Trichloro-bridged Heterobimetallic Phosphine Complexes containing Ruthenium(II) and Rhodium(III) †

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The syntheses of a series of trichloro-bridged heterobimetallic phosphine complexes of the type $[(Ph_3P)(L)ClRuCl_3RhClL_2]$ (L = PMe_2Ph, PEt_2Ph, $PBu^n{}_2Ph$, $PBu^n{}_3$, or PPh_3) from the mononuclear complexes $[RuCl_2(PPh_3)_3]$ and $[RhCl_3L_3]$ or $[RhCl_3(PF_3)(PPh_3)_2]$ are described. The structures of these complexes have been elucidated by ^{31}P n.m.r. spectroscopy, and the reactions are shown to involve phosphine-ligand transfer from rhodium to ruthenium.

IN a previous paper [1] we described the synthesis of the trichloro-bridged diruthenium(II) complex $[(Ph_3P)_2(F_3P)RuCl_3RuCl(PF_3)(PPh_3)]$ from the reaction of the mononuclear complexes $[RuCl_2(PPh_3)_3]$ and $[RuCl_2(PF_3)_2(PPh_3)_2]$. An interesting feature of the reaction was the transfer of a PF_3 ligand from one ruthenium atom to the other. In order to study this type of reaction more fully, we undertook a study of the reaction between phosphine complexes of different metals. Here we report the first syntheses of novel heterobimetallic trichloro-bridged phosphine complexes containing Ru^{II} and Rh^{III} (for a preliminary report see ref. 2). Transfer of phosphine from rhodium to ruthenium is implied by a ^{31}P n.m.r. study of the heterobimetallic complexes.

RESULTS AND DISCUSSION

When an equimolar mixture of $[RuCl_2(PPh_3)_3]$ and *mer*-$[RhCl_3(PR_3)_3]$ in acetone solution is heated under reflux deep red or purple crystalline complexes of general formula $[(R_3P)_2ClRhCl_3RuCl(PR_3)(PPh_3)]$ [$PR_3 = PBu^n{}_3$ (1), PMe_2Ph (2), PEt_2Ph (3), $PBu^n{}_2Ph$ (4), or PPh_3 (5)] are produced in high yield, *e.g.* equation (1). As the reactions proceed the colour of the acetone solution changes from brown to deep red, the rate of change being different with each particular rhodium(III) complex. Thus a noticeable colour change occurs within 30 min when $PR_3 = PBu^n{}_2Ph$, while when $PR_3 = PMe_2Ph$ the intense red solution forms within 10 min. The solubility of complexes (1)—(5) in common organic solvents is dependent on the nature of the phosphine PR_3. When $PR_3 = PBu^n{}_3$ the product is very soluble and this has precluded its isolation, although its existence is unambiguously confirmed by ^{31}P n.m.r. spectroscopy. When $PR_3 = PPh_3$, however, the product is quite insoluble and totally precipitates out of solution. The formulation of complexes (1)—(5) as $[(R_3P)_2ClRhCl_3RuCl(PR_3)(PPh_3)]$ is based on ^{31}P n.m.r. spectroscopic studies, elemental analyses, molecular-weight determinations, i.r. spectroscopy, and in part by preliminary *X*-ray studies.

$$[RuCl_2(PPh_3)_3] + mer\text{-}[RhCl_3(PR_3)_3] \xrightarrow{-2PPh_3} [(R_3P)_2ClRhCl_3RuCl(PR_3)(PPh_3)] \quad (1)$$
$$(1)\text{—}(5)$$

The proton-decoupled ^{31}P n.m.r. spectrum of $[(PhBu^n{}_2P)_2ClRhCl_3RuCl(PBu^n{}_2Ph)(PPh_3)]$ (4) which is shown in the Figure, is typical of the spectra obtained for all the complexes studied. Chemical-shift and coupling-constant data are summarised in Table 1. The two lower-field resonances are identified as an AX pattern of lines and are assigned to the PPh_3 and

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† No reprints available.

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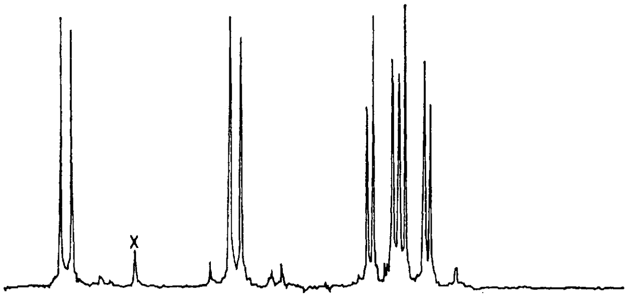
[2] R. A. Head and J. F. Nixon, *J.C.S. Chem. Comm.*, 1976, 62.

PBu^n_2Ph ligands co-ordinated to ruthenium, each line appearing as the expected doublet [$^2J(PRuP')$]. The chemical-shift differences between the two resonances is similar to the shift difference between the free ligands, the resonance at lowest field being assigned to PPh_3. The high-field pattern of lines is assigned to the resonance of the two PBu^n_2Ph ligands co-ordinated to rhodium and appears as an AB ' quartet ', each line being split into a doublet by coupling to rhodium [$^1J(RhP)$] (^{103}Rh: $I = \frac{1}{2}$, 100% natural abundance). The magnetic non-equivalence of the two phosphine ligands co-ordinated to rhodium is not unexpected, since they can only eclipse different types of ligand on ruthenium.[1] The magnitude of the coupling to rhodium [$^1J(RhP)$] is similar to values reported for monomeric rhodium(III) phosphine complexes.[3] Only one isomer for each of the complexes has been detected by ^{31}P n.m.r. spectroscopy, which contrasts with the existence of different isomers for the homobimetallic complexes discussed earlier.[1] The ^{31}P n.m.r. spectrum of (5; $PR_3 = PPh_3$) is slightly different from those recorded for other phosphines and exhibits only one resonance for the two PPh_3 groups co-ordinated to ruthenium, while the resonance of the triphenylphosphines co-ordinated to rhodium appears as the expected eight-line pattern.



Proton-decoupled ^{31}P n.m.r. spectrum of [$(PhBu^n_2P)_2ClRhCl_3RuCl(PBu^n_2Ph)(PPh_3)$]. Width 2 000 Hz, × = trace amount of [$RuCl_2(PPh_3)_3$]

TABLE 1

Phosphorus-31 n.m.r. chemical-shift and coupling-constant data for [$(R_3P)_2ClRhCl_3RuCl(PR_3)(PPh_3)$] [a]

	Rh			Ru		
PR_3	$\delta(PR_3)$ [b]	$^1J(RhP)$ [c]	$^2J(PRhP')$ [c]	$\delta(PR_3)$ [b]	$\delta(PPh_3)$ [b]	$^2J(PRuP')$ [c]
PBu^n_3	109.8 114.0	117.2	22.0	105.4	84.3	39.0
PMe_2Ph	122.6 127.3	116.0	24.4	111.6	83.4	41.5
PEt_2Ph	108.8 110.2	117.2	19.5	96.5	86.5	39.0
PBu^n_2Ph	114.7 117.0	117.2	22.0	101.0	85.5	40.0
PPh_3	119.2 121.8	122.7	15.3	91.7	91.7	

[a] In CH_2Cl_2. [b] P.p.m. relative to $P(OMe)_3$. [c] In Hz.

Analysis of the ^{31}P n.m.r. data unambiguously establishes that the formation of complexes (1)—(5) involves the transfer of one phosphine ligand from rhodium to ruthenium. This may occur *via* a two-step mechanism involving initial loss of PR_3 which then displaces a PPh_3 on ruthenium, *e.g.* as in equation (2). An alternative mechanism involves the transfer of the phosphine and formation of the trichloro-bridge in a concerted reaction, as postulated[1] for the formation of [$(Ph_3P)_2(F_3P)RuCl_3RuCl(PF_3)(PPh_3)$] from *cis*-[$RuCl_2(PF_3)_2(PPh_3)_2$] and [$RuCl_2(PPh_3)_3$]. Support for this mechanism comes from ^{31}P n.m.r. spectroscopic studies carried out on the reaction mixtures. The spectra exhibit resonances at 112 and 145 p.p.m. [relative to $P(OMe)_3$] which are characteristic of PPh_3O and PPh_3 respectively, while no lines are present at the resonance frequency of the free alkylphosphine. In addition, no evidence has been found for the postulated intermediate [$(R_3P)_2ClRhCl_3RuCl(PPh_3)_2$]. Although several workers[4-12] report ligand-transfer reactions, there appears to be little substantive evidence regarding the mechanisms involved. In the reactions of [$Pt(PR_3)_4$] [$PR_3 = PMe_2Ph$, PPh_3, or $PPh(OMe)_2$] with [$M_3(CO)_{12}$] (M = Fe, Ru, or Os)[5] it appears that free phosphine is present in solution as evidenced by the isolation of com-

$$\begin{aligned}
&[RuCl_2(PPh_3)_3] + [RhCl_3(PR_3)_3] \xrightarrow{-PPh_3,\ -PR_3} [(R_3P)_2ClRhCl_3RuCl(PPh_3)_2] \\
&\qquad\qquad \Big\downarrow {\scriptstyle +PR_3,\ -PPh_3} \qquad\qquad (2) \\
&\qquad\qquad [(R_3P)_2ClRhCl_3RuCl(PR_3)(PPh_3)]
\end{aligned}$$

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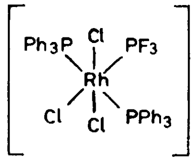
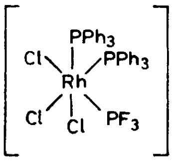
plexes of the type $[M_3(CO)_n(PR_3)_{12-n}]$ formed by simple carbonyl replacement.

In view of the transfer of a trifluorophosphine ligand between ruthenium atoms described earlier, it was of interest to study the reaction of $[RuCl_2(PPh_3)_3]$ with a rhodium(III) trifluorophosphine complex. Prior to this present work the only such complexes known were $[RhR(\eta\text{-}C_5Me_5)I(PF_3)]$ (R = I, CF_3, C_2F_5, *etc.*) prepared by King and Efraty [13] by the oxidative addition of RI to $[Rh(\eta\text{-}C_5Me_5)(PF_3)_2]$.

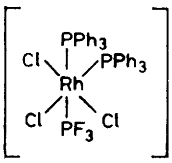
We find that when dry chlorine gas is passed through a solution of *trans*-$[RhCl(PF_3)(PPh_3)_2]$ [14] the yellow crystalline rhodium(III) complex $[RhCl_3(PF_3)(PPh_3)_2]$ (6) is obtained. The reaction is very rapid and is complete inside one minute. Prolonged passage of Cl_2 affords a deep red complex which does not contain trifluorophosphine and has not been investigated. Recently, oxidative addition of halogens, X_2 (X = Cl, Br, or I), to $[RhCl(PPh_3)_3]$ has been reported to give the rhodium(III) complexes $[RhClX_2(PPh_3)_3]$.[15]



(6a)



(6b)



(6c)

Complex (6) can exist in any of the three isomeric structures shown above. In the proton-decoupled ^{31}P n.m.r. spectrum of (6) the resonance of the PPh_3 ligands appears at highest field as a doublet [^1J(RhP) 80.6 Hz] of doublets [^2J(PRhP') 31.7 Hz] of quartets [^3J(PRhPF) 4 Hz]. The equivalence of the triphenylphosphines immediately dismisses (6c) as a possible structure. The low-field PF_3 resonance appears as the expected widely spaced quartet [^1J(PF) 1 349 Hz], each line being further split into a doublet [^1J(RhP) 227 Hz] of triplets [^2J(PRhP') 31.7 Hz]. The magnitude of the rhodium trifluorophosphine coupling constant is smaller than that of the starting rhodium(I) complex [^1J(RhP) 373.5 Hz] and, as expected, the ratio $J(Rh^{III}) : J(Rh^{I})$ = 0.61 : 1 is similar to the value of 0.58 : 1 previously reported for similar compounds.[3] The value of ^1J(RhP) for the PPh_3 groups in (6) is typical of PPh_3 *trans* to phosphorus rather than chlorine,[3] suggesting that (6) has structure (a).

The ^{19}F n.m.r. spectrum of (6) exhibits the expected doublet [^1J(PF)] of doublets [^2J(RhPF) 11 Hz] of triplets [^3J(FPRhP') 4 Hz]. Addition of PPh_3 to the sample does not lead to any change in the appearance of the spectrum, which contrasts with the behaviour of *trans*-$[RhCl(PF_3)(PPh_3)_2]$ where rapid phosphine exchange occurs resulting in loss of coupling to PPh_3 [^3J(FPRhP')].[14] This is expected, since the rhodium(I) complex is square planar and the incoming PPh_3 ligand can readily co-ordinate to the metal from above or below the plane. In (6), however, the octahedral arrangement of ligands around the metal prevents the co-ordination of the incoming ligand and hence no exchange occurs.

The reaction of (6) with $[RuCl_2(PPh_3)_3]$ leads to preferential displacement of PF_3 and complex (5) is formed in good yield.

Our results are of interest in the light of recent work by Masters and his co-workers [10-12] who identified the heterobimetallic complex $[PtPdCl_4(PR_3)_2]$ (PR_3 = PPr_3 or PBu^n_3) in mixtures of $[Pd_2Cl_4(PR_3)_2]$ and $[Pt_2Cl_4(PR_3)_2]$ by ^{31}P n.m.r. spectroscopy. It has been proposed that the exchange occurs *via* a tetrameric intermediate, although neither the intermediate nor the heterobimetallic complex has been isolated.

Attempts to synthesise heterobimetallic complexes from $[RuCl_2(PPh_3)_3]$ and *trans*-$[RhCl(PF_3)(PPh_3)_2]$ in acetone only led to the formation of some PPh_3O and the recovery of starting materials.

TABLE 2

Yields, melting points, and elemental analyses of $[(R_3P)_2ClRhCl_3RuCl(PR_3)(PPh_3)]$

				Analysis (%) [a] Found		
PR_3	Yield (%)	Colour	M.p. (θ_c/°C)	C	H	Cl
PBu^n_2Ph	87	Deep red	173—174	55.1 (55.0)	6.5 (6.5)	14.0 (13.5)
PMe_2Ph [b]	73	Purple	170—172	44.8 (45.2)	4.1 (4.4)	
PEt_2Ph [b]	81	Purple	174	47.8 (47.9)	4.7 (5.1)	18.6 (20.3)
PPh_3 [c]	91	Purple	165	59.7 (60.5)	4.3 (4.2)	12.5 (12.4)

[a] Calculated values are given in parentheses. [b] Isolated as the dichloromethane solvate. [c] P, 8.4 (8.7); total metal, 14.0 (12.3%).

EXPERIMENTAL

General procedures were as described in earlier papers in this series. Molecular weights were determined osmometrically in 1,2-dichloroethane using a Hitachi–Perkin-Elmer 115 instrument.

Preparation of $[(R_3P)_2ClRhCl_3RuCl(PR_3)(PPh_3)]$ [PR_3 = PBu^n_3 (1), PMe_2Ph (2), PEt_2Ph (3), PBu^n_2Ph (4), *or* PPh_3 (5)].—A solution of $[RuCl_2(PPh_3)_3]$ (0.350 g, 0.37 mmol) and *mer*-$[RhCl_3L_3]$ (L = PBu^n_2Ph) (0.320 g, 0.37 mmol) in acetone (80 cm³) was heated under reflux for 5.5 h. After

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20 min the initial light brown solution became deep burgundy in colour. Removal of solvent left a red oil which was recrystallised from hexane to give deep red crystals of (4). Yields, melting points, and analyses are summarised in Table 2. Infrared spectrum in Nujol mull: 3 055w, 1 590w, 1 575w, 1 486w, 1 440w, 1 417w, 1 304w, 1 277w, 1 215w, 1 192w, 1 160w, 1 105w (sh), 1 098ms, 1 083w (sh), 1 060w, 1 048w, 1 031w, 1 001w, 974w, 910w, 896w (sh), 850w, 783w, 762w (sh), 755w (sh), 747ms, 742s (sh), 733w, 730vw (sh), 725m, 700vs, 689w (sh), 620w, 540s, 534vw (sh), 521m, 512s, 508w (sh), 500vw (sh), 482w, 472w, 463vw (sh), 439w, 430w, 400w, 350vw (sh), 341w, 338vw (sh), 322vw (sh), 318w, 310vw (sh), 279w, and 261w cm^{-1}. *M* 1 175 (calc.: 1 309). Further recrystallisation of the mother liquor gave colourless crystals of triphenylphosphine oxide identified by i.r. and ^{31}P n.m.r. spectroscopy. Complexes (2), (3), and (5) were isolated using similar conditions to those described above.

(2; $PR_3 = PMe_2Ph$). This product was recrystallised from dichloromethane–hexane and was isolated as the dichloromethane solvate. Infrared spectrum in Nujol: 3 060w, 1 590w, 1 575w, 1 489w, 1 441mw, 1 326w, 1 305w, 1 281w, 1 197w, 1 163w, 1 098m, 1 092w (sh), 1 082w (sh), 1 031w, 1 004w, 956mw, 950mw, 926w (sh), 918s, 855w (sh), 850w, 844w, 766w, 758vw (sh), 753s, 748s, 709m, 702vs, 698w, 541w (sh), 536vs, 528w (sh), 524m, 510m, 501w, 469w, 450w, 436w, 430w (sh), 343w, 337w, and 317w,br cm^{-1}. *M* 996 (calc.: 1 058).

(3; $PR_3 = PEt_2Ph$). The product was recrystallised from dichloromethane–hexane and was isolated as the dichloromethane solvate. Infrared spectrum in Nujol: 3 050w,br, 1 587w, 1 570w, 1 484w, 1 435mw, 1 317w, 1 270w, 1 245w, 1 191w, 1 160w, 1 100w (sh), 1 094m, 1 083w, 1 077w (sh), 1 045w, 1 031m, 1 015w, 1 000w, 980w, 851w, 765w (sh), 755w (sh), 750w, 743s, 737w (sh), 723s, 706m (sh), 699vs, 688w (sh), 641w, 545vw (sh), 538mw (sh), 531vs, 520ms, 508w (sh), 504s, 468m, 456w (sh), 435w, 418vw, 400vw, 349mw, 330vw (sh), 320w,br, and 310w,br cm^{-1}. *M* 1 078 (calc.: 1 142).

(5; $PR_3 = PPh_3$). This product was isolated as a purple microcrystalline precipitate, washed with acetone, and dried *in vacuo*. Infrared spectrum in Nujol: 3 060w, 1 587w, 1 573w, 1 484w, 1 438mw, 1 316w, 1 268w,br, 1 197w, 1 189w, 1 160w, 1 122w, 1 097m,br, 1 088m, 1 031w, 1 003mw, 974vw, 934vw, 923vw, 854w, 763vw (sh), 759m, 750w (sh), 746s, 726w, 705w (sh), 699vs, 686w (sh), 622w, 546w (sh), 539vs, 521vs, 523vs, 509s, 466m, 442w, 429mw, 353m, 322w, 295vw (sh), and 261w,br cm^{-1}.

(1; $PR_3 = PBu^n{}_3$). This product was not isolated due to its high solubility in all the common organic solvents, but was identified by ^{31}P n.m.r. spectroscopy.

Preparation of Trichloro(trifluorophosphine)bis(triphenylphosphine)rhodium(III).—Chlorine gas was passed through a solution of *trans*-$[RhCl(PF_3)(PPh_3)_2]$ (1.020 g, 1.36 mmol) in dichloromethane (20 cm^3) causing an initial darkening (30 s) which rapidly disappeared, leaving a clear yellow solution (1 min). Removal of solvent left an orange oil which was washed with hexane (10 cm^3), and recrystallisation from dichloromethane–hexane gave yellow *crystals* of (6) isolated as the dichloromethane solvate (0.411 g, 0.45 mmol, 44%), m.p. 152—154 °C (Found: C, 49.6; H, 3.7. $C_{37}H_{32}Cl_5F_3P_3Rh$ requires C, 49.0; H, 3.5%). Infrared spectrum in Nujol: 3 060w, 1 580w, 1 575w, 1 489mw, 1 443w (sh), 1 439m, 1 322w, 1 269m, 1 197m, 1 168w, 1 100w (sh), 1 092s, 1 089w (sh), 1 079w (sh), 1 034w, 1 033m, 940vw (sh), 930vw (sh), 926vs, 920vs, 912w (sh), 900vs,br, 889vw (sh), 885vw (sh), 861w, 850w, 762mw, 760w (sh), 757w (sh), 751vs, 739vs, 734w (sh), 730vw (sh), 712vw (sh), 709vs, 699vs, 690w (sh), 621w, 545s, 525vs,br, 515w (sh), 508s, 469s, 449w, 431vw, 421w, 404w, 395m, 363m, 327m, 321vw (sh), 307vw, and 261w cm^{-1}. $\delta(PPh_3)$ 123.8 p.p.m., $\delta(PF_3)$ 50.5 p.p.m. [relative to $P(OMe)_3$], ϕ(F) 30.9 p.p.m. (relative to CCl_3F).

Reaction of $[RuCl_2(PPh_3)_3]$ *with* $[RhCl_3(PF_3)(PPh_3)_2]$.—A solution of $[RuCl_2(PPh_3)_3]$ (0.202 g, 0.21 mmol) and $[RhCl_3(PF_3)(PPh_3)_2]$ (0.173 g, 0.21 mmol) in acetone (60 cm^3) was heated under reflux for 2 h. The purple precipitate which formed was filtered off, washed with acetone (10 cm^3), and dried *in vacuo* to give (5) (0.093 g, 0.07 mmol, 63%). The i.r. spectrum was identical to that described previously.

Reaction of $[RuCl_2(PPh_3)_3]$ *with trans*-$[RhCl(PF_3)(PPh_3)_2]$. A solution of $[RuCl_2(PPh_3)_3]$ (0.149 g, 0.16 mmol) and *trans*-$[RhCl(PF_3)(PPh_3)_2]$ (0.117 g, 0.16 mmol) in acetone (100 cm^3) was heated under reflux for 4.75 h, during which time no change in colour was observed. The solution was pumped to dryness affording a brown oil. This was washed with hexane (10 cm^3) to give a powder identified by ^{19}F and ^{31}P n.m.r. spectroscopy as a mixture of the two starting materials.

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