summarised in Scheme 1. When ruthenium trichloride reacts with dimethyl(1-naphthyl)phosphine(L) in refluxing 2-methoxyethanol the major product is a deep red five-co-ordinate species $[RuCl_2L_3]$; a small amount of the ion $[Ru_2Cl_3L_6]^+$ was also formed and isolated as the BPh_4^- salt. In contrast other dialkylarylphosphines(Q) yield exclusively the salt $[Ru_2Cl_3Q_6]Cl$.[4] The formation of a co-ordinatively unsaturated species with dimethyl(1-naphthyl)phosphine presumably reflects a large steric requirement for this ligand. An analogous triphenylphosphine complex,



(I)

Scheme 1 Some interconversion reactions of ruthenium–dimethyl(1-naphthyl)phosphine complexes; 1, L in 2-methoxyethanol; 2, $NaBPh_4$–EtOH; 3, a, NaOH–EtOH, b, heat in decalin; 4, $CO\text{–}CH_2Cl_2$; 5, pyridine, or acetonitrile, in dichloromethane

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† No reprints available.

[1] A. J. Cheney, B. E. Mann, B. L. Shaw, and R. M. Slade, *Chem. Comm.*, 1970, 1176.

[2] J. M. Duff and B. L. Shaw, *J.C.S. Dalton*, 1972, 2219.

[3] J. M. Duff, B. E. Mann, B. L. Shaw, and B. L. Turtle, to be published.

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

$[RuCl_2(PPh_3)_3]$, is known.[5] That our complex is indeed five-co-ordinate is shown by its monomeric nature in chloroform solution and its ready reaction with neutral ligand. For example, when carbon monoxide is passed through a suspension of $[RuCl_2L_3]$ in dichloromethane a pale yellow solution is rapidly formed from which $[RuCl_2(CO)L_3]$ in configuration (I) may be isolated. The stereochemistry follows from the ^1H n.m.r. spectrum which has two triplets and one doublet in the methyl region (Table 2).[6] Complexes of the type $[RuCl_2Q'L_3]$ (Q' = pyridine or MeCN) were also prepared but in solution the ligand Q' dissociates. The u.v.-visible spectrum of $[RuCl_2L_3]$ in chloroform solution shows a peak at 466 nm ($\varepsilon_{max.}$ $1{\cdot}1 \times 10^3$) and this peak diminishes in intensity as pyridine is added to the solution. An isosbestic point is observed at 420 nm (ε $9{\cdot}0 \times 10^2$) suggesting an equilibrium, $[RuCl_2L_3] + Q' \rightleftharpoons [RuCl_2Q'L_3]$. The n.m.r. (methyl) patterns of the acetonitrile and pyridine adducts are complicated and also suggest that more than one species is present in solution. $[RuCl_2L_3]$ also reacts with PMe_2Ph, MeNC, α-picoline, γ-picoline, or tetracyanoethylene as shown by electronic spectroscopy but with these ligands the products isolated were not analytically pure. The complexes $[RuCl_2Q'L_3]$ (Q' = MeCN or pyridine) react with sodium tetraphenylborate in alcohols giving the chloro-bridged salt $[Ru_2Cl_3L_6]BPh_4$ which was also obtained in low yield from the original mixture formed from ruthenium trichloride and dimethyl(1-naphthyl)phosphine.

TABLE 1

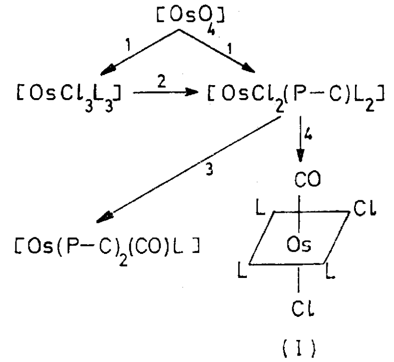
Colours, melting points, % yields, and microanalytical data for some ruthenium and osmium complexes prepared from dimethyl(1-naphthyl)phosphine

Complex [a]	% Yield	Colour	M.p./°C	Analytical data [b] C	H	N	Halide	M [b,c]
$[RuCl_2L_3]$	41	Red	202—219 [d]	58·95 (58·7)	5·4 (5·35)		9·8 (9·65)	750 (736)
$[RuCl_3L_6]BPh_4$	25	Yellow	155—159	66·1 (66·65)	5·9 (5·6)		5·7 (6·05)	
$[RuCl_2(CO)L_3]$	63	Cream	253—261 [d]	57·7 (58·1)	5·2 (5·15)		9·4 (9·25)	
$[RuCl_2(MeCN)L_3]$	69	Yellow	179—185	58·6 (58·7)	5·4 (5·45)	1·95 (1·8)	9·35 (9·1)	
$[RuCl_2(pyridine)L_3],0{\cdot}9CH_2Cl_2$	87	Yellow	168—171	56·35 (56·4)	4·9 (5·2)	1·85 (1·6)	14·8 (15·1)	
$[RuCl(P{-}C)(CO)L_2]$	52	White	247—253	60·7 (61·05)	5·05 (5·25)		5·2 (4·85)	
$[OsCl_3L_3]$	70	Maroon	214—221 [d]	50·35 (50·2)	4·55 (4·55)		12·65 (12·35)	850 (860)
$[OsCl_2(P{-}C)L_2]$	73	Green	243—247	52·45 (52·45)	4·7 (4·65)		8·7 (8·6)	740 (823)
$[Os(P{-}C)_2(CO)L]$	66	Cream	254—255	57·05 (56·9)	5·0 (4·8)		0·2 (0·0)	
$[OsCl_2(CO)L_3$	38	Off-white	271—280	52·2 (52·05)	4·6 (4·6)		8·55 (8·3)	
$[OsBr_2(P{-}C)L_2]$	46	Brown	232—240 [d]	47·1 (4·735)	4·15 (4·2)		17·55 (17·5)	890 (914)

[a] L = PMe_2(1-naphthyl); P–C = $PMe_2(C_{10}H_6)$. [b] Calculated values in parentheses. [c] In $CHCl_3$ solution. [d] With decomposition.

The complex $[RuCl_2L_3]$ was recovered unchanged when refluxed in 2-methoxyethanol for 20 h. However an attempt to reduce $[RuCl_2L_3]$ with sodium borohydride gave an unstable product which was not a metal hydride (n.m.r. evidence) and hence probably had undergone a base catalysed internal metallation. Since tertiary phosphine metal hydrides or alkylmetal compounds tend to internally metallate more readily that the corresponding chlorides [2,3] we attempted to prepare $[RuHCl(CO)L_3]$ in order to obtain a metallated complex. However treatment of $[RuCl_2(CO)L_3]$, configuration (I), with NaOH in ethanol gave a mixture of two carbonyl complexes but none of the hoped for hydrido-complex. This mixture was converted to a single complex by heating in decalin. This material is probably the monometallated carbonyl compound $[RuCl(P{-}C)(CO)L_2]$ with ν(C–C) at 1541 cm^{-1} (due to a metallated naphthyl group) but no metal hydride band. It was not sufficiently soluble for n.m.r. studies but see Tables for analytical and i.r. data. The conversion probably involves the formation of the hydrido-complex $[RuHCl(CO)L_3]$ which then eliminates hydrogen giving $[RuCl(P{-}C)(CO)L_2]$ in isomeric forms. Heating in decalin converts the mixture to a single isomer of $[RuCl(P{-}C)(CO)L_2]$.

Osmium Complexes.—The reactions have been summarised in Scheme 2. Osmium tetroxide reacts with dimethyl(1-naphthyl)phosphine(L) in the presence of conc. hydrochloric acid to give a high yield of $[OsCl_3L_3]$. The far i.r. spectrum of this compound shows bands at 265 and 307 cm^{-1} which are assigned as metal–chlorine frequencies: hence this material probably has the *mer*-stereochemistry.[7] Metal–chlorine frequencies are not



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SCHEME 2 Some interconversion reactions of osmium–dimethyl(1-naphthyl)phosphine complexes; 1, L in hydrochloric acid–2-methoxyethanol; 2, heat at 270 °C; 3, NaOH in 2-methoxyethanol; 4, carbon monoxide in 2-methoxyethanol

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[5] T. A. Stephenson and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1966, **28**, 945.

[6] J. M. Jenkins, M. S. Lupin, and B. L. Shaw, *J. Chem. Soc.* (*A*), 1966, 1787.

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

generally useful for obtaining the stereochemistry of dimethyl(1-naphthyl)phosphine complexes because of the large number of far-i.r. bands shown by the phosphine ligand. The reaction of OsO_4 with dimethyl(1-naphthyl)-phosphine also yielded a small amount of a second material shown to be the internally metallated complex $[OsCl_2(P–C)L_2]$ $(P–C = PMe_2C_{10}H_6)$. It is formed from $[OsCl_3L_3]$ either in refluxing 2-methoxyethanol or by pyrolysis *in vacuo* when the evolution of hydrogen chloride gas can be shown by i.r. spectroscopy. $[OsCl_2(P–C)L_2]$ was characterised by analytical data, molecular weight determination, and measurement of its room temperature magnetic moment, 1·85 B.M., which is typical for an osmium(III) complex[8] (*cf.* $[OsCl_3L_3]$, $\mu = 1{\cdot}96$ B.M.). $[OsCl_2(P–C)L_2]$ has $\nu(Os–Cl)$ at 267 and 281 cm^{-1} but no strong band at *ca.* 305 cm^{-1} (*cf.* $[OsCl_3L_3]$ above) suggesting that a chlorine atom *trans*-to chlorine has been displaced during the metallation. The peaks at 267 and 281 cm^{-1} are absent for $[OsBr_2(P–C)L_2]$. Unfortunately it was not possible to obtain structural information from the ^1H n.m.r. spectrum of $[OsCl_2(P–C)L_2]$ because osmium(III) complexes give rise to very broad resonances.[9] There is however strong evidence that the 1-naphthyl-group of a co-ordinated dimethyl(1-naphthyl)phosphine ligand undergoes internal metallation in the 8-position.[2] Reactions between OsO_4, L, and HBr gave only the metallated product $[OsBr_2(P–C)L_2]$ which is presumably formed *via* $[OsBr_3L_3]$.

$[OsCl_2(P–C)L_2]$ is stable in refluxing 2-methoxyethanol but in the presence of aqueous sodium hydroxide a reduction takes place yielding an osmium(II) complex which has undergone a further metallation. This complex $[Os(P–C)_2(CO)L]$ has satisfactory analytical figures and shows a strong carbonyl absorption and a C–C stretching frequency due to a metallated 1-naphthyl group (Table 2). The complex is not sufficiently soluble for its n.m.r. spectrum to be recorded. The metallation possibly proceeds *via* an intermediate carbonyl hydride, $[OsH(P–C)(CO)L_2]$ which then loses H_2, giving $[Os(P–C)_2(CO)L]$. When treated with carbon monoxide the osmium(III) complex $[OsCl_2(P–C)L_2]$ was reduced to the unmetallated osmium(II) carbonyl complex $[OsCl_2(CO)L_3]$ of configuration (I). The i.r. and ^1H n.m.r. spectra of this complex are very similar to the analogous ruthenium complex described above (Table 2). Since carbonyl formation from $[OsCl_2(P–C)L_2]$ is very slow in the absence of carbon monoxide the carbonyl group probably arises from the carbon monoxide gas rather than the alcohol. A conversion involving reduction by the alcohol can be envisaged:

$$[OsCl_2(P–C)L_2] + CO + \tfrac{1}{2}RCH_2OH \longrightarrow [OsCl_2(CO)L_3] + \tfrac{1}{2}RCHO$$

Treatment of $[OsCl_3L_3]$ with NaOH in isopropyl alcohol or sodium acetate in 2-methoxyethanol gave mixtures of products which, from the evidence of i.r. and elemental analysis, probably contained the internally metallated $PMe_2C_{10}H_6$ grouping. Pure products were not however isolated.

TABLE 2

Some i.r. (cm^{-1}) and ^1H n.m.r. data

Complex	Configuration	$\nu(CO)$ Nujol	$\nu(CO)$ $CHCl_3$	$\nu(C{=}C)$ in Nujol	^1H (methyl) N.m.r. data[a] τ	J
$[RuCl_2(CO)L_3]$	I	1935vs	1944		7·86(t)	7·4
		1919m			7·98(t)	8·0
					8·86(t)	9·3
$[RuCl(P–C)(CO)L_2]$		1942vs	1945	1541w		
$[Os(P–C)_2(CO)L]$		1922vs	1923	1538w		
$[OsCl_2(CO)L_3]$	I	1923vs	1931		7·83(t)	8·0
		1911m			7·99(t)	8·2
					8·81(d)	9·3

[a] In CH_2Cl_2 at 60 MHz, τ-value in p.p.m., multiplicity in parentheses; values of $J = |^2J(P–H) + {}^4J(P–H)|$ in Hz.

EXPERIMENTAL

Reactions were carried out in an atmosphere of argon. Yields, m.p.s, analytical, n.m.r., and i.r. data are given in Tables 1 and 2. M.p.s were determined on a Kofler hot stage and are corrected.

Action of Dimethyl(1-*naphthyl*)*phosphine on Ruthenium Trichloride*.—A solution of $RuCl_3,3H_2O$ (0·595 g, 2·4 mmol) and dimethyl(1-naphthyl)phosphine (2·25 g, 12·0 mmol) in 2-methoxyethanol (15 ml) was refluxed for 16·5 h. The suspension was filtered hot giving *dichlorotris*[*dimethyl*(1-*naphthyl*)*phosphine*]*ruthenium*(II) as red *needles* (0·72 g). The mother liquor was evaporated to dryness, the residue dissolved in methanol (15 ml) and treated with sodium tetraphenylborate (0·60 g) giving *tri-μ-chloro-hexakis*[*dimethyl*(1-*naphthyl*)*phosphine*]*diruthenium*(II) *tetraphenylborate* which recrystallised from dichloromethane–methanol as yellow *microprisms* (0·26 g).

Dichloro(*carbonyl*)*tris*[*dimethyl*(1-*naphthyl*)*phosphine*]*ruthenium*(II), *Configuration* (I).—Carbon monoxide was bubbled through a suspension of dichlorotris[dimethyl(1-naphthyl)-phosphine]ruthenium(II) (0·188 g) in dichloromethane (10 ml) for 10 min. The resulting pale yellow solution was

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[8] B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, 1964, **6**, 175.

[9] J. Chatt, G. J. Leigh, D. M. P. Mingos, E. W. Randall, and D. Shaw, *Chem. Comm.*, 1968, **419**.

evaporated to dryness and the residue recrystallised from dichloromethane–methanol giving the desired product as pale cream *prisms* (0·122 g).

Dichloro(acetonitrile)tris[dimethyl(1-naphthyl)phosphine]-ruthenium(II).—Acetonitrile (0·13 g, 3·2 mmol) was added to a suspension of dichlorotris[dimethyl(1-naphthyl)phosphine]ruthenium(II) (0·168 g, 0·23 mmol) in dichloromethane (10 ml). The suspension was stirred for 5 min giving a yellow solution which was diluted with light petroleum (b.p. 40—60°) yielding the desired product as yellow *microcrystals* (0·123 g).

$[\mathrm{RuCl_2(pyridine)(PMe_2C_{10}H_7)_3}],0{\cdot}9\mathrm{CH_2Cl_2}$ was similarly prepared in 86% yield and formed as a yellow powder. Its ^{1}H n.m.r. spectrum in deuteriochloroform showed the presence of 0·9 mol of dichloromethane.

Action of Sodium Tetraphenylborate on Dichloro(pyridine)-tris[dimethyl(1-naphthyl)phosphine]ruthenium(II).— $\mathrm{NaBPh_4}$ (0·066 g, 0·19 mmol) and $[\mathrm{RuCl_2(pyridine)(PMe_2C_{10}H_7)_3}]$ (0·133 g, 0·14 mmol) were dissolved in warm methanol (10 ml). The resulting yellow precipitate was filtered off and washed with methanol and water. It was shown to be μ-trichlorohexakis[dimethyl(1-naphthyl)phosphine]diruthenium(II) tetraphenylborate (0·087 g) by its i.r. spectrum.

$[\mathrm{RuCl_2(MeCN)L_3}]$ reacted similarly giving $[\mathrm{Ru_2Cl_3L_6}]\mathrm{BPh_4}$ in 61% yield.

Chloro[1-(8-dimethylphosphino)naphthyl](carbonyl)bis[dimethyl(1-naphthyl)phosphine]ruthenium(II).—Aqueous 1M sodium hydroxide solution (1·22 mmol) was added to a suspension of dichloro(carbonyl)tris[dimethyl(1-naphthyl)-phosphine]ruthenium(II) (0·85 g, 1·11 mmol) in ethanol (50 ml). The mixture was refluxed for 1 h and the insoluble material separated and then heated in refluxing decalin (5 ml) for 5 min. The desired product was filtered off from the cold mixture and washed with light petroleum (b.p. 30—40°). It formed *prisms* (0·425 g).

Action of Dimethyl(1-naphthyl)phosphine and Hydrochloric Acid on Osmium Tetroxide.—Dimethyl(1-naphthyl)phosphine (2·7 g, 14·4 mmol) was added to a solution of osmium tetroxide (0·63 g, 2·5 mmol) in 2-methoxyethanol (15 ml) containing conc. hydrochloric acid (1·4 ml). The solution was refluxed for 1 h and filtered hot yielding maroon prisms (1·5 g) of mer-*trichlorotris[dimethyl(1-naphthyl)phosphine]-osmium*(III). The mother liquor was cooled to 20° giving *dichloro[1-(8-dimethylphosphino)naphthyl]bis[dimethyl(1-naphthyl)phosphine]osmium*(III) as green microcrystals (0·11 g).

Dichloro[1-(8-dimethylphosphino)naphthyl]bis[dimethyl(1-naphthyl)phosphine]osmium(III).—A solution of *mer*-trichlorotris[dimethyl(1-naphthyl)phosphine]osmium(III) (0·063 g) in 2-methoxyethanol (25 ml) was refluxed for 30 min. Removal of the solvent and treatment of the residue with methanol gave the desired product (0·044 g) identified by its i.r. spectrum.

This complex was also prepared by pyrolysis of the trichloro-complex at 260° *in vacuo*. The gas evolved was shown to be HCl by its i.r. spectrum.

Dibromo[1-(8-dimethylphosphino)naphthyl]bis[dimethyl(1-naphthyl)phosphine]osmium(III).—A solution of osmium tetroxide (0·452 g, 1·78 mmol) and dimethyl(1-naphthyl)-phosphine (1·91 g, 10·2 mmol) in 2-methoxyethanol (15 ml) containing conc. hydrobromic acid (1·2 ml) was refluxed for 25 min. The desired product was obtained as brown *prisms* (0·725 g) from the reaction mixture.

Bis[1-(8-dimethylphosphino)naphthyl]carbonyl[dimethyl(1-naphthyl)phosphine]osmium(II).—A suspension of trichlorotris[dimethyl(1-naphthyl)phosphine]osmium(III) (0·208 g, 0·24 mmol) in 2-methoxyethanol (12 ml) was refluxed until a clear solution was obtained (15 min). Sodium hydroxide (1M aq., 0·8 ml, 0·8 mmol) was added and the solution was refluxed for 50 min. On cooling to 20° the product was obtained as cream *needles* (0·125 g) and was washed with methanol and water.

Dichloro(carbonyl)tris[dimethyl(1-naphthyl)phosphine]-osmium(II), *Configuration* (I).—A suspension of $[\mathrm{OsCl_3L_3}]$ (0·43 g) in 2-methoxyethanol (25 ml) was refluxed until a clear green solution of $[\mathrm{OsCl_2(P{-}C)L_2}]$ was obtained (30 min). Carbon monoxide was then passed through the refluxing solution for 20 min. The resulting clear solution was evaporated to dryness and the residue recrystallised from dichloromethane–methanol giving the desired product as off-white prisms (0·17 g).

We are very grateful to the S.R.C. for support and to Johnson–Matthey Ltd. for the generous loan of ruthenium and osmium salts.

[3/514 *Received*, 12*th March*, 1973]