Cationic and Neutral Complexes of Ruthenium-(II) and -(III) containing Tertiary Phosphines or Arsines and Nitrogen-donor Ligands [1]

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In contrast to the reaction of [$RuX_3(EPh_3)_2(HOMe)$] (X = Cl or Br; E = P or As) with N–N (N–N = 2,2′-bipyridyl or 1,10-phenanthroline) in CH_2Cl_2 which gives [$RuX_3(EPh_3)$(N–N)], the reaction in methanol gives [$RuX(EPh_3)$(N–N)$_2$]X (X = Cl or Br; E = P). For E = As these cations are only formed if [$RuCl_3(AsPh_3)$(N–N)] and N–N in methanol are reacted in the presence of Na[BPh_4]. However, reaction of [$RuCl_3(PPh_3)_2(O_2NMe)$], bipy, and Na[BPh_4] in methanol gives both [$RuCl_2(PPh_3)_2$(bipy)][BPh_4] and [$RuCl(PPh_3)$(bipy)$_2$][BPh_4] whereas [$RuCl_3(PPh_3)$(bipy)] and PhCN give [$RuCl_2(PPh_3)(NCPh)$(bipy)]Cl·H_2O. Reaction of *mer*-[$RuCl_3(PMe_2Ph)_3$] and excess of bipy in methanol followed by recrystallisation from acetone–light petroleum gives [$RuCl(PMe_2Ph)_3$(bipy)]Cl·2H_2O and [$RuCl(PMe_2Ph)_2$(bipy)($OCMe_2$)]Cl, whereas in CH_2Cl_2 [$RuCl_2(PMe_2Ph)_2$(bipy)] and a small amount of [Hbipy][$RuCl_3(PMe_2Ph)$(bipy)] is formed. With phen the product from CH_2Cl_2–hexane is [$RuCl_2(PMe_2Ph)_2$(phen)], but from methanol, followed by recrystallisation from CH_2Cl_2–light petroleum, the main product is [$RuCl(PMe_2Ph)_2$(phen)(CH_2Cl_2)]Cl together with small amounts of [Hphen][$RuCl_3(PMe_2Ph)$(phen)]·H_2O. With 3,4,7,8-tetramethyl-1,10-phenanthroline (Me_4phen), reaction with [$RuCl_3(PMe_2Ph)_3$] in methanol gives [$RuCl(PMe_2Ph)_3(Me_4$phen)]Cl which on recrystallisation from CH_2Cl_2–pentane gives [$RuCl(PMe_2Ph)_2(Me_4$phen)(CH_2Cl_2)]Cl. In contrast, reaction with 2,9-dimethyl-1,10-phenanthroline (Me_2phen) gives [$Ru_2Cl_2(Me_2$phen)$_4$]Cl_2 and [$Ru_2Cl_3(PMe_2Ph)_6$]Cl. All the complexes have been characterised by elemental analysis, ^1H and ^{31}P n.m.r. spectra, and heteronuclear-decoupling studies and attempts have been made to rationalise the observed differences in product composition.

SEVERAL successful methods of preparation of neutral Ru^{III} complexes containing tertiary phosphines and arsines have been reported elsewhere.[2] However, as reported briefly earlier,[2] when some of these reactions are carried out in more polar solvents such as methanol,

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[1] Preliminary communication, L. Ruiz-Ramírez, T. A. Stephenson, and E. S. Switkes, *J. Organometallic Chem.*, 1973, **49**, C77.

[2] L. Ruiz-Ramírez, T. A. Stephenson, and E. S. Switkes, *J.C.S. Dalton*, 1973, 1770 and refs. therein.

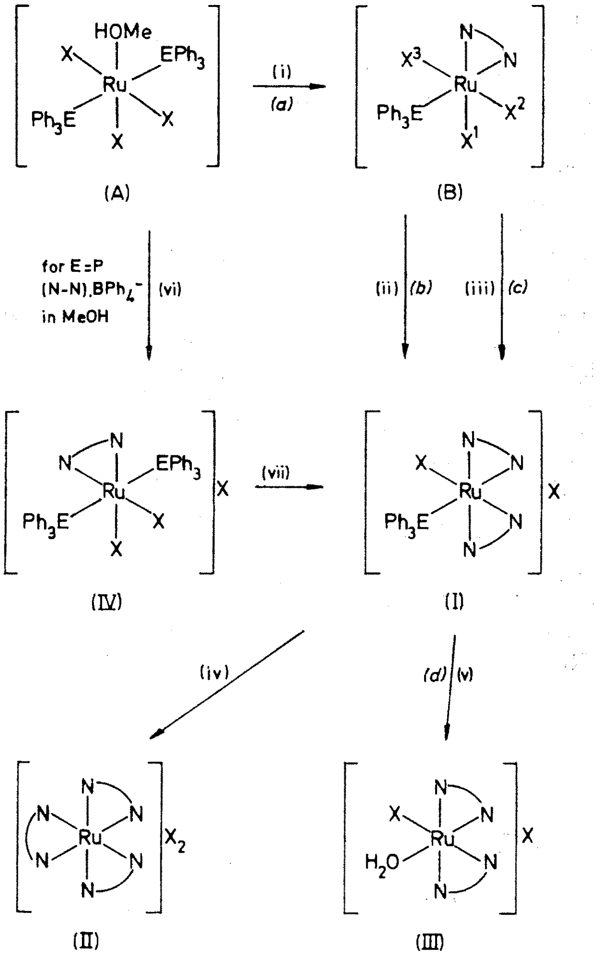
rather than dichloromethane, reduction to cationic Ru^{II} complexes occurs. Although a wide range of neutral Ru^{II} complexes has been reported, few cationic Ru^{II} complexes containing phosphine (or arsine) ligands are known.[3] Therefore we considered it of some importance to attempt to synthesise and characterise more complexes of this type, especially in view of the antibacterial activity recently demonstrated for rhodium(III) cations containing various nitrogen-donor ligands.[4]

RESULTS AND DISCUSSION

(a) *Triphenyl-phosphine and -arsine Complexes containing Nitrogen-donor Ligands.*—A range of neutral Ru^{III} complexes containing tertiary phosphines or arsines and bidentate nitrogen-donor ligands was prepared by reaction of $[RuX_3(EPh_3)_2(HOMe)]$ ($X = Cl$ or Br; $E = P$ or As) with either 2,2′-bipyridyl or 1,10-phenanthroline (N–N). When the reactions were carried out in CH_2Cl_2, the only products obtained were the neutral paramagnetic Ru^{III} complexes $[RuX_3(EPh_3)(N–N)]$ (except in the case where $E = P$, $X = Br$, and N–N = bipy, when a small amount of a yellow-brown solid identified as the halide-bridged complex $[Ru_2Br_2(PPh_3)_4(bipy)_2]Br_2$ was also isolated). The complex $[Ru_2Br_2(PPh_3)_4(bipy)_2]Br_2$ was obtained in higher yield by reaction of $[RuBr_2(PPh_3)_3]$ and bipy in CH_2Cl_2; similarly $[Ru_2Cl_2(PPh_3)_4(bipy)_2]Cl_2$ was synthesised from $[RuCl_2(PPh_3)_3]$ and bipy (see ref. 2).

However, when the reactions of $[RuCl_3(PPh_3)_2(HOMe)]$ and excess of N–N were carried out in methanol $[RuCl(PPh_3)(N–N)_2]Cl{\cdot}H_2O$, (I), were obtained together with very low yields of $[RuCl_3(PPh_3)(N–N)]$. The monomeric cations can also be prepared by reactions of $[RuCl_3(PPh_3)(N–N)]$ and excess of N–N in methanol. Similarly, reactions of $[RuCl_2(PPh_3)_3]$ with excess of N–N in methanol gave the same cations together with small amounts of $[Ru_2Cl_2(PPh_3)_4(N–N)_2]Cl_2$. The monomeric formulation is confirmed by the ready synthesis of the $[PF_6]^-$ and $[BPh_4]^-$ salts (see ref. 2). In contrast, the reaction of $[RuCl_3(AsPh_3)_2(HOMe)]$ or $[RuCl_3(AsPh_3)(bipy)]$ with excess of bipy in methanol gave $[Ru(bipy)_3]Cl_2{\cdot}6H_2O$, (II), and small amounts of purple $[RuCl(OH_2)(bipy)_2]Cl{\cdot}H_2O$, (III). However, when a mixture of $[RuCl_3(AsPh_3)(bipy)]$, bipy, and $Na[BPh_4]$ was heated under reflux in methanol the only product was $[RuCl(AsPh_3)(N–N)_2][BPh_4]$, (I) (see ref. 2).

In the Scheme possible modes of formation of complexes (I)—(III) are presented. The structures of $[RuCl_3(EPh_3)_2(HOMe)]$ (A) and $[RuCl_3(EPh_3)(N–N)]$ (B) have been previously established.[2] Thus, in step (i) N–N displaces first the labile MeOH ligand and subsequently a EPh_3 group to form the Ru^{III} complex (B). In CH_2Cl_2, further dissociation of halide groups is not encouraged and therefore (B) is the only product. However, step (ii) is facilitated when methanol is used as solvent. Here the more polar solvent encourages dissociation of the halide groups, probably initially of X^1 (*trans* to N–N) and then X^2 (or X^3) is subsequently displaced to give (I).* The displacement of halide groups is also accompanied by reduction of the metal to the bivalent state. For $E = As$ further reaction occurs in methanol, namely displacement of the $AsPh_3$ group and the remaining halide ligand by N–N to give $[Ru(N–N)_3]X_2$, (II) [step (iv)]. In addition, small amounts of $[RuCl(OH_2)(N–N)_2]Cl{\cdot}H_2O$, (III), are produced, presumably by displacement from (I) of the $AsPh_3$ group by water [step (v)]. Reactions (iv) and (v) do not occur under these conditions when $E = P$, presumably because PPh_3 is a stronger nucleophile than $AsPh_3$. However, the synthesis of $[RuCl(AsPh_3)(bipy)_2][BPh_4]$ by reaction of $[RuCl_3(AsPh_3)(bipy)]$, bipy, and



SCHEME (*a*), N–N in CH_2Cl_2; (*b*), $E = P$, excess of N–N in MeOH; (*c*), $E = As$, excess of N–N and $[BPh_4]^-$ in MeOH; (*d*), $E = As$, excess of N–N in MeOH

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* Although no direct experimental evidence is available, we suggest that all complexes (I) have a *cis* configuration by analogy with earlier studies on $[MCl_2(N–N)_2]Cl$ ($M = Co$, Cr, or Rh) which only exhibit *cis*-octahedral geometry.[5]

[3] For recent references see G. M. Bancroft, M. J. Mays, B. E. Prater, and F. P. Stefani, *J. Chem. Soc.* (*A*), 1970, 2146; B. E. Cavit, K. R. Grundy, and W. R. Roper, *J.C.S. Chem. Comm.*, 1972, 60; J. R. Sanders, *J.C.S. Dalton*, 1973, 743; T. V. Ashworth and E. Singleton, *J. Organometallic Chem.*, 1974, **77**, C31.

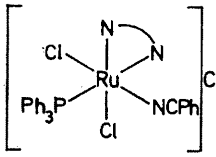
[4] For detailed refs. see M. J. Cleare, *Co-ordination Chem. Rev.*, 1974, **12**, 383.

[5] See E. D. McKenzie and R. A. Plowman, *J. Inorg. Nuclear Chem.*, 1970, **32**, 199 and refs. therein.

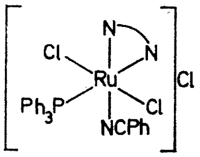
Na[BPh_4] in methanol confirms that (I) is initially formed even for E = As [step (iii)].

When [$RuCl_3(PPh_3)_2(O_2NMe)$],* excess of bipy, and Na[BPh_4] were heated under reflux in methanol two orange products formed. The less soluble species, which is obtained in higher yield (60%), analysed for the Ru^{III} cation [$RuCl_2(PPh_3)_2$(bipy)][BPh_4], (IV), and the other product is [$RuCl(PPh_3)$(bipy)$_2$][BPh_4], (I). Therefore, in methanol, preferential replacement of halide ion rather than PPh_3 occurs and the resulting Ru^{III} cation (IV) can be precipitated by [BPh_4]$^-$ ion before substantial reduction to the Ru^{II} cation (I) occurs. Hence, in polar solvents, steps (vi) and (vii) (see Scheme) also constitute an important alternative path for formation of (I).

In an attempt to synthesise mixed nitrogen-donor ligand cationic complexes, [$RuCl_3(PPh_3)$(bipy)] was treated in methanol with excess of phenyl cyanide. A yellow solid was isolated which analysed for the Ru^{III} cation [$RuCl_2(PPh_3)$(NCPh)(bipy)]$Cl{\cdot}H_2O$ ($\mu_{\text{eff.}}$ 1.78 B.M. by Evans' method).[6,†] The i.r. spectrum contained a weak band at 2 222 cm^{-1} [ν(CN)] suggesting that bonding occurs through the nitrogen.[7] Examination of the far-i.r. spectrum revealed two bands at 320 and 300 cm^{-1} [ν(RuCl)] consistent with configuration (Va). However, recrystallisation from CH_2Cl_2–pentane gave a product with a single band at 334 cm^{-1} and no changes in the rest of the spectrum. A possible explanation is facile isomerisation of (Va) to give (Vb). In this instance, the absence of Ru^{II} species {*cf.* the reaction of [$RuCl_3(PPh_3)$(bipy)] with bipy} can be attributed to the lower nucleophilicity of PhCN compared to bipy.



(Va)



(Vb)

(b) *Dimethylphenylphosphine Complexes containing Bidentate Nitrogen-donor Ligands.*—Reaction of *mer*-[$RuCl_3(PMe_2Ph)_3$] (A′) with excess of bipy in refluxing methanol followed by solvent removal and recrystallisation from acetone–light petroleum gave an orange precipitate and a red filtrate. The former, whose i.r. spectrum showed the presence of PMe_2Ph, bipy, and water ligands, analysed for [$RuCl_2(PMe_2Ph)_3$(bipy)-$(OH_2)_2$] and is conducting in CH_2Cl_2. Its ^1H n.m.r. spectrum in $CDCl_3$ (Figure 1) signifies two mutually *trans* PMe_2Ph groups with no plane of symmetry passing through the phosphorus atoms and a third PMe_2Ph group *cis* to these ligands. The proton-noise decoupled ^{31}P n.m.r. spectrum, which consisted of a triplet and doublet pattern (relative intensity 1 : 2), is in agreement with this proposed stereochemistry. In addition, there was a singlet in the ^1H n.m.r. spectrum at τ 7.73 (301 K) whose position was temperature and concentration dependent, indicating the presence of hydrogen-bonded water molecules {*cf.* [$Pt(S_2CNR_2)(PR'_3)_2]Cl{\cdot}H_2O$ [8]}.

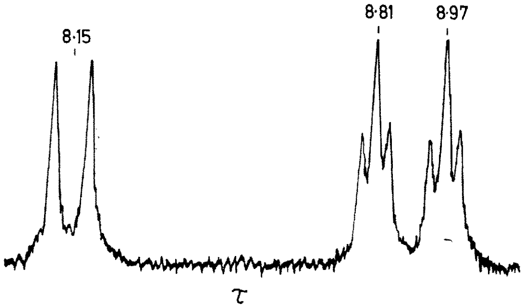
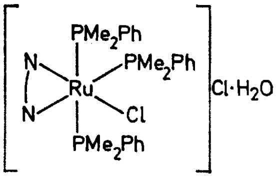


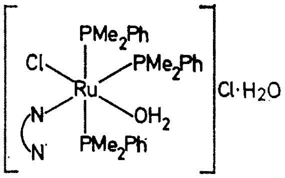
FIGURE 1 ^1H N.m.r. spectrum of [$RuCl(PMe_2Ph)_3$(bipy)]$Cl{\cdot}H_2O$ in $CDCl_3$ (methyl region) at 301 K

There are three structures which fit these n.m.r. data, namely (VIa)—(VIc). Structure (VIb) can be discounted because the conductivity data indicate a 1 : 1 electrolyte and this is verified by synthesis of [RuCl-$(PMe_2Ph)_3$(bipy)][BPh_4]$\cdot 2H_2O$; (VIc) seems even more unlikely but cannot be completely ruled out on the present evidence {*cf.* [PtCl(phen)$(PEt_3)_2$][BF_4] shown to have structure (VII) [9]}. Nevertheless, (VIa) appears to be the most likely structure.

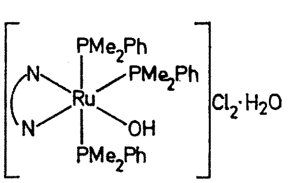
Concentration of the red filtrate gave a dark red conducting solid whose ^1H n.m.r. spectrum in $CDCl_3$ (methyl region) consisted of four doublets of equal intensity. This clearly indicates that the complex contains two mutually *cis* PMe_2Ph groups and the other ligands are so arranged that the phosphorus atoms do not lie on a plane of symmetry of the molecule.‡



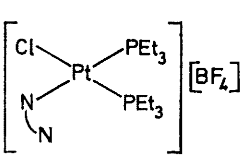
(VIa).



(VIc)



(VIb)



(VII)

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* In ref. 2, it was shown that [$RuCl_3(PPh_3)_2(O_2NMe)$] undergoes the same reactions as [$RuCl_3(PPh_3)_2$(HOMe)] providing the entering ligand is a stronger nucleophile than $MeNO_2$.

† 1 B.M. ≈ 9.27 × 10^{-24} A m^2, 1M = 1 mol dm^{-3}.

‡ On the basis of C, H, and N analyses alone this complex was initially considered to be a geometrical isomer of (VIa).[1]

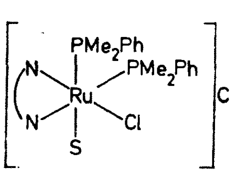
[6] D. F. Evans, *J. Chem. Soc.*, 1959, 2003.

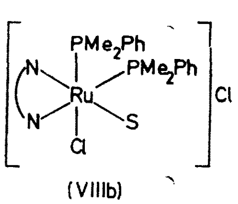
[7] R. A. Walton, *Quart. Rev.*, 1965, **19**, 126.

[8] J. M. C. Alison and T. A. Stephenson, *J.C.S. Dalton*, 1973, 254.

[9] G. W. Bushnell, K. R. Dixon, and M. A. Khan, *Canad. J. Chem.*, 1974, **52**, 1367.

The ^{31}P n.m.r. spectrum (two doublets of equal intensity) and heteronuclear decoupling studies support this conclusion (see Experimental section). In addition, there was a singlet at τ 7.86 whose position was temperature invariant. This resonance is therefore assigned to co-ordinated acetone and this conclusion is supported by the weak i.r. band at 1 620 cm^{-1} [ν(CO)] {*cf.* $[RuCl_3(AsPh_3)_2(OCMe_2)]$, ν(CO) at 1 656 cm^{-1}}.[10] The only structures which fit the above information are (VIIIa) or (VIIIb). Similar complexes of composition $[Ru(bipy)_2(S)Cl]Cl$ (S = Me_2CO, MeCN, *etc.*) have been recently reported and proved useful intermediates for synthesising a range of complexes by solvent displacement, *e.g.* $[Ru(bipy)_2Cl(py)]^+$, $[Ru(bipy)_2Cl(NO_2)]$, *etc.* (py = pyridine).[11]


(VIIIa)


(VIIIb)

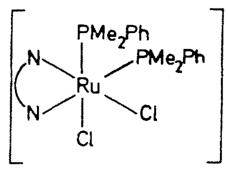
(S = Me_2CO or CH_2Cl_2)

Likewise, preliminary investigations indicate that (VIII) is a useful starting material for reactions of this type. For example, reaction of (VIII) with PMe_2Ph readily gave the orange complex (VIa). Also, the conductivity of (VIII) in CH_2Cl_2 decreased with time such that after 4—5 h the ^1H n.m.r. spectrum of the solution was identical with that of $[RuCl_2(PMe_2Ph)_2(bipy)]$ (see below). Finally, red solutions of (VIII) (S = CH_2Cl_2) and PMe_2Ph were produced when CH_2Cl_2 solutions of (VIa) were left to stand for several weeks. This suggests that (VIIIa) is the most likely structure of the solvated complex, which is consistent with the higher *trans* effect of PMe_2Ph compared to bipy. Complex (VIIIa) was also slowly formed when $[RuCl_2(PMe_2Ph)_2(bipy)]$ was left in strongly solvating solvents for several days.

$$[RuCl(PMe_2Ph)_2(bipy)(Me_2CO)]Cl \rightleftharpoons [RuCl_2(PMe_2Ph)_2(bipy)] + Me_2CO \quad (1)$$

Reaction of A′ with excess of bipy in CH_2Cl_2 gave the dark red non-conducting $[RuCl_2(PMe_2Ph)_2(bipy)]$. Its ^1H n.m.r. spectrum in $CDCl_3$ at 233 K (methyl region) consisted of four doublets, suggesting structure (IX). Again, ^{31}P n.m.r. and heteronuclear decoupling studies confirm this suggestion (see Experimental section). A minor product of this reaction was an orange-red solid which analysed for $[Hbipy][RuCl_3(PMe_2Ph)(bipy)]$. In support of this formulation, the i.r. spectrum showed extra bands in the region 1 500—1 600 cm^{-1}, assignable to the $[Hbipy]^+$ ion.[12] In hexane–CH_2Cl_2 (10 : 1 ratio by volume) only $[RuCl_2(PMe_2Ph)_2(bipy)]$ was isolated.

From earlier studies,[2] it was expected that reactions of phen would follow the same pattern as those of bipy. However, although reaction of A′ with excess of phen in methanol did give orange and red products, the orange product was not the expected $[RuCl(PMe_2Ph)_3(phen)]Cl$ but analysed for $[Hphen][RuCl_3(PMe_2Ph)(phen)]{\cdot}H_2O$. This complex is conducting in methanol and showed extra i.r. bands in the region 1 500—1 600 cm^{-1} characteristic of $[Hphen]^+$ ion.[12] The main product, which was separated from the orange solid by recrystallisation from CH_2Cl_2–light petroleum, was the expected dark red $[RuCl(PMe_2Ph)_2(phen)(CH_2Cl_2)]Cl$, (VIIIa) ($^1H$ and ^{31}P n.m.r. evidence). Although no evidence was found in this reaction for formation of $[RuCl(PMe_2Ph)_3(phen)]Cl$, addition of a large excess of PMe_2Ph to a red $CDCl_3$ solution of (VIIIa) (N–N = phen, S = CH_2Cl_2) rapidly gave an orange solution with a ^1H n.m.r. pattern very similar to that observed for the $[RuCl(PMe_2Ph)_3(bipy)]^+$ cation. The main reason for the instability of the $(PMe_2Ph)_3$ complex here is probably steric. In hexane–CH_2Cl_2 (10 : 1 v/v) reaction of A′ with excess of phen gave neutral $[RuCl_2(PMe_2Ph)_2(phen)]$, (IX).


(IX)

In view of these differences in behaviour of bipy and phen, the reaction with A′ was extended to some methyl-substituted 1,10-phenanthrolines. Reaction between 3,4,7,8-tetramethyl-1,10-phenanthroline (Me_4phen) and A′ in methanol gave a red solution which after concentration and addition of CH_2Cl_2–pentane gave orange-red $[RuCl(PMe_2Ph)_3(Me_4phen)]Cl$. This was confirmed by its proton-noise decoupled ^{31}P n.m.r. spectrum which showed the expected triplet and doublet pattern (relative intensity 1 : 2). However, recrystallisation from CH_2Cl_2–pentane gave a dark red conducting solid whose ^{31}P n.m.r. spectrum consisted of two doublets of equal intensity. Its ^1H n.m.r. spectrum in $CDCl_3$ (Figure 2) consisted of two overlapping doublets centred at τ 7.47 and 7.51 (Me of Me_4phen), two doublets at τ 7.74 and 8.00, a ' triplet ' at τ 8.64 (Me of PMe_2Ph), and a singlet at τ 4.76 (CH_2Cl_2). However, decoupling experiments revealed that the ' triplet ' is in fact two overlapping doublets and thus the complex is formulated as $[RuCl(PMe_2Ph)_2(Me_4phen)(CH_2Cl_2)]Cl$, (VIIIa).

In contrast, the reaction of A′ with excess of 2,9-dimethyl-1,10-phenanthroline (Me_2phen) in methanol gave a dark yellow solution which after concentration and addition of CH_2Cl_2–pentane gave a white crystalline

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

[11] S. A. Adeyemi, F. J. Miller, and T. J. Meyer, *Inorg. Chem.*, 1972, **11**, 994.

[12] A. A. Schilt and R. C. Taylor, *J. Inorg. Nuclear Chem.*, 1959, **9**, 211.

precipitate and a yellow filtrate from which a golden-yellow solid was isolated. The white solid was too insoluble for n.m.r. measurements but the i.r. spectrum revealed that it contained no PMe_2Ph ligands. The complex analysed for $[RuCl_2(Me_2phen)_2]$ but is strongly conducting in methanol [Λ (1 × 10^{-3}M) 150 S cm^2 mol^{-1}] suggesting the formulation $[Ru_2Cl_2(Me_2phen)_4]Cl_2$, (X) {*cf.* $[Ru_2Cl_2(N{-}N)_2(PPh_3)_4]Cl_2$ [2]}. The yellow complex was identical in analysis, i.r., and ^1H n.m.r. to the well known $[Ru_2Cl_3(PMe_2Ph)_6]Cl$.[13]

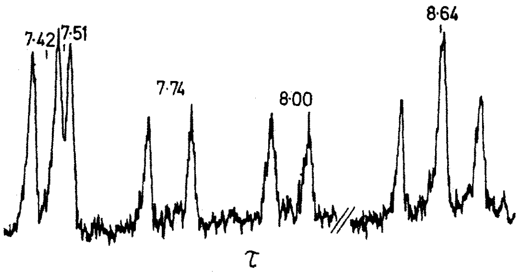
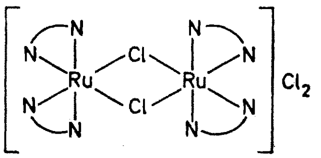


FIGURE 2 ^1H N.m.r. spectrum of $[RuCl(PMe_2Ph)_2(Me_4phen)(CH_2Cl_2)]Cl$ in $CDCl_3$ (methyl region) at 301 K



(X)

These studies clearly indicate that both solvent media and steric constraints on the ligands play an important role in these reactions. Thus, whereas bipy readily forms the $(PMe_2Ph)_3$ complex (VIa), phen and Me_4phen only give this complex with difficulty and the sterically encumbered Me_2phen gives no complexes containing itself and PMe_2Ph groups.

EXPERIMENTAL

Microanalyses were by A. Bernhardt, West Germany, and the University of Edinburgh Chemistry Department. I.r. spectra were recorded in the region 4 000—250 cm^{-1} on a Perkin-Elmer 225 grating spectrometer using Nujol and hexachlorobutadiene mulls on caesium iodide plates. Solution spectra were obtained in potassium bromide cells. ^1H N.m.r. spectra and solution magnetic moments (Evans' method) were determined on a Varian Associates HA 100 spectrometer with variable-temperature attachment and ^{31}P n.m.r. spectra on a Varian XL 100 spectrometer operating in the pulse and Fourier-transform modes at 40.5 MHz (^{31}P chemical shifts quoted in p.p.m. to high frequency of 85% H_3PO_4). Heteronuclear-decoupling experiments were carried out on the HA 100 spectrometer using a second radio-frequency field provided by the Schlumberger FS30 frequency synthesiser. Conductivity measurements were made on a model 310 Portland Electronics bridge. M.p.s were determined with a Köfler hot-stage microscope and are uncorrected.

The complexes $[RuCl(PPh_3)(bipy)_2]Cl{\cdot}H_2O$, $[RuCl(PPh_3)(bipy)_2]Y$ (Y = PF_6 or BPh_4), $[RuCl(PPh_3)(phen)_2]Y$ (Y = Cl or PF_6), $[RuCl(AsPh_3)(bipy)_2][BPh_4]$, $[Ru_2X_2(PPh_3)_4(N{-}N)_2]X_2$ (X = Cl or Br; N–N = bipy or phen), $[Ru(bipy)_3]Cl_2{\cdot}6H_2O$, and $[RuCl(OH_2)(bipy)_2]Cl{\cdot}2H_2O$ were prepared as described in ref. 2.

(2,2′-Bipyridyl)dichlorobis(triphenylphosphine)ruthenium(III) *Tetraphenylborate*.—The complex $[RuCl_3(PPh_3)_2(O_2NMe)]$ (0.10 g) was heated under reflux under nitrogen in methanol (120 cm^3) with an excess of sodium tetraphenylborate (0.10 g) and 2,2′-bipyridyl (0.04 g) for *ca.* 5 h. The initial green suspension became yellow and after *ca.* 2 h of reflux an orange *solid* started to precipitate and finally the solution became red. The solid was collected and washed with methanol (yield 60%), m.p. 195—196 °C (decomp.) (Found: C, 71.9; H, 5.3; N, 3.4. Calc. for $C_{70}H_{58}BCl_2N_2P_2Ru$: C, 71.9; H, 5.1; N, 2.4%), Λ (1.0 × 10^{-3}M) in CH_2Cl_2 = 19.3 S cm^2 mol^{-1}. The red filtrate was concentrated and the orange complex *bis(2,2′-bipyridyl)chloro(triphenylphosphine)ruthenium*(II) *tetraphenylborate* which precipitated was washed with light petroleum (b.p. 100—120 °C) and methanol (20%), m.p. 230 °C (Found: C, 73.0; H, 5.1; N, 5.5. Calc. for $C_{62}H_{51}BClN_4PRu$: C, 72.3; H, 4.9; N, 5.4%).

(2,2′-Bipyridyl)dichloro(phenyl cyanide)triphenylphosphineruthenium(III) *Chloride Monohydrate*.—The complex $[RuCl_3(PPh_3)(bipy)]$ (0.10 g) was heated under reflux under nitrogen in methanol (100 cm^3) with excess phenyl cyanide (0.08 cm^3) for *ca.* 12 h. The resulting orange solution was concentrated to dryness, the residue dissolved in dichloromethane followed by pentane addition, and a crystalline yellow solid was precipitated (72%), m.p. 165—167 °C (decomp.) (Found: C, 56.2; H, 4.0; N, 5.9. Calc. for $C_{35}H_{30}Cl_3N_3OPRu$: C, 56.5; H, 4.0; N, 5.7%), Λ (6.0 × 10^{-4}M) in CH_2Cl_2 = 8.2 S cm^2 mol^{-1}; ν(RuCl) at 320 and 300 cm^{-1}. Recrystallisation from CH_2Cl_2–pentane gave an orange isomer, m.p. 168 °C [ν(RuCl) at 334 cm^{-1}].

(2,2′-Bipyridyl)chlorotris(dimethylphenylphosphine)ruthenium(II) *Chloride Dihydrate*.—The complex $[RuCl_3(PMe_2Ph)_3]$ (0.30 g) [14] was heated under reflux in methanol (200 cm^3) under nitrogen with an excess of bipy for *ca.* 12 h. The resulting red solution containing a mixture of two components (t.l.c. evidence) was concentrated to dryness and acetone–light petroleum (b.p. 100—120 °C) was added to the residue giving the orange solid (60%), m.p. 123 °C (decomp.) (Found: C, 51.7; H, 5.4; Cl, 9.4; N, 3.7. Calc. for $C_{34}H_{45}Cl_2N_2O_2P_3Ru$: C, 52.4; H, 5.8; Cl, 9.1; N, 3.6%), Λ (1 × 10^{-3}M) in CH_2Cl_2 = 16.5 S cm^2 mol^{-1}; τ in ($CDCl_3$) (301 K) (Figure 1) 8.97 (t) and 8.81 (t) [J(PH) + J(PH)′ 6.5], 8.15 (d) [J(PH) 7.5 Hz] (P*Me*$_2$Ph), 7.73 (s) (H_2O); and 0—4 (PMe_2*Ph* and bipy); ^{31}P n.m.r., δ (in $CDCl_3$) (301 K) 6.88 (t) and 0.38 p.p.m. (d) [relative intensity 1 : 2, J(PP) 32.8 Hz].

Concentration of the red filtrate gave a red solid, *(acetone)(2,2′-bipyridyl)chlorobis(dimethylphenylphosphine)ruthenium*(II) *chloride* (30%), m.p. 115 °C (decomp.) (Found: C, 51.6; H, 5.5; Cl, 8.1; N, 4.0. Calc. for $C_{29}H_{36}Cl_2N_2OP_2Ru$: C, 52.6; H, 5.4; Cl, 10.7; N, 4.2%), Λ (1 × 10^{-3}M) in CH_2Cl_2 = 20.0 S cm^2 mol^{-1}; τ (in $CDCl_3$) (301 K) 8.71, 8.56, 8.01, 7.82 (doublets) [J(PH) 8.5 Hz] (P*Me*$_2$Ph), 7.86 (s) (acetone), and 0—4 (PMe_2*Ph* and bipy); δ (in $CDCl_3$) (301 K) 27.20 and 15.14 p.p.m. (doublets) [relative intensity 1 : 1,

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

J(PP) 36.0 Hz]. $^{1}\text{H}-\{^{31}\text{P}\}$ studies: irradiation at 40 481 715 Hz collapsed τ 8.71 and 8.56, whereas irradiation at 40 481 210 Hz collapsed τ 8.01 and 7.82 (doublets).

(2,2′-*Bipyridyl*)*chlorotris*(*dimethylphenylphosphine*)*ruthenium*(II) *Tetraphenylborate Dihydrate*.—The complex $[\text{RuCl(PMe}_2\text{Ph)}_3\text{(bipy)]Cl}\cdot2\text{H}_2\text{O}$ (0.10 g) was dissolved in methanol (10 cm^3) and a three-fold excess of $\text{Na[BPh}_4]$ (0.12 g) added. After shaking for 4 h the orange crystalline *precipitate* was filtered off, washed several times with methanol, and dried *in vacuo* at 40 °C (71%), m.p. 159—160 °C (Found: C, 65.8; H, 5.9; N, 2.7. Calc. for $\text{C}_{58}\text{H}_{65}\text{BClN}_2\text{O}_2\text{P}_3\text{Ru}$: C, 65.6; H, 6.1; N, 2.7%), Λ (4×10^{-4}M) in CH_2Cl_2 = 40.0 S cm^2 mol^{-1}; τ (in CDCl_3) (301 K) 9.03 and 8.84 (triplets) [J(PH) + J(PH)′ 6.5], 8.25 (d) [J(PH) 7.5 Hz] [PMe_2Ph], 7.70 (s) (H_2O), and 0—5 (PMe_2Ph, $[\text{BPh}_4]^-$, and bipy).

(2,2′-*Bipyridyl*)*dichlorobis*(*dimethylphenylphosphine*)*ruthenium*(II).—The complex $[\text{RuCl}_3(\text{PMe}_2\text{Ph})_3]$ (0.20 g) was heated under reflux under nitrogen in CH_2Cl_2 (100 cm^3) with an excess of bipy (0.08 g) for 12 h. After removal of a very small amount of insoluble dark red solid the resulting red solution was concentrated and addition of light petroleum (b.p. 100—120 °C) gave the dark red *solid*, m.p. 215—216 °C (decomp.) (Found: C, 51.2; H, 4.8; Cl, 11.9; N, 4.9. Calc. for $\text{C}_{26}\text{H}_{30}\text{Cl}_2\text{N}_2\text{P}_2\text{Ru}$: C, 51.6; H, 4.9; Cl, 11.7; N, 4.6%) (65%); τ (in CDCl_3) (233 K) 8.72, 8.39, 7.95, 7.79 (doublets) [J(PH) 9.0 Hz] (PMe_2Ph) and 0—4 (PMe_2Ph and bipy) (at 301 K the methyl region consisted of two broadened doublets at τ 8.66 and 7.96); δ (in (CDCl_3) (301 K) *ca.* 29 and 16 p.p.m. (br, relative intensity 1 : 1). $^{1}\text{H}-\{^{31}\text{P}\}$ studies: irradiation at 40 481 720 Hz collapsed τ 8.66 (d), whereas irradiation at 40 481 220 Hz collapsed τ 7.96 (d).

Removal of solvent from the filtrate gave an orange-red solid (20%) which analysed for 2,2′-*bipyridinium* (2,2′-*bipyridyl*)*trichloro*(*dimethylphenylphosphine*)*ruthenate*(II), m.p. 268—270 °C (decomp.) (Found: C, 53.1; H, 4.7; N, 6.8. Calc. for $\text{C}_{28}\text{H}_{28}\text{Cl}_3\text{N}_4\text{PRu}$: C, 51.3; H, 4.3; N, 8.5%). The complex $[\text{RuCl}_2(\text{PMe}_2\text{Ph})_2(\text{bipy})]$ was obtained as the sole product from $[\text{RuCl}_3(\text{PMe}_2\text{Ph})_3]$ and in hexane–CH_2Cl_2 (100 : 10 cm^3).

1,10-*Phenanthrolinium Trichloro*(*dimethylphenylphosphine*)(1,10-*phenanthroline*)*ruthenate*(II) *Monohydrate*.—The complex $[\text{RuCl}_3(\text{PMe}_2\text{Ph})_3]$ (0.20 g) was heated under reflux in methanol (200 cm^3) under nitrogen with an excess of phen for *ca.* 12 h. The resulting red solution containing a mixture of two compounds (t.l.c. evidence) was concentrated to dryness and a mixture of CH_2Cl_2–light petroleum (b.p. 100—120 °C) was added to the residue giving an orange *precipitate* (15%), m.p. 280 °C (decomp.) (Found: C, 52.9; H, 4.2; N, 7.7. Calc. for $\text{C}_{32}\text{H}_{30}\text{Cl}_3\text{N}_4\text{OPRu}$: C, 52.9; H, 4.2; N, 7.7%), Λ (1×10^{-3}M) in MeOH = 90 S cm^2 mol^{-1}. From the red filtrate a dark red *solid*, *chloro*(*dichloromethane*)*bis*(*dimethylphenylphosphine*)(1,10-*phenanthroline*)*ruthenium*(II) *chloride*, was precipitated on addition of pentane (80%), m.p. 230 °C (decomp.) (Found: C, 46.1; H, 4.3; N, 3.9. Calc. for $\text{C}_{29}\text{H}_{32}\text{Cl}_4\text{N}_2\text{P}_2\text{Ru}$: C, 48.8; H, 4.5; N, 3.9%), Λ (1×10^{-3}M) in CH_2Cl_2 = 16.4 S cm^2 mol^{-1}; τ (in CDCl_3) (301 K) 8.78, 8.52, 7.94, 7.74 (doublets) [J(PH) 8.5 Hz] (PMe_2Ph), 4.75 (s) (CH_2Cl_2), and 0—4 (PMe_2Ph and phen); δ (in CDCl_3) (301 K) 27.95 and 16.14 p.p.m. (doublets) [relative intensity 1 : 1, J(PP) 36.5 Hz]. $^{1}\text{H}-\{^{31}\text{P}\}$ irradiation at 40 481 720 Hz collapsed τ 8.78 and 8.52 (doublets), whereas irradiation at 40 481 230 Hz collapsed τ 7.94 and 7.74 (doublets).

Dichlorobis(*dimethylphenylphosphine*)(1,10-*phenanthroline*)*ruthenium*(II).—The complex $[\text{RuCl}_3(\text{PMe}_2\text{Ph})_3]$ (0.20 g) was heated under reflux in hexane–dichloromethane (100 : 10 cm^3) under nitrogen with an excess of phen for *ca.* 12 h. The resulting dark red solid was collected and washed with light petroleum (b.p. 100—120 °C) (70%), m.p. 190 °C (decomp.) (Found: C, 53.6; H, 4.6; N, 4.7. Calc. for $\text{C}_{28}\text{H}_{30}\text{Cl}_2\text{N}_2\text{P}_2\text{Ru}$: C, 53.8; H, 4.8; N, 4.5%).

Chlorotris(*dimethylphenylphosphine*)(3,4,7,8-*tetramethyl*-1,10-*phenanthroline*)*ruthenium*(II) *Chloride*.—The complex $[\text{RuCl}_3(\text{PMe}_2\text{Ph})_3]$ (0.20 g) was heated under reflux in methanol (150 cm^3) under nitrogen with an excess of Me_4phen (0.08 g) for *ca.* 10 h. The resulting red solution containing a mixture of two compounds (t.l.c. evidence) was concentrated to dryness and CH_2Cl_2–pentane was added to the residue to give an orange-red *precipitate* which was washed with light petroleum (b.p. 100—120 °C) and dried (80%), m.p. 190—200 °C (decomp.) (Found: C, 57.2; H, 5.8; N, 3.2. Calc. for $\text{C}_{40}\text{H}_{49}\text{Cl}_2\text{N}_2\text{P}_3\text{Ru}$: C, 58.2; H, 5.9; N, 3.4%), Λ (1×10^{-3}M) in CH_2Cl_2 = 18.0 S cm^2 mol^{-1}; δ (in CDCl_3) (301 K) 9.01 (t) and 1.09 p.p.m. (d) [relative intensity 1 : 2, J(PP) 32.5 Hz]. Recrystallisation of this complex from CH_2Cl_2–pentane gave red crystals of *chloro*(*dichloromethane*)*bis*(*dimethylphenylphosphine*)(3,4,7,8-*tetramethyl*-1,10-*phenanthroline*)*ruthenium*(II) *chloride*, m.p. 200—205 °C (decomp.) (Found: C, 51.6; H, 5.2; N, 3.6. Calc. for $\text{C}_{33}\text{H}_{40}\text{Cl}_4\text{N}_2\text{P}_2\text{Ru}$: C, 51.5; H, 5.2; N, 3.6%), Λ (1×10^{-3}M) in CH_2Cl_2 = 16.5 S cm^2 mol^{-1}; τ (in CDCl_3) (301 K) (Figure 2) 8.64 (' t '), 8.00, 7.74 (doublets) [J(PH) 8.5 Hz] (PMe_2Ph), 7.47, 7.51 (doublets) (Me of Me_4phen), and 4.76 (s) (CH_2Cl_2).

μ-*Dichloro-bis*[*bis*(2,9-*dimethyl*-1,10-*phenanthroline*)*ruthenium*(II) *Dichloride*.—The complex $[\text{RuCl}_3(\text{PMe}_2\text{Ph})_3]$ (0.20 g) was heated under reflux in methanol (120 cm^3) under nitrogen with an excess of Me_2phen (0.08 g) for *ca.* 12 h. The resulting dark yellow solution was concentrated to dryness and CH_2Cl_2–pentane added to the residue to give a white crystalline *precipitate*, m.p. 205—206 °C (decomp.) (Found: C, 58.7; H, 5.1; Cl, 12.4; N, 9.9. Calc. for $\text{C}_{56}\text{H}_{48}\text{Cl}_4\text{N}_8\text{Ru}_2$: C, 56.5; H, 4.1; Cl, 12.1; N, 9.4%), Λ (1×10^{-3}M) in MeOH = 150 S cm^2 mol^{-1}. Concentration of the filtrate gave yellow crystals of μ-*trichloro-bis*[*tris*(*dimethylphenylphosphine*)*ruthenium*(II)] *chloride*, m.p. 120 °C (Found: C, 46.1; H, 5.5; Cl, 12.1. Calc. for $\text{C}_{48}\text{H}_{66}\text{Cl}_4\text{P}_6\text{Ru}_2$: C, 49.4; H, 5.6; Cl, 12.2%).

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