Some Anionic Ruthenium(III)¹ and Rhodium(III) Complexes of Tertiary Monophosphines and Arsines

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Various methods of preparing ruthenium(III) anions of formula $M[RuCl_4(PR_3)_2]$ ($M = Me_4N^+$, Ph_4As^+ ; $PR_3 = PPh_3$, PMe_2Ph , PEt_3 , $P(OPh)_3$), and $M[RuX_4(AsPh_3)_2]$ ($M = Me_4N^+$, Et_4N^+ , Ph_4As^+ ; X = Cl, Br) are described including one involving 'oxidation' of $RuCl_2(PPh_3)_{3 \text{ or } 4}$ by concentrated hydrochloric acid. Methods of synthesising the isomorphous complexes $Ph_4As[RhCl_4(PR_3)_2]$ ($PR_3 = PPh_3$, PMe_2Ph) via $RhCl(PPh_3)_3$ and trans-[RhClCO(PPh_3)_2] are also described. A comparison of the stability of these anions towards solvolysis and various exchange reactions is made. From n.m.r. and i.r. spectral studies, the probable structures of the complexes are shown to be trans.

ALTHOUGH a wide variety of the complexes of ruthenium-(II) with tertiary phosphines and arsines have been synthesised,² there have been few reported preparations of the analogous compounds of ruthenium(III). Those described in the literature are as follows.

(a) A brief note on the preparation of $RuBr_3CO(PPh_3)_2$ (ref. 3). The only other ruthenium(III) carbonyl complexes are $M_2[RuCOCl_5]$ [M = NH_4^+ (ref. 4), Cs⁺ (ref. 5)], [Ru(CO)_2{(PhCH_2)_2NCS_2}_2]Cl (ref. 6), and M[RuCl_4-CO py] (M = pyH⁺, Ph_4As⁺).⁷

(b) The synthesis of $[RuCl_3(LPh_3)_2MeOH]$ (L = P, As)^{3,7} obtained by treatment of $RuCl_3, xH_2O$ with a stoicheiometric amount of triphenylphosphine in methanol and by heating $RuCl_3, xH_2O$ under reflux with an excess of triphenylarsine. The bromo-compounds can also be obtained; reaction with acetone gives $[RuCl_3(LPh_3)_2Me_2CO]$ and with pyridine $[RuCl_3(AsPh_3)-(py)_2]$.⁷

(c) Various methods for the preparation of the complexes mer-[RuX₃(LR₃)₃] (X = Cl, Br; L = As, P; R = alkyl and/or aryl) have been reported, culminating in a recent paper by Chatt *et al.*⁸ in which a general preparative method has been given. Further papers have discussed the e.s.r.⁹ and configurations ¹⁰ of these and other platinum-metal tertiary phosphine and arsine complexes.

(d) The binuclear complexes $[\operatorname{RuCl}_3(\operatorname{PR}_3)_2]_2$ and $[\operatorname{Ru}_2\operatorname{Cl}_5(\operatorname{PR}_3)_4]$ (R = Pr^u, Buⁿ) have been recently reported.¹¹ The former is formulated as a halogenbridged dimer and the latter has been shown by X-ray analysis ¹² to be analogous to the $[\operatorname{Ru}_2\operatorname{Cl}_3(\operatorname{PR}_3)_6]$ Cl complexes (postulated to contain a triple chloride bridge) ¹³ with two chloride ions replacing two phosphine groups to give a neutral complex with formal mixed oxidation states of (II) and (III).

(e) A brief report of the preparations of $R_3PH[RuCl_4-$

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¹ Preliminary communication, T. A. Stephenson, Inorg. Nuclear Chem. Letters, 1968, **4**, 687.

² For detailed references see M. S. Lupin and B. L. Shaw, J. Chem. Soc. (A), 1968, 741.

³ L. Vaska, Chem. and Ind., 1961, 1402.

⁴ J. Halpern, B. R. James, and A. L. W. Kemp, J. Amer. Chem. Soc., 1966, **88**, 5142. ⁵ M. J. Cleare and W. P. Griffith, J. Chem. Soc. (A), 1969,

⁵ M. J. Cleare and W. P. Griffith, *J. Chem. Soc.* (A), 1969, 372. ⁶ J. V. Kingston and G. Wilkinson, *L. Inorg. Nuclear Chem.*

 ⁶ J. V. Kingston and G. Wilkinson, J. Inorg. Nuclear Chem., 1966, 28, 2709.
 H H $(PR_3)_2$] $(PR_3 = PEt_3 \text{ and } PEt_2Ph)$ is available,⁷ obtained by treatment of ethanolic carbonyl-containing ruthenium solutions with excess tertiary phosphine.

Here we describe more convenient methods of preparing the ruthenium(III) anions of tertiary phosphines and arsines, particularly those of triphenyl-phosphine and -arsine which cannot be prepared by method (e), the only products being $[RuCl_2CO(LPh_3)_3]$ and $[RuCl_2-(CO)_2(LPh_3)_2]$ (L = P, As).⁷ The preparation of the isomorphous rhodium(III)-tertiary phosphine anions are also described. Various reactions of these anions will be discussed in later publications.

Ruthenium(III) Anions of Triphenyl-phosphine and -arsine.—The ready reaction of $[RuCl_3(LPh_3)_2MeOH]$ (L = P, As) with solvents and Lewis bases ⁷ prompted an attempt to displace the solvent group with halide ion to form anionic ruthenium complexes. Although an attempt with potassium chloride produced no obvious reaction, when $[RuCl_3(LPh_3)_2MeOH]$ was suspended in acetone and thoroughly shaken for several hours with a large excess of tetramethylammonium chloride, an 80% conversion of the initially formed $[RuCl_3(LPh_3)_2Me_2CO]$ into the red crystalline $Me_4N[RuCl_4(LPh_3)_2]$ occurred. Similar crystalline complexes were obtained upon treatment $[RuCl_3(LPh_3)MeOH]$ with an excess of Ph₄AsCl,HCl and Et₄NCl,H₂O.

Similarly, treatment of $[RuBr_3(AsPh_3)_2MeOH]$ in acetone with hydrobromic acid followed by addition of a large excess of Ph₄AsBr or Me₄NBr and removal of the solvent gave the purple crystalline M[RuBr₄(AsPh₃)₂] (M = Ph₄As⁺, Me₄N⁺).

In all cases, the complexes were characterised by elemental analyses, by magnetic moments at room temperature [ranging from 1.80 to 2.20 B.M. indicative of ruthenium(III) spin-paired complexes] and by conductance measurements on 10^{-3} M-solutions in nitromethane at 25° (Table 1). These gave values almost in

⁷ T. A. Stephenson and G. Wilkinson, J. Inorg. Nuclear Chem., 1966, 28, 945.

⁸ J. Chatt, G. J. Leigh, D. M. P. Mingos, and R. J. Paske, J. Chem. Soc. (A), 1968, 2636, and references therein.

⁹ A. Hudson and M. J. Kennedy, J. Chem. Soc. (A), 1969, 1116.

 J. Chatt, G. J. Leigh, and D. M. P. Mingos, J. Chem. Soc. (A), 1969, 1674.
 J. K. Nicholson, Angew. Chem. Internat. Edn., 1967, 6, 264.

¹¹ J. K. Nicholson, Angew. Chem. Internat. Edn., 1967, **6**, 264. ¹² G. Chioccola, J. J. Daly, and J. K. Nicholson, Angew. Chem. Internat. Edn., 1968, **7**, 131; G. Chioccola and J. J. Daly, J. Chem. Soc. (A), 1968, 1981.

¹³ J. Chatt and R. G. Hayter, J. Chem. Soc., 1961, 896.

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the range expected for 1:1 electrolytes in this solvent.¹⁴ A molecular-weight measurement in acetone on Me₄N- $[RuBr_4(AsPh_3)_2]$ gave a value of half that expected for a monomeric complex (since a 1 : 1 electrolyte in acetone).

The attempt to obtain the corresponding bromophosphine anion via [RuBr₃(PPh₃)₂MeOH] and MBr was unsuccessful; the red-brown solids isolated contained no large cations (i.r. evidence) and were non-electrolytes in acetone and nitromethane solution. Treatment of a suspension of $Me_4N[RuCl_4(PPh_3)_2]$ in acetone with an excess of lithium bromide immediately gave a purple solution but after complete removal of the solvent or addition of excess water, the paramagnetic product contained no Me_4N^+ (characterised by a strong band in the i.r. region at ca. 950 cm.⁻¹) and had an analysis very close to that for [RuBr₃(PPh₃)₉H₉O]H₉O. This formulation was supported by the very low conductance (Table 1) in acetone and nitromethane solutions and by the presence of weak bands at 3300 and 1600 cm.⁻¹ in the i.r. spectrum of the complex which were assigned to hydroxy stretching and bending vibrations respectively.

It is interesting to note that a similar reaction between the $[RuCl_4(AsPh_3)_2]^-$ anion and lithium bromide produced the bromo-anion, provided that the solvent was removed within minutes of the reactants; when they were not, solvation occurred to give [RuBr₃(AsPh₃)₂-H₂O]H₂O. The anion could, however, be washed with hot water without any apparent effect. Results presented later for the chloro-anions, both with reference to the rate of solvolytic attack and exchange reactions with other tertiary phosphines, clearly indicate the increased lability of the Ph3P anion compared to the Ph3As anion. It is concluded, therefore, that the inability to prepare the bromophosphine anion stems from its kinetic instability with respect to the solvated bromocomplex.

Because of this ready solvolysis, few attempts have been made to generate a series of ruthenium(III) anions $[RuX_4(LPh_3)_2]^-$ (X = SCN⁻, I⁻, etc) by metathetical reactions. In contrast, similar reactions with [RhCl_- $(PPh_3)_2$ ⁻ readily produced $[RhX_4(PPh_3)_2]^-$ (X = Br⁻, SCN⁻) which did not undergo solvolysis.

A feature of the tetraphenylarsonium salts of the ruthenium(III) triphenyl-phosphine and -arsine anions was that they crystallised with two molecular equivalents of acetone. This was shown by direct oxygen analyses and by the i.r. spectra of the complexes which contained bands characteristic of acetone at ca. 1700 (v_{CO}) and 1220 cm.-1 (vcc).15 The position of vco indicated that the acetone was probably present as molecules of solvation and not co-ordinated, [cf. v_{CO} 1656 cm.⁻¹ in [RuCl₃(AsPh₃)₂Me₂CO]⁷; 1640 cm.⁻¹ in F₃BOCMe₂].¹⁵ ¹⁴ J. E. Fergusson and R. S. Nyholm, Nature, 1959, 183, 1039;

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However, the quaternary ammonium salts crystallised out with no associated solvent. This suggests that either the solvent molecules are associated only with the tetraphenylarsonium ion or that the crystal packing is such that acetone is incorporated in the lattice cavities as in a clathrate complex.

In view of the success in preparing these ruthenium-(III) anions, an attempt was made to synthesise the unknown ruthenium(II) anion [RuCl₄(PPh₃)₂]²⁻ via RuCl₂- $(PPh_3)_{3 \text{ or } 4}$.⁷ There is only one example in the literature of a ruthenium(II) anionic complex containing a tertiary phosphine group: the rather strange [Ru₂Cl₃(PEt₂Ph)₆]-[RuCl₃(PEt₂Ph)₃] prepared by heating [Ru₂Cl₃(PEt₂-Ph), Cl at 60° in methyl acetate.^{16,17} At 120° in this solvent, [Ru₂Cl₄(PEt₂Ph)₅] is formed.^{16,18} However, the corresponding halogenocarbonyl anions Cs[RuX₃-(CO)3] (X = Cl, Br) 5 as well as $\rm M_{2}[RuX_{4}(\rm CO)_{2}]$ [M = Cs^+ (refs. 5 and 19), NH_4^+ (ref. 4); X = Cl, Br, I] and $M_2[RuCl_4CO(H_2O)] [M = Cs (ref. 5); NH_4^+ (ref. 20)]$ are well known.

However, reaction of RuCl₂(PPh₃)_{3 or 4} with an excess of Ph₄AsCl,HCl in acetone produced orange crystals of Ph₄As[RuCl₄(PPh₃)₂](Me₂CO)₂, identical to the product obtained from [RuCl₃(PPh₃)₂MeOH]. With Me₄NCl, there was no apparent reaction except on pre-treatment of the acetone solution with concentrated hydrochloric acid when the air-sensitive yellow-brown solution was converted into an air-stable reddish-brown solution. Addition of an excess of Me₄NCl to a portion of this then rapidly deposited orange $Me_4N[RhCl_4(PPh_3)_2]$. Removal of the solvent from the remainder of the acidified solution gave an air-stable, paramagnetic, yellow-brown powder which was partially ionised in nitromethane and acetone (Table 1) and had an analysis close to that for $H_3O[RuCl_4(PPh_3)_2]$. However, an i.r. spectrum of the carefully dried compound contained no evidence for either hydroxonium ion or aquo-groups and a better formulation may be H[RuCl₄(PPh₃)₂] (cf. H[RuCl₄(ophen)] obtained by reduction of [RuCl₄(o-phen)] with alcohol in the presence of hydrochloric acid).²¹ The structure of these complexes may be similar to that postulated for $H_4(Ru(CN)_6]^{22}$ with hydrogen bonding between the hydrogen and chloride groups.

Ruthenium(III) Anions of other Tertiary Monophosphines.-Although the PhaP anion can be readily obtained from RuCl₃(PPh₃)₂MeOH, similar routes for the preparation of other ruthenium(III)-tertiary phosphine anions are unavailable because the corresponding starting materials containing a labile alcoholic group are unknown. Instead, refluxing methanolic ¹³ or 2-methoxyethanolic² solutions of R₃P and RuCl₃, xH₂O gives $[Ru_2Cl_3(PR_3)_6]Cl;$ in an acidified ethanolic solution

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 ¹⁵ P. Chalandon and B. P. Susz, Helv. Chim. Acta, 1958, 41 697

¹⁶ R. H. Prince and K. A. Raspin, J. Chem. Soc. (A), 1969, 612.

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 N. W. Alcock and K. A. Raspin, J. Chem. Soc. (A), 1968, 2108.

¹⁹ R. Colton and R. H. Farthing, Austral. J. Chem., 1967, 20, 1283.

²⁰ J. Halpern and A. L. W. Kemp, J. Amer. Chem. Soc., 1966,

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J. Chem., 1963, 16, 42. ²² D. F. Evans, D. Jones, and G. Wilkinson, J. Chem. Soc., 1964, 3164; A. P. Ginsberg and E. Koubek, Inorg. Chem., 1965, 4, 1186.

mer-RuCl₃(PR₃)₃ is formed ⁸ and attempts to obtain anionic complexes by reactions of these compounds with MCl-hydrochloric acid mixtures have been unsuccessful.

An attempted preparation of the unknown complex RuCl₂(PEt₃)₃, by treatment of monomeric ²³ RuCl₂- $(PPh_3)_3$ with an excess of neat triethylphosphine gave a deep emerald-green solution. In view of the recent paper by Leigh et al.,²⁴ in which it is suggested that in solution $[RuX_2(PMe_2Ph)_3(EtOH)]$ (X = Cl or Br) readily decomposes to give green [RuX₂(PMe₂Ph)₃], the method is probably successful; only a very soluble oil could, however, be isolated. When the solution was set aside for several hours, the green colour was discharged and very pale yellow crystals were deposited; these had an crystals of $R_3PH[RuCl_4(PR_3)_2]$. This reaction has now been extended to the preparation of the phosphonium salt of Me₂PhP; reaction of an excess of Me₂PhP with a cold freshly prepared ' red solution ' produced a mixture of Me₂PhPH[RuCl₄(PMe₂Ph)₂] (ca. yield 40%), RuCl₂CO- $(PMe_2Ph)_3$, and $RuCl_2(CO)_2(PMe_2Ph)_2$. The carbonyl complexes have been well characterised by previous workers.²⁶ Treatment of the phosphonium salts with MCl in a minimum volume of solvent then gave M[RuCl₄- $(PR_3)_2$ (M = Ph₄As⁺ or Me₄N⁺).

A more direct method of obtaining these salts is by treatment of $M[RuCl_4(LPh_3)_2]$ with an excess of neat tertiary phosphine for several days under nitrogen, when almost quantitative conversion into the corresponding

1 1 1.

Molar conductivities (25°) and	I magnetic moments of some i	ruthenium ar	ia rhodium comple	exes
Complex	$\Lambda_{(0.001M)}$ (cm. ² ohm ⁻¹ mole ⁻¹)	Solvent	μ_{eff} (BM)	<i>Т</i> (°к)
Ph.As[RuCl.(AsPh.)](Me.CO)	50	MeNO.	1.97	291
1 114110[110014(1101 113)2](110200/2	36	CH.Cl.ª		
Me.N[RuCL(AsPh_)]	67	MeNO.	$2 \cdot 21$	292
$Et.N[RuCl.(AsPh_)_a]$	73	MeNO,	2.10	293
$Ph.As[RuCl.(PPh_a)a](Me_CO)a$	62. 63 0	MeNO.	2·00,0 1·96 °	295
$Me.N[RuCl.(PPh_)]$	74.4 72 0	MeNO.	1.97.4 2.02 .	294
$H[RuCl.(PPh_a)_a]$	23	MeNO	2.3	293
11[110014(1 1 13/2]	29	Me		
Ph.As[RuBr.(AsPh.)](Me.CO)	66	MeNO,	1.87	296
1 1410[110-4(37	CH CL2		
Me.N[RuBr.(AsPh.).]	73	MeÑO,	1.84	295
	82	Me ₂ CO		
RuBr.(PPh.).H.O]H.O	5	$MeNO_2$	2.00	293
	6	Me ₂ CO		
[RuCl _o (AsPh _o),MeNO _o]	4, • 5	MeNO,	2.00 .	295
[RuCl, (PPh,), MeNO,]	4	MeNO ₂	1.975	295
Me,PhPH[RuCl.(PMe,Ph),]	60	MeNO ₂	$2 \cdot 10$	293
Ph,As[RuCl,(PMe,Ph),]	51,9 49 h	MeNO ₂	1.94 \$	296
Ph,As[RuCl, (PEt,),]	64, ^h 62 g	$MeNO_2$	1·89 g	294
Ph,As,RhCl,PPh,,,,(Me,CO),	49,1 531	MeNO ₂	Diamagnetic 4	296
	43 '	CH ₂ Cl ₂ ^a	-	
$Me_{4}N[RhCl_{4}(PPh_{3})_{2}]$	80	$MeNO_{2}$	Diamagnetic	296
PhAs[RhBr, (PPh3)] (Me2CO)	54	MeNO ₂	Diamagnetic	294
Ph.As[Rh(SCN),(PPh.),]	98	Me _s CO	Diamagnetic	294

TABLE 1

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^a Ph₄AsCHCl in CH₂Cl₂; $\Lambda_{0.001M} = 48 \text{ cm.}^2 \text{ ohm}^{-1} \text{ mole}^{-1}$. ^b Prepared from RuCl₂(PPh₃)₄. ^c Prepared from RuCl₃(PPh₃)₂MeOH, ^d Prepared from RuCl₂(PPh₃)₃. ^e From RuCl₃(AsPh₃)₂MeOH. ^f From Ph₄As⁺ salt. ^e From phosphonium salt. ^h From Ph₃P anion. ⁱ From RhCl(PPh₃)₃. ^j From trans-[RhClCO(PPh₃)₂].

analysis which was consistent with the empirical formula $[RuCl_2(PEt_3)_3]$. The far-i.r. spectrum [nov(RuCl) > 270]cm.⁻¹], conductivity in nitromethane ($\Lambda_{0.001M} = 49$ ohm⁻¹ mole⁻¹ cm.²), and melting point were identical with those of a sample of [RuCl₃(PEt₃)₆]Cl, prepared from $RuCl_3, xH_2O$, Et_3P , and 2-methoxyethanol.² A similar result was obtained when RuH₂(PMe₂Ph)₄ was treated with hydrochloric acid when [Ru₂Cl₃(PMe₂Ph)₆]Cl, and not the expected [RuCl₂(PMe₂Ph)₄], was isolated.²⁵ It is concluded, therefore, that although mononuclear halide complexes of ruthenium(II) with R_3P do exist, they are unstable with respect to the halogeno-bridged binuclear complex. The only exceptions are RuCl₂-(PPh₃)_{3 or 4}.

As briefly reported earlier,⁷ treatment of a ruthenium carbonyl-containing solution with a large excess of Et₃P or Et₂PhP gives immediate precipitation of green

²³ S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, 1965, **4**, 778. ²⁴ J. Chatt, G. J. Leigh, and R. J. Paske, *J. Chem. Soc.* (A), 1969, 854.

tertiary phosphine anionic complex occurred. Care must be taken to avoid solvents in these exchange reactions because of ready solvolysis of all the anions; further, since the compounds are thermally unstable, heat must be avoided. The rate of exchange was also sensitive to whether Ph₃P or Ph₃As was being displaced and on the particular cation present. Qualitatively, this rate of exchange was found to be $[RuCl_4(PPh_3)_2]^+ >$ $[RuCl_4(AsPh_3)_2]^-$ and $Ph_4As^+ > Me_4N^+$ for the same anion. This exchange reaction was also used to prepare the first tertiary phosphite complex of ruthenium(III). Treatment of $Me_4N(RuCl_4(PPh_3)_2]$ with an excess of neat triphenyl phosphite for several months gave orange $Me_4N[RuCl_4{P(PhO)_3}_2].$

Magnetic moments and conductivity data are given in Table 1.

²⁵ K. C. Dewhirst, W. Keim, and C. A. Reilley, Inorg. Chem.,

 <sup>1968, 7, 546.
 &</sup>lt;sup>26</sup> J. M. Jenkins, M. S. Lupin, and B. L. Shaw, J. Chem. Soc. (A), 1966, 1787.

Solvolysis of Ruthenium(III) Anions.—When the red anionic complexes M[RuCl₄(LPh₃)₂] were dissolved in nitromethane, the initial yellow solutions rapidly turned green and if concentrated solutions were used, green crystals could be isolated. This colour change was accelerated by heat and the rate of conversion was qualitatively the same as that found for the exchange with tertiary phosphines. Similarly, when the green triethylphosphonium compound (and its Ph₄As⁺ salt) was dissolved in dichloromethane, the initial green solution rapidly turned yellow-brown; dissolution of the brown dimethylphenylphosphonium salt in acetone followed by addition of water rapidly gave a green solution.

Similar colour changes have been reported in related systems. For example, persistent treatment of red H[RuCl₄],2H₂O with alcohol gives a green solid ²⁷ and Griffith ^{28a} has suggested that these may be cis- and trans-isomers of the $[RuCl_4(H_2O)_2]^-$ anion. A recent X-ray analysis²⁹ of red Ph₄As[RuCl₄(H₂O)₂]H₂O has shown it to contain *cis*-aquo-groups. The brown complexes phenH[RuCl₄(phen)] and bipyH[RuCl₄(bipy)] are also known²¹ and for steric reasons must have a cisconfiguration. In contrast, e.s.r.⁹ and far-i.r.^{1,10} evidence for green $Et_3PH[RuCl_4(PEt_3)_2]$ suggest that this anion has a *trans*-configuration.

Therefore, on the basis of this evidence, the most likely explanation for the colour changes observed in this work was the existence of both cis- and trans-isomers: a red cis- and a green trans-form. However, in every case, the colour change could be suppressed by addition of an excess of MCl to the solution, and, further, the addition of MCl to the green solids (from the [RuCl₄- $(LPh_3)_2$ anions) in acetone rapidly gave the original red complexes. Furthermore, the green complexes were found to be non-conducting in nitromethane and to contain no large cation (i.r. evidence); in fact, they had melting points and analyses identical to [RuCl₃(LPh₃)₂-MeNO₂], which was obtained by treating [RuCl₃(LPh₃)₂-MeOH] with nitromethane. A similar behaviour was observed in acetonitrile solutions. Thus the red-green colour change can be ascribed to the equilibrium:

$$[\operatorname{RuCl}_4(\operatorname{LPh}_3)_2]^- + S \Longrightarrow$$

$$[\operatorname{RuCl}_3(\operatorname{LPh}_3)_2S] + \operatorname{Cl}^-(S = \operatorname{MeNO}_2, \operatorname{MeCN})$$

A similar behaviour has been found for the complexes $M[IrX_4(SbPh_3)_2]$ (M = Na, K; X = Cl, Br) which on dissolution in methanol slowly give [IrX₃(SbPh₃)₂-CH₃OH].³⁰ Rather surprisingly, the i.r. spectra of the ruthenium complexes showed no evidence for solvent co-ordination, although the nitrogen analyses clearly indicated their presence. The reason for the absence

Araneo, S. Martinengo, and F. Zingales, 1965, 95, 1435.

of characteristic solvent absorptions is unknown. Investigation of the colour change in dichloromethane of the Et_aP anion led to isolation of a red-brown solid, nonconducting in dichloromethane and nitromethane and containing no large cation (i.r. evidence).

Therefore, it is concluded that the colour changes observed arise from solvolysis of the anions and not a *cis-trans* isomerisation. It also suggests that the colour change observed when $[RuCl_4(H_2O)_2]^-$ is treated with ethanol is probably due to the formation of green $[RuCl_3(H_2O)_2(EtOH)].$

Rhodium(III) Anions of Tertiary Monophosphines. Although a substantial literature exists for a variety of rhodium(III) complexes of tertiary phosphines,285 there is only one reported example of a rhodium(III) anion containing a tertiary phosphine group, namely [RhCl₄(PMe₂Ph)₂]⁻, isolated as its phosphonium salt (2-3% yield) in the reaction of RhCl₃, 3H₂O and Me₂PhP to give mer- and fac-[RhCl₃(PMe₂Ph)₃].³¹ Reaction of the phosphonium salt with Ph₄AsCl,HCl then gave Ph₄As[RhCl₄(PMe₂Ph)₂]. Attempts to prepare this anion in larger yields by treatment of mer- [RhCl3-(PMe₂Ph)₃] with an excess of Me₄NCl have proved unsuccessful since only slow isomerisation to the faccomplex occurred (cf. the recent report by Shaw et al.³² on photochemical isomerisation of platinum-metal phosphine complexes).

However, when a suspension of RhCl(PPh₃)₃ in acetone was treated with a large excess of Ph₄AsCl,HCl, conversion into orange crystalline Ph₄As[RhCl₄(PPh₃)₂] occurred during several hours. As for the ruthenium anion, the complex crystallises out with two molecular equivalents of solvent acetone. With Me₄NCl, the same anion was isolated (with no solvent acetone) provided that the suspension was pretreated with concentrated hydrochloric acid. Attempts to obtain the unknown rhodium-(I) anion $[RhCl_2(PPh_3)_2]^-$, analogous to the well-known [RhCl₂(CO)₂]^{-,33} with a stoicheiometric quantity of Ph₄AsCl,HCl were unsuccessful; only the rhodium(III) anion and unchanged RhCl(PPh₃)₃ were isolated from the reaction mixture.

The rhodium(III) anion was also obtained as a sideproduct (ca. 20% yield) by prolonged treatment of trans-[RhCl(CO)(PPh₃)₂] with a large excess of Ph₄AsCl,HCl in an acetone-chloroform mixture. The main product was trans-[RhCl₃CO(PPh₃)₂], previously obtained by direct interaction of chlorine with trans-[RhCl(CO)-(PPh3)2].34 Although carbonyl groups have been replaced in metal carbonyls by halide ion to give halogenocarbonyl anions,³⁵ this appears to be the first reported reaction involving carbonyl displacement by halide ion in a monocarbonyl complex.

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²⁸ W. P. Griffith, 'The Chemistry of the Rarer Platinum Metals,' Interscience, London, 1967, (a) p. 141; (b) ch. 6.
²⁹ T. E. Hopkins, A. Zalkin, D. H. Templeton, and M. G. Adamson, *Inorg. Chem.*, 1966, 5, 1427.
³⁰ A. Araneo and S. Martinengo, *Gazzetta*, 1965, 95, 825; A. Araneo C. Martinengo, *Gazzetta*, 1965, 95, 825; A.

³¹ P. R. Brookes and B. L. Shaw, J. Chem. Soc. (A), 1967, 1079.

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As for the ruthenium anions, treatment of this triphenylphosphine anion with neat Me₂PhP gave Ph₄As- $[RuCl_4(PMe_2Ph)_2]$; however with Et_3P and $(PhO)_3P$, only the unchanged arylphosphine anion could be isolated. The decreased lability of the rhodium anions, compared with ruthenium was also illustrated by the relative stability of these complexes in solution; whereas the ruthenium ions underwent rapid solvolysis, the rhodium ions appeared quite stable in nitromethane, acetonitrile, etc. Furthermore, treatment of the rhodium triphenylphosphine chloro-anion with various lithium salts gave $[RhX_4(PPh_3)_2]^-$ ions $(X = Br^- \text{ and } SCN^-)$ which were quite stable in solution. Unlike reactions of mer-[RhCl₃(PMe₂Ph)₃] with lithium salts, which require

' triplet ' indicative of trans-Me₂PhP groups. The complex Ph₄As[RhCl₄(PMe₂Ph)₂] reported in this paper has an identical m.p. and n.m.r. and far-i.r. spectral properties (except for the absence of the characteristic doublet of the Ph₄As⁺ ion at 351 and 339 cm.⁻¹ in ref. 31) to that reported by Shaw et al.³¹ Similar i.r. evidence suggests a trans-structure for the $[RuCl_4(PEt_3)_2]^-$ ion and this has been recently substantiated by e.s.r. measurements ⁹ on $Et_3PH[RuCl_4(PEt_3)_2]$.

For the chloro-Ph₃P and -Ph₃As anions, no strong bands below 300 cm.⁻¹ are found in their far-i.r. spectra. Superposition of the far-i.r. spectra of the chloro- and bromo-ions enables v(MX) to be assigned and the ratio of v(MCl): v(MBr) (1.25-1.30) is in the range found by

TABLE 2

Far-i.r. absorptions (400-200 cm.⁻¹) for some ruthenium and rhodium complexes; metal-halogen frequencies are tentatively assigned

	and tomotory abbiguou	
Complex	Frequency of other bands (cm. ⁻¹)	ν (M–X) cm. ⁻¹
PhAs[RuCl ₄ (AsPh ₃),](Me ₂ CO),	358s, 338m, 332s, 319vs, 296m,* 253w, 245w, 225m, 220w	311vs,* 296m *
Ph,As[RuBr,(AsPh,),](Me,CO),	352s, 347m,* 328s, 322s,* 306w, 224m, 220w	246s
PhAs RuCl (PPh3) (Me2CO)	358s, 344m,* 228w	317vs, 307vs
PhAs RhCl (PPh3) (Me2CO)	356s, 342m,* 290w, 236m, 230w *	334vs, 323s *
Ph ₄ As[RhBr ₄ (PPh ₃) ₂](Me ₂ CO)	357s, 347m,* 229m	263s
Ph_As[RuCl_(PMe_Ph),	354s, 341s, 322s,* 240w, 217w, 213w	311vs, 299vs
Ph ₄ As[RhCl ₄ (PMe ₂ Ph) ₂]	364s, 351s, 339s, 326s,* 213m	316vs , 303 m
Ph ₄ As RuCl ₄ (PEt ₃),	392m, 360m, 351m, 253m, 244m, 224m	308vs, 300vs
Me ₄ N[RuCl ₄ (AsPh ₃) ₂]	346w, 328s,* 316vs, 292m,* 226m	312vs, 303s *
$Me_4N[RuBr_4(AsPh_3)_2]$	340w, 328s, 318s, 309m,* 257m,* 226m	250s
$Me_4N[RuCl_4(PPh_3)_2]^d$	325s,* 226w	314vs, 307m *
$Me_4N[RhCl_4(PPh_3)_2]$	340s,* 268 w, 242w, 230m	326vs
$Me_4N[RuCl_4(PEt_3)_2]$	392m, 228m	315s,* 308vs
$Et_4N[RuCl_4(AsPh_3)_2]$	338m,* 320vs, 272w, 220w	308s *
Me ₂ PhPH[RuCl ₄ (PMe ₂ Ph) ₂]	322m,* 214w	312vs, 302s *
$Et_{3}PH[RuCl_{4}(PEt_{3})_{2}]$	344w, 272w, 228m	308vs
$H[RuCl_4(PPh_3)_2]$	340s, 312s,* 229m	333s
RuCl ₃ (AsPh ₃) ₂ CH ₃ NO ₂ ^e	316 vs, 267w, 220w	312s *
RuCl ₃ (PPh ₃) ₂ CH ₃ NO ^f	330s,* 227m	327vs
[Ru Cl ₃ (PEt ₃) ₆]Cl	392m, 232m, 227m	266m
mer-[RuCl _a (PPh ₃) ₃]	348(m), 278w, 230w	318vs, 312s,* 302m *
mer-RuCl ₃ (PMePh) ₃	352m, 222m	330vs, 302m, 272s
* Shoulder.		

• From $\operatorname{RuCl}_{2}(\operatorname{PPh}_{3})_{4}$. • From trans -[RhClCO(PPh}_{3})_{2}]. • From Ph}_{3}P anion. • From $\operatorname{RuCl}_{2}(\operatorname{PPh}_{3})_{3}$. • From $\operatorname{RuCl}_{3}(\operatorname{AsPh}_{3})_{3}$ - CH₃OH. • From Ph₄As⁺ salt. • Prepared as in ref. 8.

several hours at reflux temperature for complete exchange,³¹ these exchange reactions occurred quite rapidly at room temperature.

Conductance data on these diamagnetic rhodium(III) anions are given in Table 1.

Configuration of Ruthenium(III) and Rhodium(III) Anions.—The far-i.r. spectra $(400-200 \text{ cm.}^{-1})$ of the various complexes are given in Table 2. There is a close similarity between the i.r. spectra (4000-200 cm.⁻¹) of the paramagnetic $[RuCl_4(PMe_2Ph)_2]^-$ ion and the diamagnetic $[MCl_4(PMe_2Ph)_2]^-$ (M = Rh³¹ and Ir³⁶) ions; in particular, the absence of strong bands below 300 cm.⁻¹, assignable to v(MCl), suggests there is no chloride trans to a tertiary phosphine. Although the ¹H n.m.r. of the paramagnetic ruthenium ion shows only a weak, broad methyl resonance (cf. ref. 10), that of the corresponding rhodium³¹ and iridium³⁷ anions show a well-defined other workers ³⁸ and supports these assignments. However, unlike *mer*-[MCl₃(PR²₂R¹)₃](M = Ru,¹⁰ Rh,^{10,31} Os,¹⁰ Ir,^{10,36} and Re¹⁰; $R^2 = R^1 = alkyl \text{ or } R^2 = alkyl$, $R^1 = aryl$) strong bands, assignable to v(RuCl) below 300 cm^{-1} are also absent in the far-i.r. spectra. Thus, it appears that the criteria established by Shaw and his co-workers for distinguishing between chloride trans to chloride or trans to tertiary phosphine may be invalid for triphenylphosphine (and arsine) complexes. The reason for this presumably arises from the fact that Ph₂P is a weaker σ -donor than Et₃P or Me₂PhP and that in octahedral complexes of the platinum metals, the transbond weakening effect of a ligand seems to depend on its σ bond properties.³⁹

Although far-i.r. evidence is, therefore, by no means conclusive, the ready exchange of Me₂PhP, etc., for Ph₂L

 ³⁶ J. M. Jenkins and B. L. Shaw, J. Chem. Soc., 1965, 6789.
 ³⁷ J. M. Jenkins and B. L. Shaw, J. Chem. Soc. (A), 1966, 1047; J. Chatt, R. S. Coffey and B. L. Shaw, J. Chem. Soc., 1965, 7391.

³⁸ J. R. Durig, B. R. Mitchell, D. W. Sink, J. N. Willis, jun., and A. S. Wilson, Spectrochim. Acta, 1967, 23A, 1121, and references therein.

³⁹ B. L. Shaw and A. C. Smithies, J. Chem. Soc. (A), 1968, 2784.

J. Chem. Soc. (A), 1970

under very mild reaction conditions to give transisomers strongly suggests that the starting materials are also trans. However, in view of the different isomers obtained during oxidative addition reactions of trans- $[IrX(CO)L_2]$ (X = halogen, L = tertiary phosphine, arsine, or olefin) and recent observations on the influence of solvent on the isomer formed in some of these reactions,⁴⁰ this evidence is also not conclusive.

In Ph₄As[Rh(SCN)₄(PPh₃)₂], the unsplit ν (CN) absorption (2105 cm.⁻¹) is consistent with a *trans*-configuration. Comparison with the i.r. spectrum of the chloro-anion

results from 400—200 cm.⁻¹. Conductivity measurements were made on a Mullard conductivity bridge: magnetic susceptibilities were determined by the Faraday method. N.m.r. spectra were obtained on a Bruker Spectrospin HFX3 at 90 MHz and X-ray powder photographs in Lindemann glass tubes were taken with a Debije–Scherrer Powder Camera, 15.75-cm. radius with cobalt radiation; *ca.* 10 hr. exposure.

Analytical data for the ruthenium(III) and rhodium(III) anions are given in Table 3.

Materials.—These were obtained from the following sources. Commercial ruthenium trichloride and rhodium

TABLE 3												
Analytical	data	for	ruthenium	(111)	and	rhodium((111)	anions				

	Found (%)						Required (%)							
Complex	c	н	As	X ª	N	0	P	ĉ	н	As	X ª	N	0	\mathbf{P}
Ph ₄ As[RuCl ₄ (AsPh ₃) ₂](Me ₂ CO) ₂	58.5	4.4	17.7	11.0		2.7		58.5	4.6	16.6	10.5		$2 \cdot 4$	
$Me_4N[RuCl_4(AsPh_3)_2]$	51.6	4.5	15.8	15.4	1.9			51.7	$4 \cdot 5$	16.1	15.3	1.5		
$Et_4N[RuCl_4(AsPh_3)_2]$	$53 \cdot 9$	5.5		14.5				53.6	$5 \cdot 1$		14.4			
Ph As[RuCl (PPh)](Me CO)	[▶] ∫ 63·6	4 ∙8					J	62.6	4.9		11.3		2.5	
$1 n_4 n_5 [n_0 n_4 (1 1 n_3 / 2) (n_2 0 0 / 2)]$	0 62.3	$4 \cdot 5$		11.1		$2 \cdot 5$		020	10		11.0		20	
Me.N[RuCl.(PPh.).]	^b {56·9	4 ·9		16.8	1.7		$\{7, 1\}$	57.1	5.0		16.9	16.9 1.7		7.4
	a (57.0	5.0		16.9	1.7	<u> </u>	7.3				200	- •		• •
$Ph_4As[RuBr_4(AsPh_3)_2](Me_2CO)_2$	51.6	4 ∙0	15.8	21.9		$2 \cdot 7$		51.7	4.1	14.8	20.9		$2 \cdot 1$	
$Me_4N[RuBr_4(AsPh_3)_2]$	43.2	4 ·0		28.1				43.4	3.8		28.9			
$Me_{2}PhPH[RuCl_{4}(PMe_{2}Ph)_{2}]$	44.0	5.4		20.9			,	43.8	5.2		21.6			
Ph.As[RuCl.(PMe.Ph).]	52.7	4.7		15.8			ł	$53 \cdot 2$	4.7		15.7			
	1 (53.8	4.9		101			J				16 5			
$Pn_4As[KuCl_4(PEt_3)_2]$	1 26 9	70		10.1				94.7	7.6		10.9			
$Me_4 N[KUOI_4(PEt_3)_2]$	J 30.2	1.0						34.1	1.0					
$Pn_4As[KuDr_4(PEt_3)_2]$	41.9	4.7						41.0	4.5					
$Me_4N[KuCl_4]P(PnO)_3]_2$	00.1	4.9	G. A	11.0		9.0	h	51.7	4.9					
Ph ₄ As[RhCl ₄ (PPh ₃) ₂](Me ₂ CO) ₂	b 02.7	4.0	0.4 20	11.0		2.9	5.0	62.4	4 ·9	5.9	11.2		2.5	4.9
Mo NIPHCI (DDb)]	" (01·7	4.0	9.9	16.5	1.7	2.3	9.0 J	56.0	5.0		16.9	1.7		
$Me_4N[MCI_4(FFII_3)_2]$ Db Ac[PbBr / DDb)]/Ma CO)	50.9	4.9		94.9	1.1			54.4	4.0		99.1	1.1		
$Ph_{4}As[RhDi_{4}(PPh_{3}/2)(Me_{2}OO)]$	61.2	4.9		24.9	4.5			61.4	4.0		20.1	4.5		
$Ph \Delta s[PhC1 (PMe Ph)]$	52.9	4.0			T .0			53.2	4.7			Ŧ 0		
x manastrent (x mogt m/g)	00.7	10						00 2						

* Found S, 11.1%; Required 10.3%.

^a X = Cl or Br. ^b From RuCl₃(PPh₃)₂CH₃OH. ^e From RuCl₂(PPh₃)₄. ^d From RuCl₂(PPh₃)₃. From phosphonium salt ^f From Ph₃P anion. ^e From RhCl(PPh₃)₃. ^h From trans-RhCl(CO)(PPh₃)₂.

shows there is no additional band in the M-NCS range (780—860 cm.⁻¹) but that a weak extra band occurs at 638 cm.⁻¹, close to the range expected for the (predominantly) C-S stretching mode of vibration of an S-bonded thiocyanate ligand (690—720 cm.⁻¹).⁴¹ The region 690—720 cm.⁻¹ is obscured by bands due to the triphenylphosphine ligands.

Finally, X-ray powder photographs of $Ph_4As[MCl_4-(PPh_3)_2]$ (M = Ru and Rh) are identical indicating that the compounds are isomorphous; this also provides support, although by no means proves, that the compounds have the same isomeric form.

EXPERIMENTAL

Microanalyses were by the Microanalytical Laboratory, Imperial College or A. Bernhardt, West Germany. Molecular weights were determined on a Perkin-Elmer Hitachi osmometer (model 115) at 35°. I.r. spectra were recorded in the region 4000—400 cm.⁻¹ on a Perkin-Elmer model 125 spectrometer and in the region 400—200 cm.⁻¹ by means of a Grubb-Parsons DM4 mark II spectrometer; an R.I.I.C. Fourier spectrometer F.S. 520 with a Melinex beam divider and an effective resolution of 5 cm.⁻¹ was also used to obtain trichloride, Johnson Matthey Ltd: triphenylphosphine, triphenylarsine, tetramethyl- and tetraethyl-ammonium chloride, dimethylphenylphosphine, B.D.H. Laboratories; triethylphosphine, B. Newton Main Ltd; tetraphenylarsonium chloride and HCl, Koch-Light Ltd.

Ruthenium Complexes

Tetraphenylarsonium Tetrachlorobis(triphenylarsine)ruthenate(III) .--- Diacetone.--- Trichlorobis(triphenylarsine)(methanol)ruthenium(III) (0.15 g.) was suspended in solvent acetone (35 ml.) and thoroughly shaken with tetraphenylarsonium chloride and hydrochloric acid (0.80 g.) for several hours to produce complete conversion of the initially formed brown trichlorobis(triphenylarsine)-(acetone)ruthenium(III) to deep red crystals of the complex; these were washed with cold acetone (20 ml.), water (15 ml.), methanol, and diethyl ether and were then dried in vacuo at 40° for several hours (0.27 g., 70%), m.p. 195° (decomp.) (v_{CO} 1709 cm.⁻¹; v_{CC} 1219 cm.⁻¹). The complex is reasonably stable in dichloromethane but decomposes in hot acetone.

⁴⁰ A. J. Deeming and B. L. Shaw, *Chem. Comm.*, 1968, 751, and references therein.

⁴¹ J. L. Burmeister, Co-ordination Chem. Rev., 1968, 3, 225.

Tetramethylammonium Tetrachlorobis(triphenylarsine)ruthenate(III).—This was prepared as for the Ph_4As^+ salt with [RuCl₃(AsPh₃)₂MeOH] (0.25 g.) and Me₄NCl (1.20 g.) in an acetone (25 ml.)-methanol (6 ml.) mixture. Orange-red crystals of the *complex* were deposited and purified as above (0.23 g., 83%), m.p. 262—263° (decomp.). The complex is insoluble in dichloromethane.

Tetraethylammonium Tetrachlorobis(triphenylarsine)ruthenate(III).—This was prepared as for the other salts from [RuCl₃(AsPh₃)₂MeOH] (0.25 g.) and Et₄NCl,H₂O (1.00 g.) in acetone (30 ml.); it was obtained as orange-brown crystals (0.24 g., 82%), m.p. 218° (decomp.). This compound is more soluble than the Me₄N⁺ salt.

Tetraphenylarsonium Tetrachlorobis(triphenylphosphine)ruthenate(III).—Diacetone.—Method (A). This was prepared as for the corresponding triphenylarsine salt from [RuCl₃-(PPh₃)₂MeOH] (0.15 g.) and Ph₄AsCl,HCl (0.80 g.) in acetone (30 ml.); it was obtained as orange crystals (0.20 g., 79%), m.p. 207° [v_{CO} 1708 cm.⁻¹; v_{CC} 1216 cm.⁻¹].

Method (B). Dichlorotetrakis(triphenylphosphine)ruthenium(II) (0·15 g.) dissolved under nitrogen in warm acetone (25 ml.) gave a yellow-brown solution to which Ph₄AsCl,HCl (0·60 g.) in acetone (5 ml.) was added. An air-stable, redbrown solution was produced which on prolonged shaking deposited orange crystals of the *complex* which were purified as above (0·11 g., 70%), m.p. 208° (v_{CO} 1708 cm.⁻¹; v_{CO} 1216 cm.⁻¹). The same product is formed if RuCl₂(PPh₃)₃ is used.

Tetramethylammonium Tetrachlorobis(triphenylphosphine)ruthenate(III).—This was prepared as for the Ph_4As^+ salt with [RuCl₃(PPh₃)₂MeOH] (0.15 g.) and Me₄NCl (0.60 g.) and gave orange crystals (0.12 g., 80%), m.p. 220° (decomp.). This compound is insoluble in dichloromethane.

Reaction of Dichlorotris(triphenylphosphine)ruthenium(II) with Hydrochloric Acid.-RuCl₂(PPh₃)₃ (0.15 g.) dissolved under nitrogen in warm acetone gave a yellow-brown solution which upon addition of concentrated hydrochloric acid (2 ml.) immediately gave an air-stable red-brown solution. Removal of the solvent from this under reduced pressure gave a yellow-brown solid which was washed with light petroleum (b.p. 60-80°) and diethyl ether and dried in vacuo at 40° for several hours (0.10 g., 86%), m.p. 122-125° (decomp.) (Found: C, 54.7; H, 5.0; Cl, 18.1% H[RuCl₄(PPh₃)₂] requires C, 56.3; H, 4.2; Cl, 18.5%). A closer formulation is H₃O[RuCl₄(PPh₃)₂] (Requires C, 55.0; H, 4.2; Cl, 18.0; O, 2.0%) but the i.r. spectrum shows no evidence for aquo or hydroxonium groups; in view of the i.r. spectrum of [RuCl₃(LPh₃)₂MeNO₂] (no evidence for MeNO₂), this may be inconclusive. An oxygen analyses was, in fact, obtained (5.5%) but the delay was considerable and some hydrolysis has probably occurred.

When a methanol (3 ml.) solution of Me₄NCl (0.60 g.) was added to the red-brown solution, orange crystals of *tetramethylammonium tetrachlorobis*(*triphenylphosphine*)*ruthenate*-(III) were slowly deposited (0.09 g., 68%), m.p. 220-222° (decomp.). The same compound can be obtained from $\operatorname{RuCl}_2(\operatorname{PPh}_3)_4$.

Tetraphenylarsonium Tetrabromobis(triphenylarsine)ruthenate(III).—Diacetone.—[RuBr₃(AsPh₃)₂MeOH] (0.30 g.) was suspended in acetone (35 ml.) and treated with concentrated hydrobromic acid (3 ml.) to give a deep redbrown solution. Ph₄AsBr (0.80 g.) was added to this solution and the mixture was thoroughly shaken for several hours. Concentration of the solution under reduced pressure gave dark purple crystals of the *complex*, which were washed with small portions of cold acetone, hot water, ethanol, and diethyl ether and then dried *in vacuo* at 40° for several hours (0.30 g., 65%), m.p. 180° (decomp.) (v_{CO} 1701 cm.⁻¹; v_{CC} 1211 cm.⁻¹). The compound can also be made by treating the corresponding chloro-salt with an excess of lithium bromide in acetone; removal of the solvent under reduced pressure (within 5 min.) gave the purple solid, purified as above (m.p. 182°) (v_{CO} 1700 cm.⁻¹). The compound is soluble in dichloromethane and nitromethane to give purple solutions; the latter rapidly turns red-brown.

Tetramethylammonium Tetrabromobis(triphenylarsine)ruthenate(III).—This was prepared as for the Ph_4As^+ salt from [RuBr₃(AsPh₃)₂MeOH] (0·30 g.) and concentrated hydrobromic acid (3 ml.), Me₄NBr(0·80 g.) in an acetone (35 ml.) methanol (6 ml.) mixture. A purple solution was obtained which upon removal of the solvent under reduced pressure gave a purple-black solid, which was washed with methanol and diethyl ether (0·20 g., 60%), m.p. 230—231° (decomp.) [Found: M(acetone) 608. Required, 553 (for 1:1 electrolyte)].

Reaction of Tetramethylammonium Tetrachlorobis(triphenylarsine)ruthenate(III) with Lithium Bromide.—Me₄N-[RuCl₄(AsPh₃)₂] (0·30 g.) was shaken with lithium bromide (1·50 g.) in acetone (30 ml.) to give a purple solution. After 3—4 min., a portion (10 ml.) of this was decanted off and an excess of water was added to it; the purple precipitate was filtered off and washed with water, methanol, and diethyl ether (0·11 g., 87%), m.p. 230° (decomp.); its i.r. spectrum was identical with that of Me₄N[RuBr₄-(AsPh₃)₂].

The remaining solution was left for a further 2 hr. Removal of the solvent from this under reduced pressure gave a dark brown *residue* which was washed with water and diethyl ether and dried *in vacuo* at 40° for several hours (0·15 g., 80%), m.p. 154—156° (decomp.) (Found: C, 43·8; H, 3·6% [RuBr₃(AsPh₃)₂H₂O]H₂O requires C, 43·5; H, 3·5%). The i.r. spectrum shows weak bands at 3400 and 1600 cm.⁻¹; no band at 950 cm.⁻¹ corresponding to Me₄N⁺.

Reaction of Tetramethylammonium Tetrachlorobis(triphenylphosphine)ruthenate(III) with Lithium Bromide.—This was prepared as for the triphenylarsine complex from $Me_4N[RuCl_4(PPh_3)_2]$ (0.30 g.) and lithium bromide (1.50 g.) in acetone (20 ml.). The purple solution was filtered after 2—3 min., and an excess of distilled water was added to it. The resulting red-brown *precipitate* was washed with water and diethyl ether (0.28 g., 87%), m.p. 148—150° (decomp.) (Found: C, 48.0; H, 3.5; Br, 26.5% [RuBr₃(PPh_3)₂H₂O]-H₂O requires C, 48.0; H, 3.8; Br, 26.6%). The same product is obtained if the solvent is removed under reduced pressure or if RuBr₃(PPh_3)₂MeOH is treated with a mixture of Me₄NBr and HBr.

Trichlorobis(triphenylarsine)(nitromethane)ruthenium(III). —Ph₄As[RuCl₄(AsPh₃)₂] (0·20 g.) was gently warmed with nitromethane (5 ml.) and the solution was cooled. The initial yellow solution slowly turned green and after *ca*. 30 min., green crystals of the *complex* were deposited; these were washed with water, methanol, and diethyl ether and dried *in vacuo* at 40° for several hours (0·10 g., 76%), m.p. 198—199° (decomp.) (Found: C, 51·5; H, 3·9; N, 1·8%. C₃₇H₃₃As₂Cl₃NO₂Ru requires C, 50·4; H, 3·8; Cl, 12·2; N, 1·6%).

Similarly, a solution of $\text{RuCl}_3(\text{AsPh}_3)_2\text{MeOH}$ (0.20 g.) in nitromethane (5 ml.) when warmed gently, rapidly (2 min.)

deposited lime-green crystals of the complex (0.16 g., 78%), m.p. 200° (decomp.) (Found: C, 50.0; H, 4.0; Cl, 12.7; N, **1·3%**).

With $Me_4N[RuCl_4(AsPh_3)_2]$, a mixture of unchanged solid and green complex is obtained when the reaction mixture is set aside for several hours. Treatment of the green complex in acetone with an excess of Me₄NCl regenerated red $Me_4N[RuCl_4(AsPh_3)_2]$ (2 hr.).

Trichlorobis(triphenylphosphine)(nitromethane)ruthenium-(III).—This was prepared as for the Ph₃As complex from $Ph_4As[RuCl_4(PPh_3)_2]$ (0.20 g.) and nitromethane (5 ml.); the reaction almost immediately gave green crystals of the complex (0.10 g., 80%), m.p. 180° (decomp.) (Found: Cl, 13.6; N, 2.0%. C₃₇H₃₃Cl₃NO₂P₂Ru requires C, 13.5; N, 1.8%). Similarly, $Me_4N[RuCl_4(PPh_3)_2]$ and $MeNO_2$ (10 min.) gave the complex.

Dimethylphenylphosphonium Tetrachlorobis(dimethylphenylphosphine)ruthenate(III).—Carbon monoxide was bubbled through a boiling solution of commercial ruthenium trichloride hydrate (1.10 g.) in ethanol (75 ml.) for 5 hr. to give a deep red solution. An excess of dimethylphenylphosphine (2.50 g.) was added to the cool solution; the mixture when kept at 0° for 1 hr. gave yellow crystals of $[RuCl_2CO(PMe_2Ph)_3]$ [v_{CO} 1961, configuration (I)] and $[RuCl_{2}(CO)_{2}(PMe_{2}Ph)_{2}][v_{CO} 1996 \text{ cm}.^{-1}, \text{ configuration (VI)}].^{26}$ Partial removal of the solvent under reduced pressure from the filtered solution gave more carbonyl complexes mixed with dark brown crystals of the *complex*; these were washed with benzene (to remove the carbonyl complexes) and diethyl ether and dried in vacuo at 40° (1.05 g., 40%), m.p. 157° (decomp.) [vPH 2450 cm.-1]. The compound is soluble in dichloromethane, acetone, nitromethane, and chloroform but is insoluble in ethanol and water.

Tetraphenylarsonium Tetrachlorobis(dimethylphenylphosphine)ruthenate(III).-Method (A).-The phosphonium salt (0.30 g.) was dissolved in acetone (10 ml.) and an excess of Ph₄AsCl,HCl was added (120 g.) to it, red-brown crystals of the complex (0.36 g., 90%), m.p. 215° (decomp.) were deposited.

Method (B). Neat Me₂PhP (1.5 ml.) was added to crushed $Ph_4As[RuCl_4(PPh_3)_2]$ (0.15 g.) which was then set aside at room temperature under nitrogen for 4 days. The excess phosphine was then decanted off and the red-brown complex was washed with acetone and diethyl ether (0.10 g., 95%), m.p. 212° (decomp.). With $Me_4N[RuCl_4(PPh_3)_2]$ and Me₂PhP, the i.r. spectrum after 4 days showed the presence of Ph₃P and indicating incomplete exchange. The complex is soluble in CH₂Cl₂ and MeNO₂ but insoluble in ethanol and water.

Tetraphenylarsonium Tetrachlorobis(triethylphosphine)ruthenate(III).-This was prepared as for the Me,PhP salt from $Ph_4As[RuCl_4(PPh_3)_2]$ (0.15 g.) and neat Et_3P (1.0 ml.) during 6 days. The greenish-brown complex was washed with water and diethyl ether and dried in vacuo (0.09 g., 93%), m.p. 198° (decomp.). With the corresponding Ph₃As salt, 30 days are required to give the Et₃P salt. The complex was also prepared from Et₃PH[RuCl₄(PEt₃)₂] and Ph₄AsCl,HCl in acetone [m.p. 200° (decomp.)]. The compound is soluble in CH₂Cl₂, and methanol to give green solutions which rapidly turn yellow-brown.

Tetramethylammonium Tetrachlorobis(triethylphosphine)ruthenate(III).—This was prepared as the preceding complex from $Me_4N[RuCl_4(PPh_3)_2]$ (0.20 g.) and neat Et_3P (1.0 ml.). The complex was obtained as green crystals (8 days) (0.13 g.,

90%), m.p. 170° (decomp.). With the Ph_3As anion, ca. 15% conversion into the green Et₃P anion occurred during 30 days. The complex is very soluble and unstable in solution (e.g. in dichloromethane) and the green solution rapidly turns yellow-brown; the brown solid isolated contained no Me₄N⁺.

Tetraphenylarsonium Tetrabromobis(triethylphosphine)ruthenate(III).--Ph4As[RuBr4(AsPh3)2] (0.10 g.) was treated with neat Et_3P (1.0 ml.) for 2 months to give a dark green solid which was washed with water and diethyl ether (0.06 g., 93%), m.p. 196-198° (decomp.).

Tetramethylammonium Tetrachlorobis(triphenylphosphite)ruthenate(III).—Me₄N[RuCl₄(PPh₃)₂] (0.10 g.) was treated with neat triphenylphosphite (1.0 ml.) for 3 months to give the crystalline orange complex; this was washed with diethyl ether and dried in vacuo at 40° (0.19 g., 95%), m.p. 158-160° (decomp.). The i.r. spectrum shows unmistakable evidence for (PhO)₃P [cf. RuCl₂{P(PhO)₃}₄]⁴² plus an extra band at 940 cm.⁻¹ (Me₄N⁺).

Tri-µ-chloro-hexakis(triethylphosphine)diruthenium(II) Chloride.— $\operatorname{RuCl}_2(\operatorname{PPh}_3)_3$ (0.20 g.) was treated under nitrogen with neat Et₃P (1.5 ml.). A deep emerald-green solution was rapidly formed (20 min.) and after several hours the green colour was discharged and pale yellow crystals of the complex were deposited; these were washed with diethyl ether and dried in vacuo at 40° (0.20 g., 92%), m.p. 145° (decomp.) (Found: C, 40.3; H, 8.4; Cl, 13.2%. Calc. for C₃₆H₉₀Cl₄P₆Ru₂: C, 41.1; H, 8.6; Cl, 13.5%). The intermediate green colour was also obtained in acetone solution but removal of the solvent gave an oil, which was very soluble in diethyl ether, and light petroleum, etc.

Rhodium(III) Complexes

Tetraphenylarsonium Tetrachlorobis(triphenylphosphine)rhodate(III).—Diacetone Method (A). Tristriphenylphosphinechlororhodium(I) 43 (0.60 g.) was suspended in solvent acetone (40 ml.) and Ph₄AsCl,HCl (1.5 g.) was added to it; the mixture was shaken for several hours under nitrogen until all the purple starting material was converted into orange-yellow crystals of the complex. These were washed with water, acetone, and diethyl ether and dried in vacuo for several hours at 40° (0.60 g., 73%), m.p. 206°) (v_{CO} 1710 cm.⁻¹; v_{OC} 1221 cm.⁻¹).

(B). Method trans-Chlorocarbonylbis(triphenylphosphine)rhodium(1) 44 (0.30 g.) was heated under reflux with Ph₄AsCl,HCl (0.80 g.) in a chloroform (15 ml.)-acetone (7 ml.) mixture for ca. 30 min. and was then set aside for several days. The yellow solution slowly turned red and a mixture of unchanged [RhCl(CO)(PPh₃)₂] (v_{CO} 1961 cm.⁻¹) and trans-[RhCl₃CO(PPh₃)₂] (v_{CO} 2105 cm.⁻¹) was deposited. The solution was filtered, more acetone (10 ml.) was added, and the mixture was set aside for a further 24 hr. Orangered crystals of the *complex* were obtained and were worked with chloroform, acetone, water, methanol, and diethyl ether (0.14 g., 25%), m.p. 206–208°) (v_{CO} 1709; v_{CC} 1219 cm.⁻¹). The compound is sparingly soluble in chloroform but soluble in CH₂Cl₂ and MeNO₂.

Tetramethylammonium Tetrachlorobis(triphenylphosphine)rhodate(III).-RhCl(PPh₃)₃ (0.60 g.) was suspended in an acetone (15 ml.)-methanol (25 ml.) mixture and treated with concentrated hydrochloric acid (6 ml.); it was then

⁴² S. D. Robinson, Chem. Comm., 1968, 521.
 ⁴³ J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, J. Chem. Soc. (A), 1966, 1711.

44 L. M. Vallarino, J. Chem. Soc., 1957, 2287.

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shaken for 1 hr. with Me₄NCl (2.7 g.). The solution was filtered and set aside 24 hr. when orange-yellow crystals of the *complex* were deposited; these were purified as above (0.40 g., 73%), m.p. 230–234° (decomp.).

Tetraphenylarsonium Tetrabromobis(triphenylphosphine)rhodate(III)-Acetone.—A suspension of Ph₄As[RhCl₄(PPh₃)₂] (0·10 g.) was shaken with lithium bromide (3·0 g.) in acetone (35 ml.) for 24 hr. The yellow-brown solution was filtered, two-thirds of the solvent were removed under reduced pressure, and the unchanged lithium bromide and chloride were filtered off; removal of the remainder of the solvent gave a yellow-brown *powder*, which was washed with water and diethyl ether and dried *in vacuo* at 40° (0·10 g., 88%), m.p. 170° (decomp.) (v_{CO} 1705 cm.⁻¹; v_{CO} 1220 cm.⁻¹). The compound is very soluble in acetone and methanol.

Tetraphenylarsonium Tetrathiocyanatobis(triphenylphosphine)rhodate(III).—This was prepared as for the bromocomplex, with lithium thiocyanate (2.0 g.); removal of the solvent from the yellow solution gave the lemon-yellow powder which was purified as above (0.09 g., 91%), m.p. 96—98°) (v_{ON} 2105 cm.⁻¹). The compound contained no acetone (i.r.) and is very soluble in acetone and methanol.

Tetraphenylarsonium Tetrachlorobis(dimethylphenylphos-

phine)rhodate(III).—This was prepared as for the corresponding ruthenium complex from the Ph₃P anion (0·15 g.) which was treated with neat Me₂PhP (1·5 ml.) for 10 days under nitrogen; the red-brown *complex* was purified as before (0·09 g., 92%), m.p. 224—226° (decomp.); the n.m.r. in CH₂Cl₂ showed methyl resonance (1:2:1 triplet) at τ 8·07 apparent coupling constant J(P-H) 4·0 c./sec.

Similar attempts to prepare the rhodium(III) anions of Et_3P and $(PhO)_3P$ gave only the unchanged Ph_3P anion.

Reaction of mer-Trichlorotris(dimethylphenylphosphine)rhodium(III) with Tetramethylammonium Chloride.—mer-[RhCl₃(PMe₂Ph)₃] (0·20 g.) was dissolved in chloroform (10 ml.) and Me₄NCl (2·0 g.) in methanol (10 ml.) was added to it. After several days, a crystalline pale yellow solid was deposited, m.p. 217—221° (decomp.), which had an i.r. spectrum identical with that of fac-[RhCl₃(PMe₂Ph)₃].³¹ More of this complex was obtained when the reaction mixture was set aside but no anionic complex was isolated from the residue.

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