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Interaction of $[RuCl_2(PR_3)_3]$ (R = Ph, *p*-tolyl) with some Rh(III), Ir(III) and Pt(IV) Tertiary Phosphine Complexes

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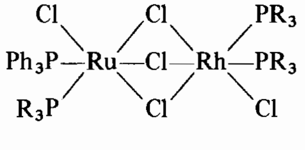
Abstract

Reactions of $RuCl_2(PR_3)_3$ [PR_3 = PPh_3 or P(*p*-tolyl)$_3$ with several monomeric phosphine complexes of rhodium(III), iridium(III) and platinum(IV) have been studied. The reactions with *mer*-$MCl_3(P'R_3)_3$ (M = Rh, $P'R_3$ = PEt_2Ph, PMe_2Ph; M = Ir, $P'R_3$ = $PBuPh_2$, $PMePh_2$, PEt_2Ph) involves a phosphine ligand transfer between metal atoms to afford novel dark coloured heterobimetallic complexes containing a triple chloro-bridge. The reactions of $RuCl_2(PR_3)_3$ with $PtCl_4(P'R_3)_2$ ($P'R_3$ = PEt_2Ph, PBu_2Ph), however, do not give evidence for the formation of dinuclear complexes containing the ($RuCl_3Pt$) unit, but a reduction of Pt^{IV} to Pt^{II} occurs with transfer of phosphine ligands between the two metals. The formulation of these complexes has been established by ^{31}P NMR spectroscopy.

Introduction

In 1976 Head and Nixon [1] reported the first syntheses of novel heterobimetallic trichloro-bridged phosphine complexes containing ruthenium(II) and rhodium(III). These complexes were prepared by treatment of $RuCl_2(PPh_3)_3$ with *mer*-$RhCl_3(PR_3)_3$ (PR_3 = PBu^n_3, PMe_2Ph, PEt_2Ph, PBu^n_2Ph, PPh_3) in a 1:1 ratio in refluxing acetone. The resulting deep-red or purple crystalline products were formulated as $[(PPh_3)(PR_3)ClRuCl_3RhCl(PR_3)_2]$ on the basis of analytical data and ^{31}P NMR spectroscopic studies. In particular, the ^{31}P NMR spectra of the above complexes have unambiguously established [2] the structures shown above and indicate that there has been a transfer of a phosphine ligand from rhodium to ruthenium (*vide infra*). In many of the reactions involving ruthenium(II) phosphine complexes, the identification of the products is greatly assisted by ^{31}P NMR spectroscopy. For example, three isomeric fluorophosphine complexes containing the ($RuCl_3Ru$) unit were fully characterised by their characteristic ^{31}P and ^{19}F NMR spectra [3].

$$RuCl_2(PPh_3)_3 + mer\text{-}RhCl_3(PR_3)_3 \xrightarrow{-2PPh_3}$$



Elemental analytical data alone are often unsatisfactory in establishing the exact nature of these types of metal complexes, since often only small differences occur in carbon and hydrogen analyses for different products. Furthermore, the presence of small amounts of free phosphine and phosphine oxide often present in reaction mixtures is readily monitored by ^{31}P NMR spectroscopy. Although X-ray crystallographic data exist for the homodinuclear complexes such as $[Ru_2Cl_5(PBu_3)_4$ [4, 5] and $[RuCl_2Cl_4(SC)(PPh_3)_4]$ [8], an attempted structural determination on the heterobimetallic compound $[(PBu_2Ph)(PPh_3)ClRuCl_3RhCl(PBu_2Ph)_2]$ by X-ray crystallography was unsuccessful owing to disorder in the crystal, although the heavy atoms were located [7].

In an attempt to extend our understanding of the factors affecting the formation of heterobimetallic complexes of platinum metal phosphine compounds, we have carried out reactions between $RuCl_2(PR_3)_3$ [PR_3 = PPh_3 or P(*p*-toly)$_3$] and several rhodium(III), iridium(III) and platinum(IV) phosphine complexes of the type *mer*-$MCl_3(PR_3)_3$ (M = Rh, Ir) and $PtCl_4(PR_3)_2$. Some unpublished work by Head [7] showed that no analogous ($RuCl_3Os$) systems could be obtained *via* treatment of $RuCl_2(PPh_3)_3$ with *cis*-$OsCl_2(PF_3)_2(PR_3)_2$ (PR_3 = PPh_3, PMe_2Ph) or using *mer*-$OsCl_3(PMe_2Ph)_3$. Masters and co-workers [8–10] have identified the presence of heterobimetallic complexes of the type $[PtPdCl_4(PR_3)_2]$ (PR_3 = PPr_3, PBu^n_3) in solutions containing mixtures of $Pd_2Cl_4(PR_3)_2$ and $Pt_2Cl_4(PR_3)_2$ by ^{31}P NMR spectroscopy. It was proposed that these

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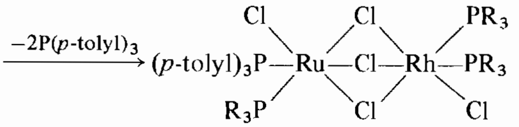
complexes arose *via* a tetrameric intermediate, although neither this intermediate nor the heterobimetallic complexes have been isolated.

Results and Discussion

We have studied the reaction of *mer*-$RhCl_3(PR_3)_3$ [11], ($PR_3 = PEt_2Ph$, PMe_2Ph), with $RuCl_2[P(p\text{-tolyl})_3]_3$ [12], using similar conditions to those mentioned above. Tri-(*p*-tolyl)phosphine was chosen to try to enhance the solubility of the resulting complexes and thereby hopefully facilitate single crystal isolation. The resulting compounds have the same deep-red colour similar to that reported [1, 2] for the analogous triphenylphosphine complexes and the products are formulated as $[\{P(p\text{-tolyl})_3\}(PR_3)ClRuCl_3RhCl(PR_3)_2]$ [$PR_3 = PEt_2Ph$ (**I**), PMe_2Ph (**II**)] on the basis of their ^{31}P NMR spectra.

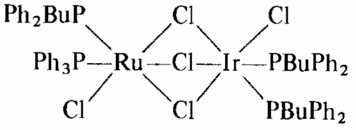
$RuCl_2[P(p\text{-tolyl})_3]_3$ + *mer*-$RhCl_3(PR_3)_3$



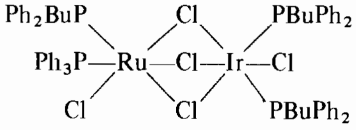
The proton decoupled ^{31}P NMR spectrum of $[\{P(p\text{-tolyl})_3\}(PEt_2Ph)ClRuCl_3RhCl(PEt_2Ph)_2]$ (**I**) is very similar in appearance to the analogous $[(PPh_3)(PEt_2Ph)ClRuCl_3RhCl(PEt_2Ph)_2]$ compound [1, 2], except that the resonance of tri-*p*-tolylphosphine occurs at slightly higher field than that of PPh_3. The NMR spectrum of (**I**) exhibits the expected AX pattern at lowest field which is readily assigned to the resonances of the $P(p\text{-tolyl})_3$ and PEt_2Ph ligands coordinated to ruthenium, each line being split further into a doublet by coupling to the other phosphine, $^2J(PRuP')$. The $P(p\text{-tolyl})_3$ ligand resonance occurs at lower field than diethylphenylphosphine and the chemical shift difference between the two resonances is found to be similar to the shift difference between the free ligands. At high field an AB quartet is observed, which can be assigned to the two diethylphenylphosphine ligands attached to rhodium, each line of this quartet being split into a doublet due to coupling to rhodium, $^1J(Rh{-}P)$, (^{103}Rh: I = 1/2, 100% natural abundance). The observation of an AB quartet indicates that the two diethylphenylphosphines coordinated to rhodium are chemically and magnetically non-equivalent since they can only eclipse different types of ligand on ruthenium [3]. The magnitude of the rhodium phosphorus coupling constant, $^1J(Rh{-}P)$, in these new heterobimetallic complexes is not very different from values known for several rhodium(III) phosphine compounds [13]. The ^{31}P NMR of complex (**II**) ($PR_3 = PMe_2Ph$) exhibits a similar type of pattern to that described above. Chemical shift and coupling constant data for the new complexes, together with those of the analogous compounds containing triphenylphosphine reported by Head and Nixon [1, 2] are summarised in Table I.

In view of the formation of heterobimetallic complexes containing Ru^{II} and Rh^{III} outlined above, the analogous reactions using monomeric octahedral iridium(III) phosphine complexes of the type *mer*-$IrCl_3(PR_3)_3$ [14] ($PR_3 = PBuPh_2$, $PMePh_2$, PEt_2Ph) wer carried out. It was found that on heating $RuCl_2(PPh_3)_3$ with the appropriate $IrCl_3(PR_3)_3$ complex in refluxing acetone, a reaction occurred, as evidenced by the formation of a dark-red solution from which red solids could be isolated. ^{31}P NMR studies proved essential in determining the exact nature of the products of these reactions.

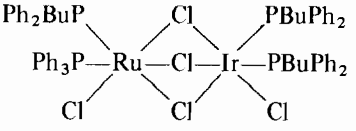
The complex obtained from the reaction of $RuCl_2(PPh_3)_3$ and $IrCl_3(PBuPh_2)_3$ analysed reasonably well for $[(PPh_3)(PBuPh_2)ClRuCl_3IrCl(PBuPh)_2)_2]$, (**III**), and the formulation as a dinuclear complex is supported by ^{31}P NMR spectroscopy. The proton decoupled ^{31}P NMR spectrum of (**III**) (Fig. 1) showed the existence of two isomers. Two of AX patterns of lines (labelled i and o) at low field are assigned to PPh_3 and $PBuPh_2$ ligands coordinated to Ru^{II} for each isomer. Each line appears as the expected doublet [$^2J(PRuP')$]. The ^{31}P chemical shift values (Table II) for phosphine attached to ruthenium(II) are entirely consistent with data for the analogous ruthenium–rhodium dinuclear complexes discussed earlier. The similar magnitude of $^2J(PRuP')$ (around 40 Hz) is consistent with the formulation of complex (**III**) shown below, which can exist in three isomeric forms [**a**–**c**].



IIIa



IIIb



IIIc

TABLE I. ^{31}P NMR Chemical Shift and Coupling Constant Data for Complexes of the Type $(P')(PR_3)ClRuCl_3RhCl(PR_3)_2$[a].

Rhodium				Ruthenium				Ref.
PR_3	δPR_3[b]	$^1J(Rh-P)$[c]	$^2J(PRhP')$[c]	P'	δPR_3[b]	$\delta P'$[b]	$^2J(PRuP')$[c]	
PBu^n_3	109.8 114.0	117.2	22.0	PPh_3	105.4	84.3	39.0	2
PBu^n_2Ph	114.7 117.0	117.2	22.0	PPh_3	101.0	85.5	40.0	2
PPh_3	119.2 121.8	122.7	15.3	PPh_3	91.7	91.7	–	2
PEt_2Ph	108.8 110.2	117.2	19.5	PPh_3	96.5	86.5	39	2
PEt_2Ph (**I**)	108.5 111.4	117.2	19.5	P(*p*-tolyl)$_3$	96.2	88.6	39	This work
PMe_2Ph	122.6 127.3	116.0	24.4	PPh_3	111.6	83.4	41.5	2
PMe_2Ph (**II**)	122.7 127.4	114.7	24.4	P(*p*-tolyl)$_3$	111.0	85.2	41.5	This work

[a] CH_2Cl_2 solutions. [b] P.p.m. rel. TMP. [c] Hz.

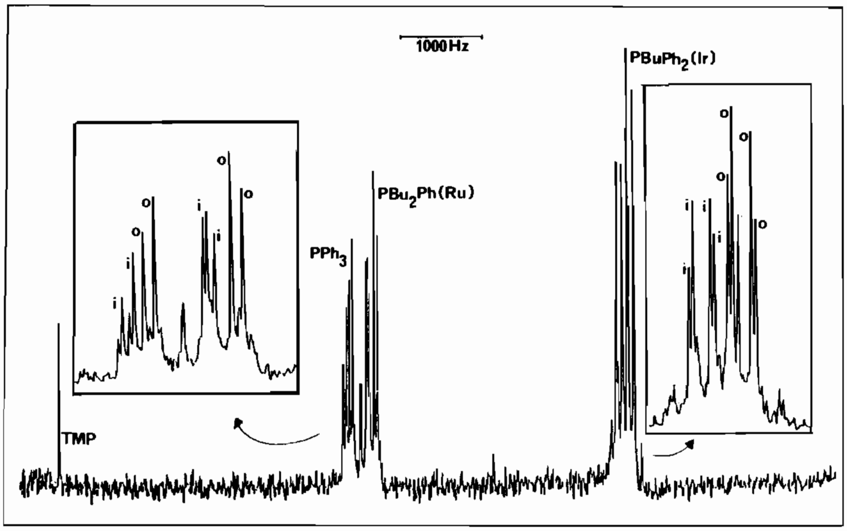
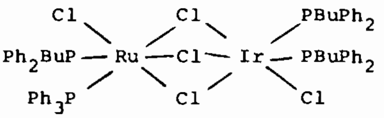
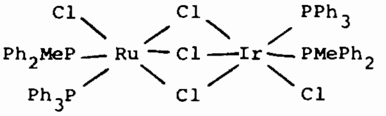
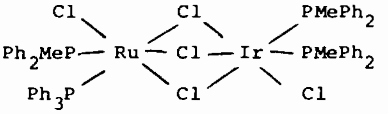
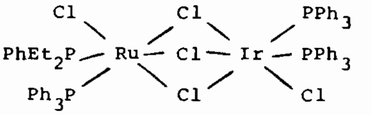


Fig. 1. Proton decoupled ^{31}P NMR spectrum of [$(PPh_3)(PBuPh_2)ClRuCl_3IrCl(PBuPh_2)_2$], (**III**).

The ^{31}P chemical shifts of the $PBuPh_2$ ligands attached to Ir^{III} lies, as expected, to much higher field in view of the increase in oxidation state of the metal. Furthermore, the chemical shift values are at higher field than those found for phosphines coordinated to Rh^{III} in the analogous ($RuCl_3Rh$) systems. This is consistent with other literature data on a variety of transition-metal complexes [13], where it has been found that the largest down field shift occurs when phosphines are attached to the first-row transition element with second-row phosphine complexes having higher field phosphine shifts and third-row compounds the highest δP values.

The magnitude of $^2J(P'IrP')$ in (**III**) is smaller than that found in the related rhodium compounds and this parallels known behaviour of *cis*-phosphine couplings in monomeric Ir^{III} and Rh^{III} phosphine complexes. The analogous ruthenium(II)–rhodium(III) complexes [$(PPh_3)(PR_3)ClRuCl_3RhCl(PR_3)_2$] [1, 2] exist as one isomer. Three geometrical isomers (a–c) are possible for (**III**) and the ^{31}P NMR spectrum indicates that only two are present, but it is difficult to make any stereochemical assignments.

TABLE II. Chemical Shift and Coupling Constant Data for Some Dinuclear Triple Chloro-Bridged Complexes Containing Ruthenium(II) and Iridium(III)[a].

Complex	Ruthenium			Iridium			
	δPPh_3[b]	$\delta P'R_3$[b]	^{2}(PP')[a]	PR_3	PR_3[b]	$P'R_3$[b]	^{2}J(PP')[a]
 **III** [d]	86.1 (87.9)	93.1 (95.4)	39.1 (39.1)	$PBuPh_2$	168.2 (171.5)	170.0 (173.5)	12.2 (12.2)
 **IV** [a]	84.5	100.0	41.5	PPh_3	165.1	170.2	14.6
 **V** [a]	83.7	99.7	41.5	$PMePh_2$	178.5	180.0	14.6
 **VII**	85.1	92.7	30.1	PPh_3	165.2[f]	–	12.2
Complex (VI)	85.0 88.0 (A) 92.5 (B) 100.5	–	30.1 (AB)		–	–	–

[a] CH_2Cl_2 solutions unless otherwise stated. [b] p.p.m. relative to TMP. [c] Hz. [d] Values for the other isomer in parentheses. [e] Benzene solution. [f] δAB.

Although analytical data on the product obtained from treatment of $RuCl_2(PPh_3)_3$ with $IrCl_3(PMePh_2)_3$ in refluxing acetone, fitted reasonably well for $[(PPh_3)(PMePh_2)ClRuCl_3IrCl(PMePh_2)(PPh_3)]$, (**IV**), the $^{31}P\{H\}$ NMR spectrum shows, in addition to the pattern of lines expected for (**IV**), evidence for the presence of the complex $[(PPh_3)(PMePh_2)ClRuCl_3IrCl(PMePh_2)_2]$, (**V**), in the approximate ratio 2:1. The resonances for (**IV**) appear as an AX pattern at low field and can be assigned to the PPh_3 and $PMePh_2$ ligands attached to ruthenium(II), each line appearing as the expected doublet [^{2}J(PRuP')]. Two doublets are also observed at high field and these are assigned to resonances of PPh_3 and $PMePh_2$ coordinated to iridium, with the PPh_3 being assigned to the resonance at lowest field (Table II). The ^{31}P NMR spectrum also exhibits a superposition of a similar pattern to that of (**IV**) at low field, indicating that complex (**V**) has similar ligands on ruthenium(II) as in (**IV**). However, at high field an AB quartet is observed, which suggests the presence of two magnetically non-equivalent $PMePh_2$ phosphines.

Treatment of $RuCl_2(PPh_3)_3$ with $IrCl_3(PEt_2Ph)_3$ in refluxing acetone for 6 h led to a complicated type of reaction and a red crystalline solid **(VI)** precipitated from the reaction mixture, leaving a red solution from which the complex [$(PPh_3)(PEt_2Ph)ClRuCl_3IrCl(PPh_3)_2$], **(VII)**, was obtained as an oil. Complex **(VI)** is fairly unstable in the solid state and is extremely sensitive to traces of oxygen in solution.

Its $^{31}P\{^1H\}$ NMR spectrum exhibits a broad resonance at low field, an AB quartet pattern of lines, and a singlet at high field. These resonances indicate that complex **(VI)** is not monomeric and the appearance of a broad pattern is consistent with some type of inter-molecular ligand exchange of phosphines. The AB pattern suggests the presence of two magnetically non-equivalent phosphine ligands coordinated to the same ruthenium atoms and the singlet resonance is indicative of two magnetically equivalent phosphines.

The IR spectrum of **(VI)** exhibits a band at 1653 cm^{-1} which is attributed to $\nu(C{=}O)$ of coordinated acetone [15]. Complex **(VI)** seems to be formed in a reaction not involving the iridium phosphine complex since in a separate experiment involving $RuCl_2(PPh_3)_3$ and acetone, the identical product **(VI)** was obtained as evidenced by its IR spectrum. Head [7] also obtained **(VI)** by treatment of $RuCl_2(PPh_3)_3$ and *cis*-$RuCl_2(CO)_2(PPh_3)_2$ in refluxing acetone whose ^{31}P NMR and IR spectra are identical to those discussed above. Complex **(VI)** could not be characterised with the present available data, but Wilkinson *et al.* [15] have reported a similar red complex formulated as [$RuCl_2(acetone)(PPh_3)_2]_2$, which contains coordinated acetone [$\nu(C{=}O) = 1660$ cm^{-1}] and complex **(VI)** may have a similar structure.

The proton decoupled ^{31}P NMR spectrum of **(VII)** showed a similar pattern of lines at low field to those observed for complexes **(III)**–**(V)** indicating the presence of two types of phosphine on Ru^{II}. At high field, however, a distorted AB quartet was observed which could be assigned to two magnetically non-equivalent PPh_3 ligands attached to iridium (III) on chemical shift grounds. Some unreacted $IrCl_3(PEt_2Ph)_3$ is also observed in the spectrum.

In summary, the ^{31}P NMR data of the products of the reaction between $RuCl_2(PPh_3)_3$ and $IrCl_3(PR_3)_3$ unambiguously establish that the triple chloro-bridged dinuclear mixed metal complexes are formed containing both Ru^{II} and Ir^{III}. In complexes **(III)**–**(V)** and **(VII)** the reaction involves the transfer of one phosphine ligand from iridium to ruthenium similar to that observed in the ($RuCl_3$-Rh) systems [1, 2]. The formation of both complexes [$(PPh_3)(PMePh_2)ClRuCl_3IrCl(PMePh_2)(PPh_3)$], **(IV)** and [$(PPh_3)(PMePh_2)ClRuCl_3IrCl(PMePh_2)_2$], **(V)** suggests that there is a subsequent attack of free triphenylphosphine on the iridium in **(V)**. In the case of $IrCl_3(PEt_2Ph)_3$, the complex [$(PPh_3)(PEt_2Ph)ClRuCl_3IrCl(PPh_3)_2$], **(VII)**, presumably arises by substitution of both PEt_2Ph ligands on Ir^{III} in the intermediate [$(PPh_3)(PEt_2Ph)ClRuCl_3IrCl(PEt_2Ph)_2$] by triphenylphosphine.

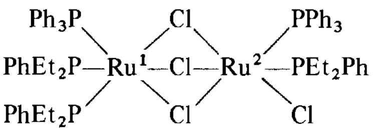
The observation of two types of resonances at low field in the ^{31}P NMR spectra of complexes **(I)** → **(VII)** unambiguously suggests that one dialkylphenylphosphine ligand has been transferred from rhodium or iridium to ruthenium during the formation of the dinuclear complex. Two types of mechanisms have been postulated for this kind of ligand transfer [2] which may occur *via* a two step mechanism involving an initial loss of PR_3 phosphine ligand from Rh or Ir to form an intermediate, followed by subsequent displacement of a $P(aryl)_3$ from ruthenium by the PR_3 group. An alternative mechanism involves a simultaneous transfer of phosphine with the formation of a trichloro-bridge in solution and this has been postulated [3] for the formation of complex [$(PPh_3)_2(PF_3)RuCl_3RuCl(PF_3)(PPh_3)$] in view of the volatility of the PF_3 ligand.

Although the above results indicate the generality of this type of reaction involving ligand transfer between Rh^{III} and Ru^{II}, it did not prove possible to obtain a single crystal of **(I)** or **(II)** suitable for an X-ray study. An attempt was also made to replace the bridging chlorine ligands in [$(PPh_3)(PBu^n_2Ph)ClRuCl_3RhCl(PBu^n_2Ph)_2$] with thiophenyl groups by treatment with NaSPh, without success, mixtures of products being obtained.

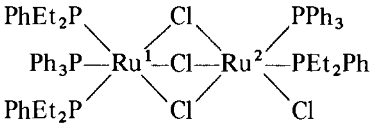
Reactions of $RuCl_2L_3$ [$L = PPh_3$ or $P(p\text{-}tolyl)_3$] with Some Platinum(IV) Phosphine Complexes

When a mixture of $RuCl_2L_3$ [$L = PPh_3$ or $P(p\text{-}tolyl)_3$] and $PtCl_4(PR_3)_2$ ($PR_3 = PEt_2Ph$, PBu^n_2Ph) is reacted in refluxing acetone, a reduction of the platinum (IV) complexes occurs with subsequent transfer of the phosphine ligand from ruthenium (II) to the resulting divalent platinum complex. The reducing agent in the reaction is presumably triphenylphosphine, although the expected oxidised species, PCl_2Ph_3, has not been positively identified, but $OPPh_3$, its hydrolysis product, has been observed in these reactions. The products of these reactions, which are readily identified on the basis of ^{31}P NMR spectroscopic studies, have been found to depend on solvent, ratio of reactants and reaction time.

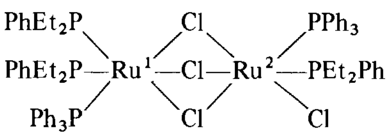
Treatment of $RuCl_2(PPh_3)_3$ with $PtCl_4(PEt_2Ph)_2$ in the ratio ~1.3:1 in refluxing acetone for 6 h gave a red crystalline precipitate [**(VI)** *vide supra*]. Evaporation of the solution to dryness gave a product which on treatment with benzene gave a dark-red solution together with a precipitate of $PtCl_2(PPh_3)_2$. From the solution a dark-red crystalline product formulated as $[(PPh_3)(PEt_2Ph)ClRuCl_3Ru(PEt_2Ph)_2(PPh_3)]$, **(VIII)** (by ^{31}P NMR) was obtained. Complex **(VIII)** can exist in one of the three isomeric structures [**d–f**] shown below.



VIIId



VIIIe



VIIIf

The proton decoupled ^{31}P NMR spectrum of **(VIII)** is shown in Fig. 2 and exhibits two low field resonances, identified as an AX pattern of lines. These are assigned to the triphenylphosphine and diethylphenylphosphine coordinated to Ru^2, each line appearing as the expected doublet $^2J(PRu^2P')$. The two diethylphenylphosphine groups on Ru^1 are magnetically non-equivalent and exhibit an AB pattern of lines, each line being further split into a doublet by coupling to triphenylphosphine $^2J(PRuP')$. These resonances appear as triplets owing to overlapping of lines and a similar pattern which has a lower field chemical shift than that of the diethylphenylphosphine groups is assigned to triphenylphosphine coordinated on Ru^1. Head and Nixon [3] reported that the trifluorophosphine complex $[(PPh_3)_2(PF_3)RuCl_3RuCl(PF_3)(PPh_3)]$ exists as three isomers having structures similar to **d–f**, ^{31}P and ^{19}F NMR studies showed that the major isomer is **d**. By analogy, therefore, complex **(VIII)** is tentatively assigned to structure **d**. The ^{31}P spectrum of the platinum product **(IX)** exhibits a singlet with its platinum satellites and the phosphorus chemical shift and the magnitude of $^1J(Pt-P)$ is identical with that recorded for a known sample of *cis*-$PtCl_2(PPh_3)_2$ (see Table III).

Interestingly, when equimolar amounts of $RuCl_2(PPh_3)_3$ and $PtCl_4(PEt_2Ph)_2$ are reacted together in acetone, the previously described red product **(VI)** is precipitated, and a reduction of the platinum(IV) complex occurred with the formation of a mixture of *cis*-$PtCl_2(PPh_3)(PEt_2Ph)$, **(X)** and *cis*-$PtCl_2(PEt_2Ph)_2$, **(XI)**, as evidenced by ^{31}P NMR spectroscopy. The proton decoupled ^{31}P NMR of this mixture is shown in Fig. 3 and chemical shift and coupling constant data are listed in Table III. As expected, the *cis*-$PtCl_2(PPh_3)(PEt_2Ph)$, **(X)**, shows two doublets [**a**, **b**], each exhibiting platinum satellites, the lower field resonance **a** being assigned to coordinated triphenylphosphine. The coupling constant between platinum and triphenylphosphine, $^1J(Pt-PPh_3)$, is, as expected, larger than $^1J(PtPEt_2Ph)$ and the value of $^1J(Pt-P)$ is that expected for a *cis*-isomer of a

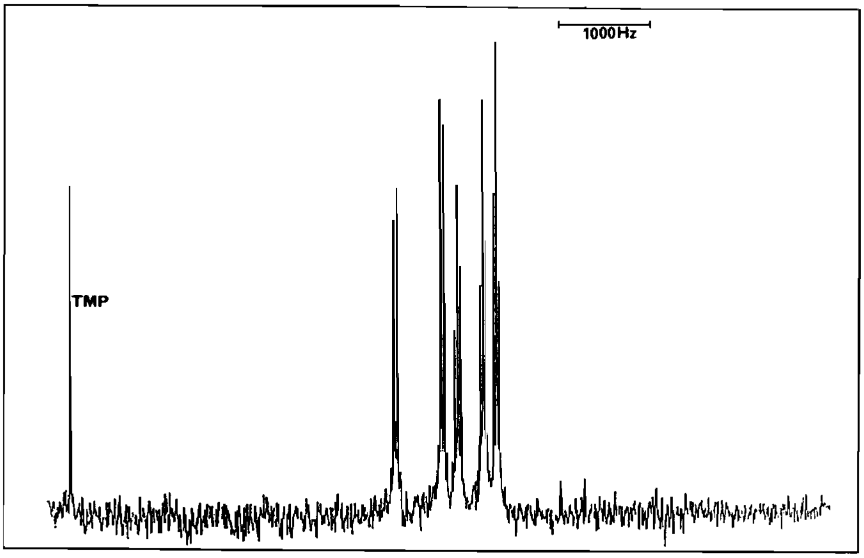


Fig. 2. Proton decoupled ^{31}P NMR spectrum of $[(PPh_3)(PEt_2Ph)ClRuCl_3Ru(PEt_2Ph)_2(PPh_3)]$, (VIII).

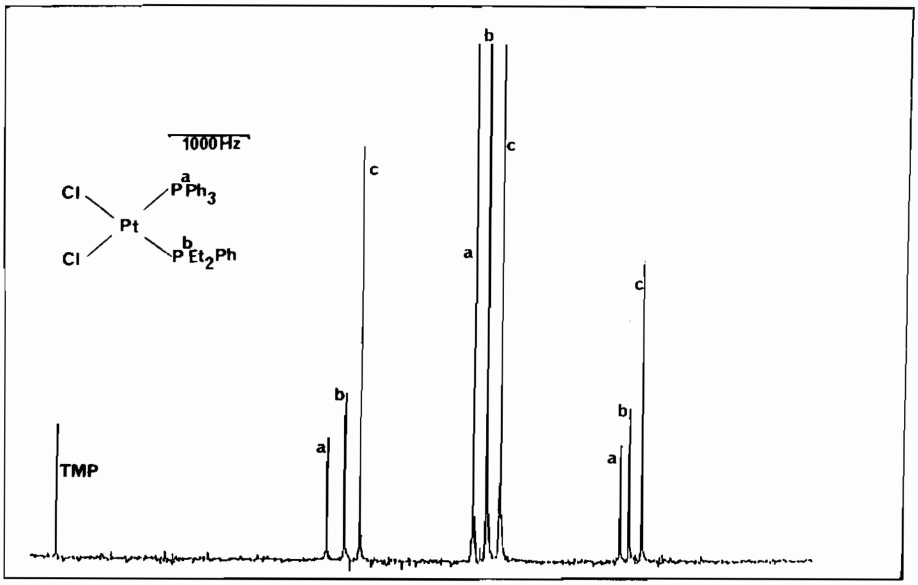


Fig. 3. Proton decoupled ^{31}P NMR spectrum of *cis*-$PtCl_2(PPh_3)(PEt_2Ph)$ [c = *cis*-$PtCl_2(PEt_2Ph)_2$].

square planar platinum(II) phosphine complex [13, 16]. At higher field, a singlet c with its platinum satellites is also observed and is assigned to the complex *cis*-$PtCl_2(PEt_2Ph)_2$, **(XI)**, since its phosphorus chemical shift and $^1J(Pt-P)$ coupling constant are identical to that reported previously for this compound by Grim and co-workers [16].

Recrystallisation of the filtrate from the above reaction afforded dark-red crystalline material, **(XII)**, whose ^{31}P NMR spectrum is similar to that of the product $RuCl_2(PBu^n Ph_2)_3$ [7], obtained from the reaction of $RuCl_2(PPh_3)_3$ and $PtCl_4(PBu^n Ph_2)_2$. Complex **(XII)** is tentatively formulated as $RuCl_2(PEt_2Ph)_3$ and the presence of a sharp singlet at 113.2 p.p.m. in the $^{31}P\{^1H\}$ NMR spectrum is assigned to the ionic species $[(PEt_2Ph)_3RuCl_3Ru(PEt_2Ph)_3]Cl$ which has been shown by Stephenson *et al.* [17] to exist with $[(PEt_2Ph)_3RuCl_3RuCl(PEt_2Ph)_2]$ in solution.

The mixed phosphine complex *cis*-$PtCl_2(PPh_3)(PBu^n{}_2Ph)$, **(XIII)**, is obtained by refluxing an equimolar mixture of $RuCl_2(PPh_3)_3$ and $PtCl_4(PBu^n{}_2Ph)_2$ in dichloromethane solution for 3 h. The $^{31}P\{^1H\}$ NMR spectrum of **(XIII)** exhibits two types of resonance, each appearing as a doublet $^2J(PPtP')$ with its platinum satellites. The lower field resonance is assigned to triphenylphosphine coordinated to platinum(II) and the magnitude of $^1J(PtP)$ is typical of a *cis*-isomer. An additional weak singlet with its platinum satellites is readily assigned to *cis*-$PtCl_2(PPh_3)_2$, **(IX)**, on the basis of phosphorus chemical shift and the magnitude of $^1J(Pt-P)$ [13]. Crystallisation of the filtrate gave a dark-red product formulated as $RuCl_2(PBu^n{}_2Ph)_3$, **(XIV)**, whose ^{31}P NMR spectrum is similar to that of **(XII)**.

The bis(dibutylphenyl)phosphine complex *cis*-$PtCl_2(PBu^n{}_2Ph)_2$, **(XV)**, is obtained as the major product from the reaction of $RuCl_2[P(p\text{-tolyl})_3]_3$ with $PtCl_4(PBu^n{}_2Ph)_2$ in refluxing acetone for 4 h. An attempt was made to crystallise a product from the filtrate without success. However, the proton decoupled ^{31}P NMR spectrum of the crude material showed the presence of further amounts of **(XV)**, and in addition, two types of doublet patterns, each

TABLE III. ^{31}P NMR Chemical Shift and Coupling Constant Data^a for *cis*-$PtCl_2(PR_3)(P'R_3)$ Complexes.

PR_3	$P'R_3$	$\delta PR_3{}^b$	$\delta P'R_3{}^b$	$^1J(Pt-PR_3)^c$	$^1J(PtP'R_3)^c$	$^2J(PPtP')$
PPh_3	PPh_3	126.2	–	3677^d	–	–
PPh_3	PEt_2Ph	128.8	133.1	3687	3579	17.1
PEt_2Ph	PEt_2Ph	–	137.4	–	3545^e	–
PPh_3	$PBu^n{}_2Ph$	128.7	138.1	3696	3567	17.1
PBu^n_2Ph	$PBu^n{}_2Ph$	–	142.8	–	3543^f	–
$P(p\text{-tolyl})_3$	PBu^n_2Ph	131.1	138.8	3665	3594	17.1

^{a}CH_2Cl_2 solution. ^{b}P.p.m. upfield from TMP. ^{c}Hz. ^{d}Lit. [7], $^1J(PtPPh_3)$ = 3684. ^{e}Lit. [16], $^1J(PtPEt_2Ph)$ = 3530 Hz. ^{f}Lit. [16], $^1J(PtBu^n_2Ph)$ = 3551 Hz.

with platinum satellites which can be unambiguously assigned to the complex *cis*-$PtCl_2(PBu^n{}_2Ph)$-$[P(p\text{-tolyl})_3]$, **(XVI)**, (see Table **III**). A broad resonance at 107.5 p.p.m. is also observed, which is indicative of some sort of inter-molecular ligand exchange process involving a ruthenium complex whose identity remains uncertain.

The results obtained above on the reaction between $RuCl_2L_3$ [L = PPh_3, $P(p\text{-tolyl})_3$] and $PtCl_4(PR_3)_2$ do not give any direct evidence for the involvement of any dinuclear complex containing Ru^{II} and Pt^{IV}, but the products do indicate that there has been a transfer of phosphine ligands between the two metals in addition to the reduction of the platinum (IV) complexes. The isolation of $PtCl_2(PR_3)_2$ products suggests that the involvement of the above dinuclear species is unlikely and indicates that the first step is presumably reduction of $PtCl_4(PR_3)_2$. It may be that the relative insolubility of some of the $PtCl_2(PPh_3)_2$ and $PtCl_2(PR_3)$-(PPh_3) complexes determines the detailed course of the reaction.

Experimental

General Procedures

Reactions were carried out either under an atmosphere of dry nitrogen gas or *in vacuo*.

Solvents were dried by standard methods and distilled under dry nitrogen gas prior to use.

^1H NMR spectra were recorded on either a Perkin Elmer R32 instrument operating at 90 MHz, or on a Varian T60 spectrometer operating at 60 MHz. Tetramethylsilane was used as an external standard. High field ^1H NMR spectra were recorded on a Perkin Elmer R32 instrument operating at 90 MHz.

^{31}P NMR spectra were recorded on a Jeol PFT100 Fourier Transform spectrometer operating at 40.49 MHz, using 8 mm spinning tubes. A capillary containing either a ~10% solution of trimethylphosphite (TMP) in deuterobenzene or trimethylphosphate (TMPO) in deuterodichloromethane, was inserted into the sample tube and used as an external standard. Chemical shifts δP are reported relative to TMP = 0 (δP TMPO = +137.6 p.p.m.) and shifts to high field of TMP are given a positive sign.

Infrared spectra in the range 4000–250 cm^{-1} were recorded on a Perkin Elmer 457 spectrophotometer and frequencies are considered to be accurate to ±2 cm^{-1} in the region below 2000 cm^{-1}. Solid compounds and in some cases oily products, were investigated in Nujol mulls between potassium bromide or caesium iodide plates.

Elemental analyses for carbon, hydrogen, nitrogen and chlorine were carried out by Mr. and Mrs. A. G. Olney of this laboratory.

Melting points were determined either on an electrothermal melting point apparatus, or between microscope class cover slips on a Kofler hot stage, and are uncorrected.

Triphenylphosphine (Koch-Light) was recrystallised from methylated spirits while tris-*p*-tolylphosphine (Maybridge Chemicals) was used as supplied.

$RuCl_2(PPh_3)_3$ was prepared by the direct reduction of $RuCl_3 \cdot 3H_2O$ by triphenylphosphine in refluxing methanol solution [18].

The iridium compounds, $IrCl_3(PR_3)_3$ (PR_3 = $PMePh_2$, PBu^nPh_2, PEt_2Ph) were obtained by a slightly different procedure from that described by Jenkins and Shaw [19]. Na_2IrCl_6 in ethanol was heated under reflux, in the presence of concentrated HCl (1 cm^3) for 1 h, during which time a greenish colour developed. The solution was cooled to room temperature, the phosphine (PR_3) was added, and the mixture was heated under reflux for 3–5 h. Removal of solvent gave a residue which was extracted with boiling benzene. The solution was pumped to dryness and recrystallisation from ethylmethyl ketone gave the desired yellow products.

The following starting materials were prepared according to literature methods:

$RhCl_3(PR_3)_3$ [20] (PR_3 = PMe_2Ph, PEt_2Ph)

$RuCl_2[P(p\text{-tolyl})_3]_3$ [21]

$PtCl_4(PR_3)_2$ (PR_3 = PEt_2Ph, $PBu^n{}_2Ph$) [22]

and their purity was established by their IR and $^{31}P\{^1H\}$ NMR spectra.

Preparation of $[P(p\text{-tolyl})_3](PEt_2Ph)ClRuCl_3RhCl(PEt_2Ph)_2$, *(I)*

A solution of $RuCl_2[P(p\text{-tolyl})_3]_3$ (0.300 g, 0.276 mmol) and *mer*-$RhCl_3(PEt_2Ph)_3$ (0.196 g, 0.276 mmol) in acetone (35 cm^3) was heated under reflux for 4 h, during which time the solution changed colour from brown to dark-red. Removal of solvent left an oily material which was washed with hexane and crystallised from dichloromethane/hexane to give dark-red crystals of chloro(diethylphenylphosphine)(tri-*p*-tolylphosphine)ruthenium (**II**) tri-μ-chlororhodium(III) chlorobis(diethylphenylphosphine) (0.25 g, 0.211 mmol; 76%) (Found: C, 54.4; H, 5.4. $C_{51}H_{66}Cl_5P_4RhRu$ requires: C, 51.83; H, 5.6%). IR spectrum: 3050 vw, 1952 w, br, 1633 vw, 1597 m, 1560 w, br, 1498 m, 1312 w, 1270 w, 1245 w, 1192 m, 1157 vw, 1088 m, 1040 m, 1027 m, 845 w, br, 805 s, 763 m, 748 m, 735 s, 712 s, 700 s, 640 m, 625 m, 608 m, 527 vs, 515 s, 500 s, 467 w, 445 w, 435 w, 346 w, 318 w, br cm^{-1} (Nujol mull). Confirmation of the formulation comes from $^{31}P\{^1H\}$ NMR studies (see text).

Tri-*p*-tolylphosphine was obtained from the hexane washings and identified by IR spectroscopy.

Preparation of [P(p-tolyl)$_3$](PMe$_2$Ph)ClRuCl$_3$RhCl(PMe$_2$Ph)$_2$, (**II**)

This product was obtained using similar conditions to those described above and isolated as a dark-red, impure solid (0.34 g) (by ^{31}P NMR) (Found: C, 51.5; H, 5.2. $C_{45}H_{54}Cl_5P_4RhRu$ requires: C, 49.22; H, 4.95%). IR spectrum: 3050 w, sh, 1960 vw, br, 1598 m, 1560 w, br, 1498 m, 1310 w, 1295 w, 1278 w, 1210 w, 1175 s, 1155 w, sh, 1112 vs, 1090 m, sh, 1037 w, 1018 w, 998 vw, 943 m, 920 s, sh, 907 s, 845 m, 805 s, 746 m, 713 s, 693 m, 678 w, 657 s, 630 w, 610 w, 530 vs, 487 m, 460 vw, 445 w, 425 w, 341 w, 315 w, br cm^{-1} (Nujol mull).

Reaction of RuCl$_2$(PPh$_3$)$_3$ with IrCl$_3$(PBuPh$_2$)$_3$

A mixture of $RuCl_2(PPh_3)_3$ (0.457 g, 0.476 mmol) and *mer*-$IrCl_3(PBuPh_2)_3$ (0.500 g, 0.487 mmol) in acetone (45 cm^3) was heated under reflux for 3^1/$_2$ h. After an hour the initial brown solution became dark-red in colour. The solvent was removed and the residue stirred in hexane (20 cm^3). Recrystallisation from dichloromethane/hexane gave red crystals of chloro(diphenylbutylphosphine)(triphenylphosphine)ruthenium(II) tri-μ-chloroiridium(III) chlorobis(diphenylbutylphosphine), (**III**), (0.348 g, 0.238 mmol; 50%) (Found: C, 53.3; H, 4.9. $C_{66}H_{72}Cl_5IrP_4Ru$ requires: C, 54.3; H, 4.94%). IR spectrum: 3060 w, 1635 w, 1593 vw, 1577 vw, 1348 vw, 1322 vw, 1278 m, 1225 m, 1195 m, 1167 m, 1100 s, 1082 w, sh, 1055 vw, 1035 w, 1006 m, 976 w, 905 m, 853 vw, 774 w, sh, 754 s, 728 m, 703 vs, 673 w, sh, 622 vw, 550 s, 538 vs, 524 s, 510 m, 470 m, 455 m, 438 w, 329 m cm^{-1} (Nujol mull).

Triphenylphosphine was isolated from the hexane washings and identified by IR spectroscopy.

Reaction of RuCl$_2$(PPh$_3$)$_3$ with IrCl$_3$(PMePh$_2$)$_3$

This reaction was carried out using similar conditions to those described above and the product was recrystallised from dichloromethane/hexane. The isolated dark-red crystals were shown to be a mixture of chloro(diphenylmethylphosphine)(triphenylphosphine)ruthenium(II) tri-μ-chloroiridium(III) chlorodiphenylmethylphosphine)(triphenylphosphine) (**IV**), and chloro(diphenylmethylphosphine)(triphenylphosphine)ruthenium(II) tris-μ-chloroiridium(III) chlorobis(diphenylmethylphosphine), (**V**), (0.61 g) (see text) (Found: C, 53.1; H, 4.1%). IR spectrum: 3050 w, 1620 w, br, 1588 w, 1575 w, 1319 w, 1287 w, 1268 w, sh, 1195 m, 1164 m, 1105 m, sh, 1093 s, 1080 m, sh, 1032 m, 1005 m, 977 w, 950 vw, 920 w, 895 s, 850 w, 750 s, 726 m, 700 s, 687 m, sh, 620 w, 545 s, 520 s, 500 m, sh, 470 m, 435 m, br, 364 w, 325 m cm^{-1} (Nujol mull).

Triphenylphosphine was isolated from hexane washings and identified by IR spectroscopy.

Reaction of RuCl$_2$(PPh$_3$)$_3$ with IrCl$_3$(PEt$_2$Ph)$_3$

A solution of $RuCl_2(PPh_3)_3$ (0.288 g, 0.300 mmol) and $IrCl_3(PEt_2Ph)_3$ (0.24 g, 0.300 mmol) in acetone (25 cm^3) was heated under reflux for 6 h, during which time a red precipitate formed, which was filtered off, washed with acetone (10 cm^3) and dried *in vacuo*, giving red crystals of the unidentified complex (**VI**) (0.024 g) (Found: C, 57.9; H, 5.5%). IR spectrum: 3060 w, 1715 m, 1653 m, 1588 vw, 1574 vw, 1320 w, 1247 w, 1228 w, 1197 w, 1160 w, 1097 m, 1086 m, sh, 1043 w, 1032 w, 1003 w, 980 vw, 930 vw, 854 w, 773 w, 763 m, 755 s, 749 vs, 728 w, 715 m, sh, 712 vs, 700 vs, 687 m, 633 w, 621 w, 585 vw, 550 m, sh, 542 vs, 532 vs, 522 m, sh, 512 w, 505 w, 470 m, 430 m, br, 327 w, 295 w cm^{-1} (Nujol mull).

Removal of solvent from the acetone solution afforded a red oil which was washed with hexane (15 cm^3) and identified by ^{31}P NMR spectroscopy as a mixture of unreacted $IrCl_3(PEt_2Ph)_3$ and chloro(diethylphenylphosphine)(triphenylphosphine)ruthenium(II) tri-μ-chloroiridium(III) chloro-bis(triphenylphosphine, (**VII**).

Reaction of RuCl$_2$(PPh$_3$)$_3$ with PtCl$_4$(PEt$_2$Ph)$_2$ in the Approximate Ratio 1.3:1

A solution of $RuCl_2(PPh_3)_3$ (0.76 g, 0.793 mmol) and $PtCl_4(PEt_2Ph)_2$ (0.400 g, 0.600 mmol) in acetone (40 cm^3) was heated under reflux for 3 h, during which time a red precipitate formed. The mixture was filtered and the precipitate was washed with acetone and dried *in vacuo* to give red crystals of complex (**VI**) (0.24 g). The IR spectrum of the product was identical to that recorded in the previous preparation.

On cooling the filtrate, a white precipitate formed, which was filtered, washed with acetone (10 cm^3) and dried *in vacuo* to give the white microcrystalline complex *cis*-dichlorobis(triphenylphosphine)platinum(II) (0.080 g, 0.102 mmol; 17%), identified by its ^{31}P NMR spectrum (see text).

The filtrate was reduced to dryness, washed with hexane (15 cm^3) and recrystallisation from dichloromethane/hexane gave dark-red crystals of bis(diethylphenylphosphine) (triphenylphosphine) ruthenium(II) tri-μ-chlororuthenium(II) chloro-(diethylphenylphosphine)(triphenylphosphine), (**VIII**). Found: C, 52.5; H, 4.5. $C_{66}H_{75}Cl_4P_5Ru_2$ requires: C, 57.98; H, 5.53%). IR spectrum: 3060 w, 1595 w, 1580 w, 1320 w, 1285 vw, sh, 1274 m, 1248 m, 1197 m, 1165 m, 1105 m, 1097 m, 1037 m, 1080 w, 1052 w, 1035 m, 1006 w, 998 w, 982 vw, 927 w, 897 vw, 855 w, 768 m, 755 s, 748 s, 743 s, 723 s, 712 vs, 703 vs, 644 m, 621 w, 560 s, 538 s, 525 vs, 505 vs, 458 m, 453 s, 434 s, 413 w, 340 w, sh, 325 s, 302 w cm^{-1} (Nujol mull). ^{31}P NMR spectrum (p.p.m.): Ru^2, δPPh$_3$, 87.0; δPEt$_2$Ph, 99.5 [$^2J(PRuP')$ = 36.6 Hz]; Ru^1 δPPh$_3$, 103.5, δPEt$_2$Ph, 110.3

and 113.9 [$^2J(PRuP') = 29.3$ Hz] (CH_2Cl_2 solution).

The ^{31}P NMR spectrum of the product, obtained by removal of solvent from the mother liquor, exhibits the typical pattern of *cis*-$PtCl_2(PPh_3)_2$ (accounting for the low yield of the platinum complex which crystallised out previously), together with triphenylphosphine oxide.

The experiment was repeated using a 1:1 ratio of reactants in refluxing acetone (40 cm^3) for $3^1/_2$ h, during which time a precipitate formed. The mixture was filtered and the precipitate was washed with acetone (10 cm^3) and dried *in vacuo*, to give red crystals (0.247 g), whose IR spectrum is identical to complex (**VI**) previously obtained. After removal of solvent, benzene (15 cm^3) was added, and a white solid product obtained (0.245 g), which was filtered and washed with benzene (10 cm^3). The ^{31}P NMR spectrum established the presence of a mixture of *cis*-dichloro(diethylphenylphosphine)(triphenylphosphine)(platinum(II) and *cis*-dichlorobis(diethylphenylphosphine)platinum(II).

Benzene was removed and the oily product was recrystallised from dichloromethane/hexane to give dark-red crystals of the ruthenium complex (**XII**) (0.232 g), whose ^{31}P NMR spectrum also shows the presence of the two *cis*-platinum complexes mentioned above. (Found: C, 51.7; H, 5.0. $C_{30}H_{45}Cl_2P_3Ru$ requires: C, 53.73; H, 6.76%). IR spectrum: 3050 w, 1627 w, 1582 w, 1578 w, 1340 vw, 1310 vw, 1275 vw, 1264 m, 1260 w, sh, 1240 w, 1185 m, 1165 vw, 1152 m, 1112 w, sh, 1085 m, 1077 m, 1070 w, sh, 1038 w, 1022 s, 994 w, 987 w, 920 vw, 847 vw, 760 m, 748 m, 739 m, 730 m, 718 w, sh, 710 m, 700 s, 693 vs, 680 w, sh, 636 m, 615 vw, 540 w, 515 vs, 510 s, 495 s, 457 w, 443 m, 424 m, 402 w, 330 w, sh, 315 m cm^{-1} (Nujol mull).

Reaction of $RuCl_2(PPh_3)_3$ with $PtCl_4(PBu^n{}_2Ph)_2$

A mixture of $RuCl_2(PPh_3)_3$ (0.613 g, 0.639 mmol), $PtCl_4(PBu^n{}_2Ph)_2$ (0.500 g, 0.639 mmol) and dichloromethane (40 cm^3) was heated under reflux for 3 h, during which time the initial brown colour changed to a dark-red solution. Removal of solvent left an oil and addition of benzene (15 cm^3) gave a white product which, after filtration and washing with benzene (10 cm^3), and drying *in vacuo*, gave white crystals of *cis*-dichloro(dibutylphenylphosphine)(triphenylphosphine)platinum(II) (0.194 g, 0.259 mmol; 40.5%) as the major product, with a trace of *cis*-$PtCl_2PPh_3)_2$ (see text) (Found: C, 52.6; H, 5.2. $C_{32}H_{38}Cl_2P_2Pt$ requires: C, 51.21; H, 5.10%). IR spectrum: 3050 w, 1658 vw, 1583 vw, 1310 w, 1220 vw, 1182 w, 1155 w, 1090 ms, 1068 vw, 1023 vw, 994 w, 980 vw, 900 w, br, 860 vw, br, 792 vw, 750 ms, 742 s, 739 ms, 735 w, 717 w, 708 w, sh, 701 s, 695 s, 692 s, 687 s, 613 vw, 548 w, sh, 540 s, 525 m, 513 s, 497 m, 478 vw, 762 vw, 745 vw, 424 w, 317 m, 290 m cm^{-1} (Nujol mull).

The filtrate was reduced to dryness and recrystallisation from dichloromethane/hexane gave dark-red crystals of an impure sample of the ruthenium complex (**XIV**) (0.522 g) (Found: C, 51.5; H, 5.1. $C_{42}H_{89}Cl_2P_3Ru$ requires: C, 60.13; H, 8.29%). IR spectrum: 3050 w, 1675 vw, 1583 w, 1568 w, 1513 vw, 1312 vw, 1262 w, 1200 w, sh, 1185 m, 1155 w, 1114 w, 1080 ms, 1070 w, sh, 1025 w, 994 w, 965 w, 915 vw, 887 w, 850 w, br, 790 w, sh, 740 ms, 723 w, sh, 718 ms, 694 s, 678 ms, 615 w, 540 m, 515 s, 495 ms, 456 w, 418 m, 348 vw, sh, 322 w, sh, 315 m cm^{-1} (Nujol mull).

Reaction of $RuCl_2[P(p\text{-}tolyl)_3]_3$ with $PtCl_4(PBu^n{}_2Ph)_2$

A solution of $RuCl_2[P(p\text{-tolyl})_3]_3$ (0.300 g, 0.276 mmol) and $PtCl_4(PBu^n{}_2Ph)_2$ (0.216 g, 0.276 mmol) in acetone (50 cm^3) was heated under reflux for 4 h. Removal of solvent and addition of benzene (15 cm^3) gave a white product which was filtered off, washed with benzene (5 cm^3) and dried *in vacuo*. The ^{31}P NMR spectrum of this product showed it to be *cis*-dichlorobis(dibutylphenylphosphine)platinum(II) (0.100 g, 0.141 mmol). IR spectrum: 3050 w, 1585 vw, 1570 vw, 1314 w, 1300 w, 1275 vw, br, 1220 vw, sh, 1207 m, 1197 w, sh, 1185 w, 1155 vw, 1148 vw, 1100 ms, 1090 ms, 1075 w, sh, 1053 vw, 1035 w, 1005 w, 993 w, 974 vw, 965 vw, 910 m, 895 m, 887 m, sh, 785 m, 780 w, sh, 764 w, 744 s, 730 w, sh, 722 s, 716 s, 695 s, 625 vw, br, 520 w, sh, 500 s, 482 w, 470 w, 433 w, 418 w, 405 m, 340 vw, 308 ms, 285 ms cm^{-1} (Nujol mull).

The benzene solution was evaporated, but attempts to isolate a product were unsuccessful. The residue was washed with hexane, giving a red solid (0.366 g), whose ^{31}P NMR spectrum showed three types of resonances, two of which could be readily assigned to the platinum phosphine complexes, and the third to an unidentified ruthenium complex (see text).

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