

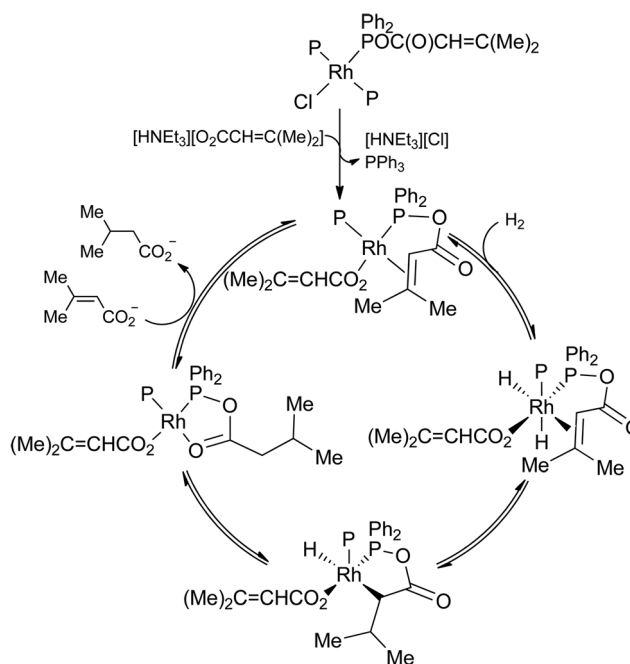
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The coordination chemistry and solution behaviour of Rh(I) and Ru(II) complexes derived from mixed anhydride ligands of carboxylic acids and phosphorus acids were explored. Similar to the free ligand systems, mixed anhydride complexes rearranged in solution *via* a number of pathways, with the pathway of choice dependent on the mixed anhydride employed, the auxiliary ligands present as well as the nature of the metal centre. Plausible mechanisms for some of the routes of rearrangement and by-product formation are proposed. Where stability allowed, new complexes were fully characterised, including solid state structures for four of the unrearranged mixed anhydride complexes and two of the interesting rearrangement products.

The coordination chemistry of mixed anhydrides of the general formula $[R_2POC(O)R']$ and their application in catalysis remain a rather uncharted area of chemistry with only a small number of reports in the literature relating to this topic.¹⁻⁹ Earlier, we reported that mixed anhydride ligands derived from diphenylphosphinous acid and acrylic acids react readily with $[\{RhCl(cyclooctene)_2\}_2]$ to form complexes of the general formula $[\{RhCl(Ph_2PO_2CCR=CR'R^n)_2\}]$, containing the allylic-mixed anhydride bound in a chelating manner *via* the phosphorus atom and the C=C double bond.^{1,3} In a later study, we showed that these ligands can be used for the regioselective hydrogenation of the parent acrylic acid when reacted with hydrogen in the presence of rhodium based precursors such as Wilkinson's catalyst.⁸ Within these catalytic systems the substrate is initially fixed to the catalyst by a phosphorus ester bond and then released, following hydrogenation, by a base catalysed transesterification reaction at phosphorus involving a fresh substrate molecule (Scheme 1). Based on the principle of microscopic reversibility the reverse reaction, *i.e.* the



Scheme 1 Mechanism for the catalytic hydrogenation of 3-methylbut-2-enoic acid using a Rh(I) mixed anhydride based catalyst (P = PPh₃).

dehydrogenation of saturated mixed anhydrides, should in theory also be possible. This should proceed through catalytic C-H activation and may provide a potential new route to the functionalisation of otherwise inert C-H bonds.

Until recently, mixed anhydride ligands have perhaps been best known for their propensity to undergo spontaneous and

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irreversible condensation and rearrangement reactions in the uncoordinated state; a characteristic that limits their application in catalysis.^{7,10–12} In addition, Rh(I) and Ru(II) complexes of $\text{Ph}_2\text{PO}_2\text{CCH}=\text{CHR}$ ($\text{R} = \text{H}$ or Me), are also known to undergo metal promoted rearrangements to give complexes containing $\text{Ph}_2\text{POPPh}_2$ (POP).^{7,9} Despite this, mixed anhydrides have shown promise as ligands in catalysts for isomerising¹³ and asymmetric hydroformylation,¹⁴ enantioselective hydrogenation reactions¹⁵ and as precursors to complex diaryl phosphonate esters for medicinal application.¹⁶

We have recently shown that mixed anhydrides derived from propanoic acid, sodium propanoate or phenylacetic acid can be stabilised by changing from chlorodiphenylphosphine as the phosphorus containing precursor to chlorophosphites during their preparation.¹⁷ By this approach, a series of mixed anhydrides was prepared that can be divided into three classes, namely (I) those devoid of electron withdrawing atoms (with the exception of the acyloxy group) and steric bulk in the vicinity of the phosphorus (1–2), (II) those with electron withdrawing atoms, but little steric bulk at P (3–4) and (III) those with both electron withdrawing atoms at P and nearby *tert*-butyl groups which shelter the phosphorus from neighbouring molecules (5–8; Fig. 1). Within this series, ligands belonging to the third category are superior in terms of stability.¹⁷

Herein, we wish to report on the coordination chemistry of all three classes of these ligands in Rh(I) and Ru(II) complexes, with emphasis on their stability in solution and various pathways of rearrangement.

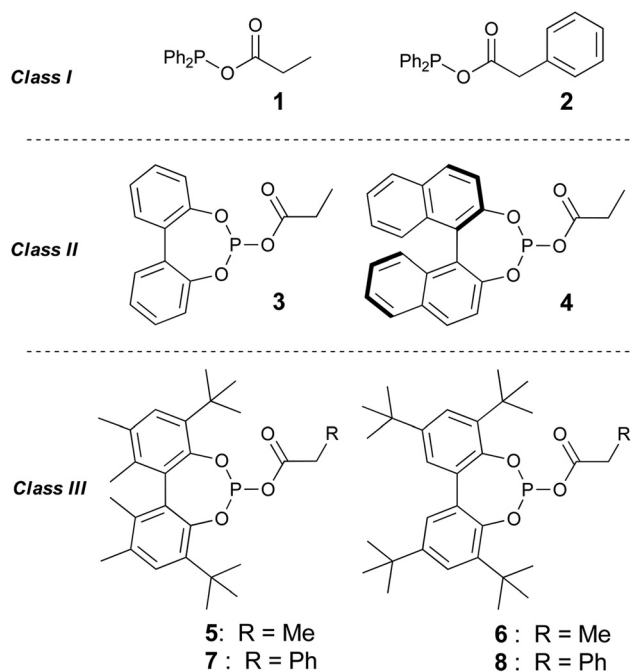


Fig. 1 The three classes of mixed anhydride ligands 1–8.

Results and discussion

All new species were identified and characterised using standard analytical techniques. The $^{31}\text{P}\{^1\text{H}\}$ NMR data collected for compounds 9–26 are summarised in Table 1, with additional analytical data listed in the Experimental section and ESI†. In addition, the crystal and molecular structures of complexes 16–18 and 23–25 were determined by single crystal X-ray-diffraction and are given in the text, but not described in detail (for a discussion see the ESI†).

Rh(I) complexes with class I mixed anhydride ligands

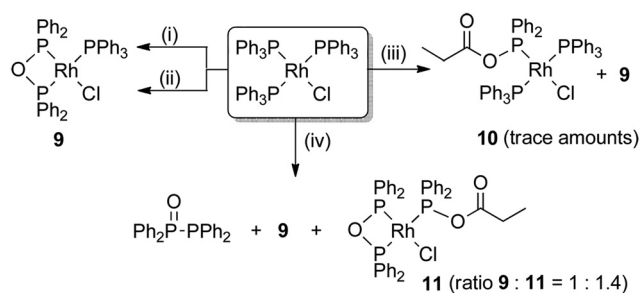
Rh(I) Complexes with PPh_3 auxiliary ligands. Although earlier studies with mixed anhydrides derived from acrylic acid and vinylacetic acid have indicated metal complexes of sterically undemanding mixed anhydrides to be prone to rearrangement,^{7,9} the known simple mixed anhydride (propanoyloxy)diphenylphosphine (**1**)¹⁸ was still evaluated as a ligand to Rh(I). Thus, **1** was reacted in a 1 : 1 ratio with $[\text{RhCl}(\text{PPh}_3)_3]$ in thf at -10°C for 80 min. Not surprisingly, NMR analysis of the crude product mixture revealed the presence of a significant amount of the rearrangement product $[\text{RhCl}(\text{PPh}_3)(\text{POP})]$ (**9**) (where $\text{POP} = \text{Ph}_2\text{POPPh}_2$),^{4,7} at the complete expense of the desired complex, $[\text{RhCl}(\text{PPh}_3)_2(\text{Ph}_2\text{POC}(\text{O})\text{CH}_2\text{CH}_3)]$ (**10**) [Scheme 2(i)]. Compound **9** was detected by the presence of three sets of doublets of doublets of doublets at δ 106.1, δ 80.9 and δ 24.7 in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum; a spectral profile which is in good agreement with the literature values reported for **9**.⁷ Compound **9** also represented the major by-product in earlier studies involving $[\text{RhCl}(\text{PPh}_3)_3]$ and mixed anhydrides of vinylacetic or acrylic acid, with its formation suggested to be metal promoted with disruption of the ligand following coordination to the metal centre.^{4,7} Shorter reaction times [40 min, Scheme 2(ii)] did not alter the products but changing from thf to dichloromethane as reaction solvent resulted in $^{31}\text{P}\{^1\text{H}\}$ NMR spectra revealing, in addition to **9**, a doublet of triplets at δ 138.2 ($J_{\text{P-Rh}} = 213.4$ Hz and $J_{\text{P-P}} = 37.5$ Hz) and a doublet of doublets at δ 32.6 ($J_{\text{P-Rh}} = 128.7$ Hz and $J_{\text{P-P}} = 37.5$ Hz) that correspond well with trace amounts of *trans*- $[\text{RhCl}(\text{PPh}_3)_2(\text{Ph}_2\text{POC}(\text{O})\text{CH}_2\text{CH}_3)]$ (**10a**) [Scheme 2(iii)]. The observed coupling behaviour is consistent with coordination of **1** only through phosphorus, and is comparable with data reported for the related complex $[\text{RhCl}(\text{PPh}_3)_2(\text{PO}_2\text{CCH}_2\text{CH}_2\text{CH}_3)]$ [δ 131.0 (dt) and δ 33.0 (dd)].⁸

Reacting $[\text{RhCl}(\text{PPh}_3)_3]$ with an excess of **1** (1 : 2 or 1 : 6 mole ratio) led to the isolation of a mixture of rearrangement products which could not be separated. Species detected in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra included $[\text{RhCl}(\text{PPh}_3)(\text{POP})]$ (**9**) and a considerable amount of the free ligand disproportionation product, $\text{Ph}_2\text{PP}(\text{O})\text{Ph}_2$. Furthermore, strong evidence for the presence of an additional new complex $[\text{RhCl}(\text{Ph}_2\text{POC}(\text{O})\text{CH}_2\text{CH}_3)(\text{POP})]$ (**11**), bearing **1** intact, was also observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum [with a ratio **9** : **11** of 1 : 1.4 Scheme 2(iv)]. Resonances at δ 121.3 (dt), δ 107.6 (ddd) and δ 82.8 (dt) could be assigned tentatively to **11**.

Table 1 $^{31}\text{P}\{^1\text{H}\}$ NMR data for the Rh(i) complexes 9–26

Compound ^a	Chemical shifts δ (ppm) ^b			Coupling constants J (Hz)					
	P _A	P _B	P _C	Rh–P _A	Rh–P _B	Rh–P _C	P _A –P _B	P _A –P _C	P _B –P _C
9 [RhCl(P _A Ph ₃)(Ph ₂ P _B OP _C Ph ₂)]	24.7 (ddd)	80.9 (ddd)	106.1 (ddd)	132.2	127.0	167.8	380.9	121.8	29.7
10a <i>trans</i> -[RhCl(P _A Ph ₃) ₂ (Ph ₂ P _C OC(O)CH ₂ CH ₃)]	32.6 (dd)	—	138.2 (dt)	128.7	—	213.4	—	37.5	—
10b <i>cis</i> -[RhCl(P _{A/B} Ph ₃) ₂ (Ph ₂ P _C OC(O)CH ₂ CH ₃)]	31.1 (ddd)	^c	129.7 (ddd)	133.2	^c	175.9	40.9	383.6	17.3
11 [RhCl(Ph ₂ P _B OP _C Ph ₂)(Ph ₂ P _A OC(O)CH ₂ CH ₃)]	121.3 (ddd)	82.8 (dt)	107.6 (ddd)	158.9	124.7	163.3	450.0	28.9	124.7
12 [RhCl(P _{A/B} Ph ₃) ₂ (Ph ₂ P _C OP _D Ph ₂)] [Cl]	Accurate values can only be determined by simulation, for accurate assignments see literature. ⁷								
13 [RhCl(Ph ₂ P _A OC(O)CH ₂ CH ₃) ₂]	135.1	—	—	228.1	—	—	—	—	—
14 [RhCl(Ph ₂ P _{A/B} OC(O)CH ₂ CH ₃) ₂] (P ₂ O coordinated) ^d	139.5 (bm)	177.5 (bm)	—	Fluxional – not determined due to line broadening					
15 [RhCl(Ph ₂ P _A OP _A Ph ₂) ₂]	87.1 (d)	—	—	161.3	—	—	—	—	—
16 [RhCl{(Ph ₂ P _A O) ₂ H}(C(O)CH ₂ CH ₃) ₂]	83.7 (d)	—	—	160.5	—	—	—	—	—
17 [RuCl ₂ (Ph ₂ P _A OC(O)CH ₂ CH ₃) ₂]	188.6 (s)	—	—	—	—	—	—	—	—
18 [RuCl ₂ (Ph ₂ P _A OC(O)CH ₂ CH ₃)(Ph ₂ P _B OH)] ₂	188.3 (d)	132.5 (d)	—	—	—	—	44.2	—	—
19 [RhCl(P _A Ph ₃) ₂ (3)] ^e	36.1 (dd)	—	134.5 (dt)	132.7	—	321.8	—	46.6	—
20 [RhCl(P _A Ph ₃) ₂ (P _C OP _C)] ^f	21.7 (dd)	—	79.9 (dt)	113.0	—	260.5	—	19.0	—
21 [RhCl(P _A Ph ₃) ₂ (4)] ^e	35.2 (dd)	—	133.9 (dt)	132.9	—	322.5	—	46.2	—
22 [RhCl(P _{A/B} Ph ₃) ₂ (P _C OP _C)] ^g	20.6 (ddd)	20.5 (ddd)	84.7 (ddd)	113.3	111.3	261.1	370.5	17.2	21.2
23 [RhCl(P _{A/B} Ph ₃) ₂ (5)] ^e	34.4 (ddd)	37.2 (ddd)	129.3 (ddd)	138.2	138.2	331.3	349.5	44.3	44.3
24 [RhCl(P _{A/B} Ph ₃) ₂ (6)] ^e	33.8 (ddd)	38.2 (ddd)	124.9 (ddd)	135.3	135.3	331.8	347.9	48.3	48.3
25 [RhCl(P _{A/B} Ph ₃) ₂ (7)] ^e	34.9 (ddd)	37.8 (ddd)	131.1 (ddd)	134.9	134.9	332.7	344.3	46.3	46.3
26 [RhCl(P _{A/B} Ph ₃) ₂ (8)] ^e	33.8 (ddd)	38.7 (ddd)	127.0 (ddd)	134.9	134.9	334.0	346.9	46.3	46.3

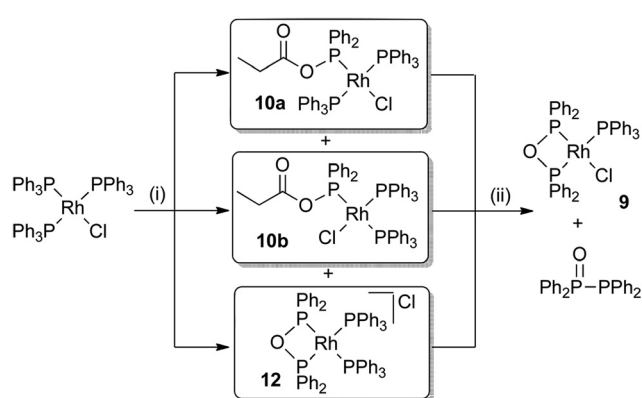
^a Note: identical labels given to different phosphorus atoms present within the same complex indicate magnetic equivalence. ^b Chemical shifts relative to 85% H₃PO₄ (CD₂Cl₂, 25 °C) with multiplicity given in parenthesis. ^c Could not be measured owing to extensive overlap of resonances in the relevant region. ^d Significant line broadening observed as a result of an unresolved dynamic process. ^e Phosphorus present in coordinated (acyl)phosphites listed as P_C. ^f P_COP_C represents 4,4'-oxydinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphine. ^g P_COP_C represents 6,6'-oxydibenzo[*d,f*][1,3,2]dioxaphosphine.



Scheme 2 Reaction conditions: (i) **1** (1:1 ratio), thf, −10 °C, 80 min.; (ii) **1** (1:1 ratio), thf, −10 °C, 40 min.; (iii) **1** (1:1 ratio), CH₂Cl₂, −10 °C, 30 min.; (iv) **1** in excess (1:2 or 1:6 mole ratio), CH₂Cl₂, −10 °C, 1 h.

In order to determine whether [RhCl(PPh₃)₂(Ph₂POC(O)CH₂CH₃)] (**10**) perhaps forms as the major product during the early stages of the reaction but then rapidly decays to form **9**, low temperature *in situ* NMR studies were performed. A solution of **1** in deuterated chloroform was added immediately after dissolution to solid [RhCl(PPh₃)₃] at −30 °C. Without delay, a small volume of the resulting solution was transferred to an NMR tube and analysed by low temperature (−10 °C) $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy at regular intervals (every 5 min for 50 min).

Although the measured spectra were very different from those from earlier attempts, surprisingly little variation was observed between spectra within the series. Despite the presence of Ph₂PP(O)Ph₂, significant amounts of the desired complex *trans*-[RhCl(PPh₃)₂(Ph₂POC(O)CH₂CH₃)] (**10a**), together with the related *cis*-isomer (**10b**), were observed. In



Scheme 3 Species observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra recorded (i) during *in situ* NMR experiments, **1** (1:1.2 mole ratio), CDCl₃, −10 °C; (ii) for a sample taken of the same solution after standing for 2 h at −10 °C.

addition, a set of resonances corresponding to the ionic complex, [Rh(PPh₃)₂(Ph₂POPPH₂)] [Cl], (**12**) was also observed [Scheme 3(i)].

In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the *cis*-isomer **10b**, coordinated **1** gives rise to a doublet of doublets of doublets at δ 129.7 ($J_{\text{P-Rh}} = 175.9$ Hz, $J_{\text{P-Ptrans}} = 383.6$ Hz and $J_{\text{P-Pcis}} = 40.9$ Hz), slightly upfield from those of the *trans* analogue **10a**. Unfortunately, owing to the presence of several resonances from PPh₃ containing products within the same $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, extensive overlap of resonances within the region δ 24– δ 35 is observed. As a result, resonances corresponding to

the PPh_3 ligand *cis* to **1** in **10b** could only be assigned tentatively.

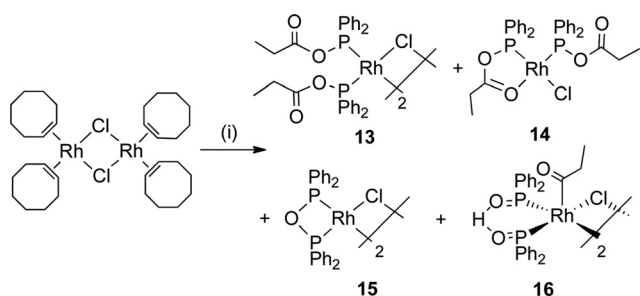
The chemically equivalent, but magnetically inequivalent phosphorus atoms for the POP and PPh_3 ligands in **12**, represent an AA'XX' spin system, giving rise to second-order spectral effects in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. Complex resonances at δ 98.0 and δ 26.4 could be assigned tentatively to the POP and PPh_3 ligands, respectively. Unfortunately, the signal to noise ratios in all spectra recorded during *in situ* NMR experiments were too low to allow for a better interpretation of these signals. However, a very similar spectral profile has been reported for $[\text{Rh}(\text{PPh}_3)_2(\text{Ph}_2\text{POPPh}_2)][\text{PF}_6]$ which contains the same cation.⁷

Since no major product decay was observed during the *in situ* NMR experiment, the original reaction mixture was allowed to stand for a further 70 min at -10°C , and again analysed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. The spectrum obtained this time differed significantly from earlier spectra, with signals from both isomers of **10** as well as compound **12** completely absent, while signals corresponding to the familiar rearrangement product **9** [Scheme 3(ii)] were now present. These observations suggest that such rearrangements may be heavily dependent on the reaction time, concentration and temperature. Moreover, the detection of **10a** and **10b** as intermediates prior to the formation of **9** supports the premise that the rearrangement is metal promoted and not the result of a direct reaction between $\text{Ph}_2\text{PP}(\text{O})\text{Ph}_2$ and $[\text{RhCl}(\text{PPh}_3)_3]$.

Rh(i) complexes devoid of PPh_3 auxiliary ligands. In light of the difficulties experienced with the metal promoted rearrangement of **1**, the possibility that PPh_3 may facilitate such rearrangements was considered. A Rh(i) precursor devoid of any PPh_3 ligands, such as the chloro-bridged rhodium dimer $[\{\text{RhCl}(\text{COE})_2\}_2]$ (where COE = cyclooctene), was therefore employed. In earlier work, this complex had proved highly successful in the preparation of Rh(i) complexes of higher substituted mixed anhydrides.³ Treatment of a solution of $[\{\text{RhCl}(\text{COE})_2\}_2]$ in dichloromethane with four equivalents of **1** at -10°C for 30 min, after work-up, gave a mixture which could not be separated, containing minor amounts ($\sim 7\%$) of the desired unrearranged dimer $[\{\text{RhCl}(\text{Ph}_2\text{PO}_2\text{CCH}_2\text{CH}_3)_2\}_2]$ (**13**; Scheme 4); detected as a doublet at δ 135.1 in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. This was a significant improvement on earlier attempts, since the PPh_3 containing Rh(i) analogue **10** was only observed *in situ* and could not be isolated. Furthermore,

the product mixture also contained a significant amount ($\sim 71\%$) of the monomeric complex, $[\text{RhCl}(\text{Ph}_2\text{PO}_2\text{CCH}_2\text{CH}_3)_2]$ (**14**), where one of the (propanoyloxy)diphenylphosphine (**1**) ligands is coordinated in a chelating fashion *via* both the phosphorus atom and the carbonyl oxygen, while the second is coordinated only *via* phosphorus. Bonding of this type, although not favoured in the presence of superior donors, is not uncommon for such complexes and has been reported for the cationic complex $[\text{Rh}(\text{PPh}_3)_2(\text{Ph}_2\text{PO}_2\text{CCH}=\text{CMe}_2)][\text{SbF}_6]$.⁶

The unambiguous NMR assignments of **14**, as well as the determination of the relevant $J_{\text{Rh-P}}$ and $J_{\text{P-P}}$ values, was complicated by substantial line broadening as a consequence of an unresolved dynamic process involving the free and co-ordinated carbonyl oxygens of ligands **1**. However, the high field chemical shift of the broad multiplet observed at δ 177.5 in the $^{13}\text{P}\{^1\text{H}\}$ NMR is consistent with the incorporation of **1** in a five membered metallocycle by bonding through both phosphorus and oxygen.¹⁹ Likewise, the chemical shift observed for a broad multiplet at δ 139.5 is consistent with coordination of **1** to a Rh(i) centre only *via* phosphorus. Despite their apparent superior stability, complexes **13** and **14** still undergo rearrangement in solution to afford the POP dimer $[\{\text{RhCl}(\text{POP})\}_2]$ (**15**, $\sim 11\%$) and more interestingly, $[\{\text{RhCl}(\text{Ph}_2\text{PO})_2\text{H}\}(\text{C}(\text{O})\text{CH}_2\text{CH}_3)_2]$ (**16**, $\sim 11\%$); a diphenylphosphinito dimer containing propanoyl moieties directly coordinated to the Rh(III) centres (yields based on NMR intensities; Scheme 4). Although **15** could only be assigned tentatively using $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy [δ 87.1 (d)], the identity of **16** [δ 83.7 (d)] could be verified crystallographically (Fig. 2; for discussion see ESI†).



Scheme 4 Product mixture obtained for reactions of $[\{\text{RhCl}(\text{COE})_2\}_2]$ with **1**. Conditions: (i) **1** (4 equivalents), CH_2Cl_2 , -10°C , 30 min.

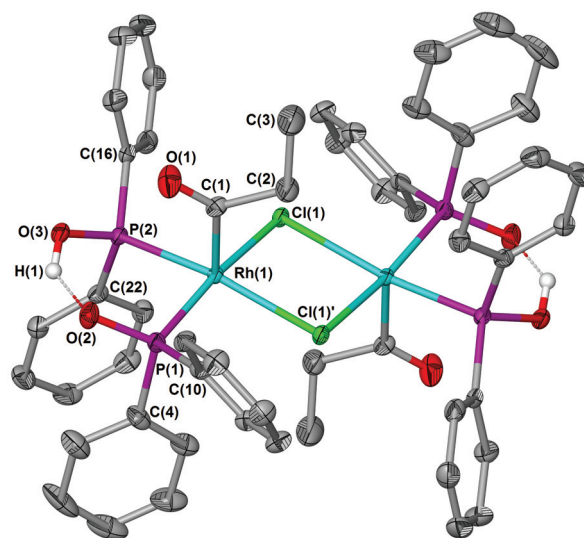
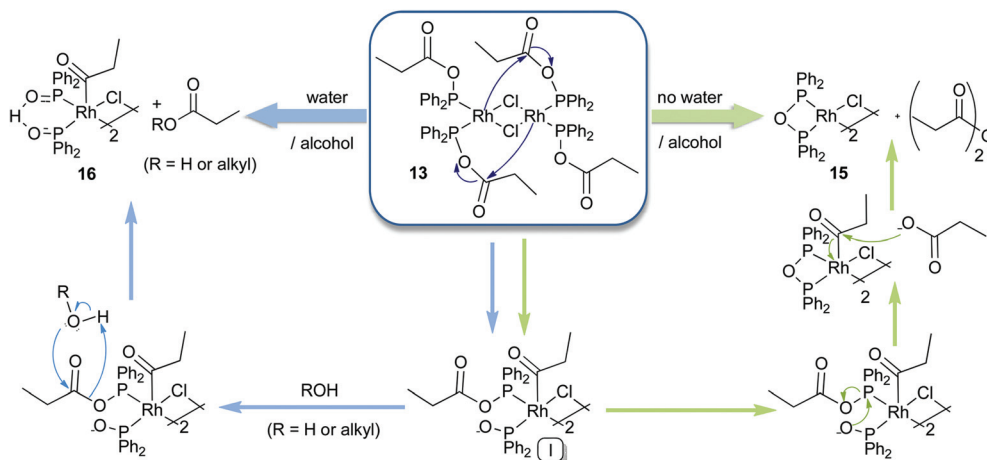


Fig. 2 Molecular structure of **16** with thermal ellipsoids set at 50% probability. Hydrogen atoms (with the exception of O-H) and solvent molecules are omitted for clarity. Selected bond lengths and angles: Rh(1)–C(1) 1.991(2), Rh(1)–Cl 2.4522(10), Rh(1)–P(1) 2.2517(9), Rh(1)–P(2) 2.2508(8), O(1)–C(1) 1.186(3), P(1)–O(2) 1.5574(18), P(2)–O(3) 1.5354(17), Rh(1)–C(1)–O(1) 125.98(19), Rh(1)–C(1)–C(2) 111.95(16), P(1)–Rh(1)–P(2) 88.24(3), Cl(1)–Rh(1)–Cl(1') 83.24(2), P(2)–Rh(1)–Cl(1) 92.85(2), P(1)–Rh(1)–Cl(1') 93.56(2), P(1)–Rh(1)–Cl(1) 170.73(2), C(1)–Rh(1)–P(1) 89.94(7), C(1)–Rh(1)–P(2) 91.50(7), C(1)–Rh(1)–Cl(1) 99.23(7).



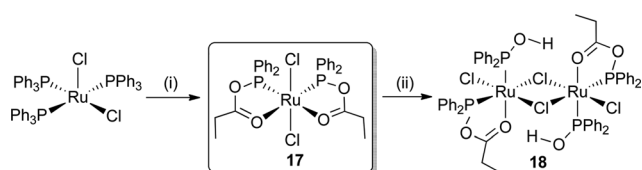
Scheme 5 Proposed mechanism for the formation of rearrangement product **15** in the absence of water or alcohol (■ left) and **16** in the presence of water or alcohol (■ right).

Numerous reports on transition metal complexes containing hydrogen bonded $[(\text{Ph}_2\text{PO})_2\text{H}]$ ligands, similar to **16**, exist in the literature with several routes to their preparation described.^{20–24} In the majority of cases, such complexes are prepared either by the reaction of metal complexes with diphenylphosphinous acid or by the hydrolysis of metal complexes of chlorodiphenylphosphine or diphenylphosphinite. Although no formal mechanistic studies have been performed, a plausible mechanism for the rearrangement of **13** to **15** in the absence of water or alcohol, and to **16** in the presence of water or alcohol is proposed in Scheme 5. All reactions were performed under dry and inert conditions, but a water-propan-2-ol mixture is employed during the preparation of, $[\text{RhCl}(\text{COE})_2]_2$, and this may thus be the source of such trace contaminants.

Ru(II) complexes with class I mixed anhydride ligands

The reaction of $[\text{RuCl}_2(\text{PPh}_3)_3]$ with 2 equivalents of **1** gave $[\text{RuCl}_2(\text{Ph}_2\text{PO}_2\text{CCH}_2\text{CH}_3)_2]$ (**17**), with **1** coordinated in a chelating fashion *via* both the phosphorus and carbonyl oxygen atoms [Scheme 6(i)]. This has been shown before to be the preferential mode of bonding for mixed anhydride Ru(II) complexes of the general form $[\text{RuCl}_2(\text{Ph}_2\text{PO}_2\text{CCH}=\text{RR}')_2]$.⁹

In contrast to known literature examples where the P-atoms occupy mutually *trans* positions, spectroscopic evidence suggests that the P-atoms in **17** occupy positions *cis* with respect to one another. In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **17** the



Scheme 6 Preparation of **17** and subsequent rearrangement to form **18**. Conditions: (i) **1**, (2 mole equivalents), CH_2Cl_2 , R.T., 2 h; (ii) standing in solution overnight.

magnetically equivalent phosphorus atoms give rise to a sharp singlet at δ 188.6, very high field in comparison to the values observed for coordinated **1** in the related Rh(I) complexes [see ESI, Fig. S1(a)†]. This serves as further confirmation for the coordination of **1** in a chelating fashion, as the resultant five membered metallocycle would lead to a high field shift in the phosphorus resonances.¹⁹ Furthermore, in the IR-spectrum of **17** the C=O bonds vibrate at a much lower frequency [single absorption at 1649 cm^{-1} $\nu(\text{C}=\text{O})$], than that typically observed for such bonds [$\sim 1700\text{ cm}^{-1}$].^{6,25} This is consistent with reduced double bond character as a result of coordination to a metal centre. In contrast to the Rh(I) complexes of **1**, compound **17** could be isolated in high purity and yield without the interference of unwanted side-reactions. Furthermore, **17** could also be stored in the solid state for prolonged periods of time, provided that an inert atmosphere was maintained.

The greater stability of **17** compared to the Rh(I) analogues comes as no surprise, since one can expect the relatively more electron poor Ru(II) centre to be less likely to participate in any rearrangements that necessitate oxidation of the metal centre or nucleophilic attack on the carbonyl carbon of **1** by the metal.

Despite the enhanced stability, **17** rearranges within hours when left standing in solution to afford the chloro-bridged Ru(II) dimer **18**, where one of the two mixed anhydrides per Ru(II) centre has been converted to diphenylphosphinous acid [Scheme 6(ii)]. Although no significant change in the chemical shift of coordinated **1** is observed when **17** rearranges to **18**, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **18** displays a mutual P–P coupling of 44.2 Hz between coordinated **1** [δ 188.3 (d)] and the generated Ph_2POH [δ 132.5 (d); see ESI, Fig. S1(b)†].

During all initial attempts to crystallise **17** by slow diffusion of pentane into dichloromethane or chloroform solutions of **17**, orange prisms of **18** crystallised from solution instead, allowing for its structure determination by X-ray crystallography (Fig. 3). Single crystals of **17** could eventually be obtained by diffusion of diethyl ether into a toluene solution of **17** at room temperature (Fig. 4).

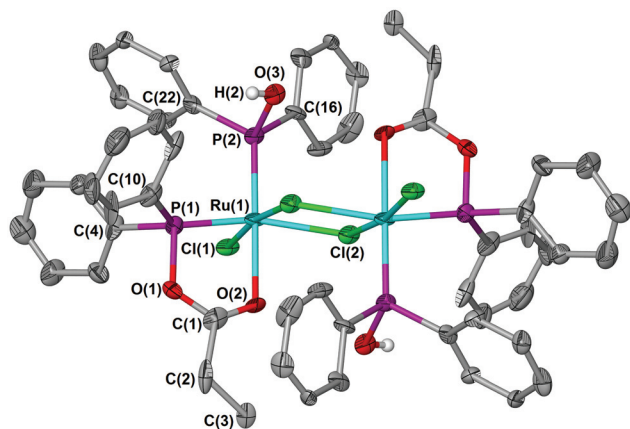


Fig. 3 Molecular structure of the rearrangement product **18** with thermal ellipsoids set at 35% probability. Hydrogen atoms (except O–H) and solvent molecules are omitted for clarity. Selected bond lengths and angles: Ru(1)–Cl(1) 2.379(3), Ru(1)–Cl(2) 2.486(4), Ru(1)–P(1) 2.189(4), Ru(1)–P(2) 2.227(4), Ru(1)–O(2) 2.227(8), P(1)–O(1) 1.729(9), O(1)–C(1) 1.311(16), O(2)–C(1) 1.215(14), P(2)–O(3) 1.637(8), Ru(1)–O(2)–C(1) 115.7(8), Ru(1)–P(1)–O(1) 100.6(3), Ru(1)–P(2)–O(3) 114.6(3), P(1)–Ru(1)–O(2) 81.1(3), P(1)–Ru(1)–P(2) 98.43(13), P(1)–Ru(1)–Cl(1) 91.85(11), P(1)–Ru(1)–Cl(2) 164.45(11), P(2)–Ru(1)–O(2) 179.4(3), P(2)–Ru(1)–Cl(1) 91.44(10), P(2)–Ru(1)–Cl(2) 96.40(11), Cl(1)–Ru(1)–Cl(2) 92.41(10).

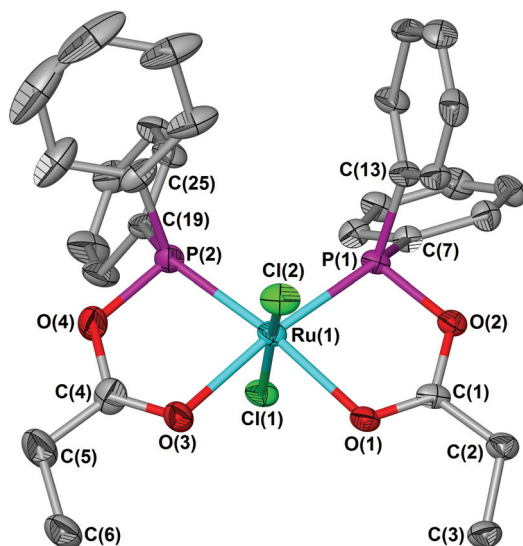


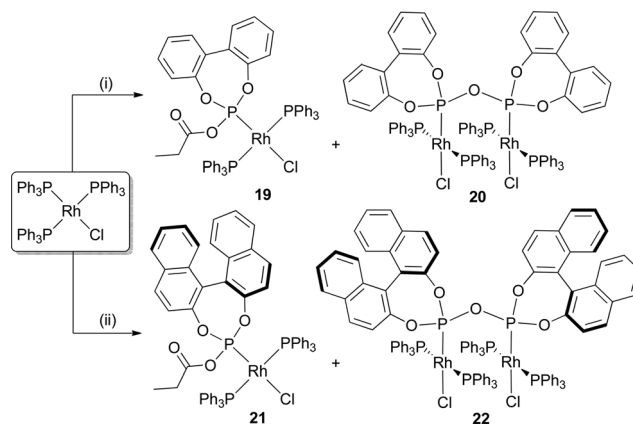
Fig. 4 Molecular structure of **17** with ellipsoids set at 35% probability and hydrogen atoms and solvent molecules omitted for clarity. Selected bond lengths and angles: Ru(1)–Cl(1) 2.379(3), Ru(1)–Cl(2) 2.388(3), Ru(1)–P(1) 2.182(3), Ru(1)–P(2) 2.182(3), Ru(1)–O(1) 2.169(6), Ru(1)–O(3) 2.173(6), P(1)–O(2) 1.716(6), P(2)–O(4) 1.706(7), Ru(1)–O(1)–C(1) 117.3(5), Ru(1)–O(3)–C(4) 117.2(6), Ru(1)–P(1)–O(2) 101.8 (2), Ru(1)–P(2)–O(4) 101.9(3), P(1)–Ru(1)–O(3) 172.94(18), P(2)–Ru(1)–O(1) 173.48(15), P(1)–Ru(1)–O(1) 80.45(16), P(2)–Ru(1)–O(3) 81.04(19), P(1)–Ru(1)–P(2) 105.93(9), O(1)–Ru(1)–O(3) 92.6(3), Cl(1)–Ru(1)–Cl(2) 168.81(8), Cl(1)–Ru(1)–O(1) 86.92(15), Cl(1)–Ru(1)–O(3) 83.49(16), Cl(2)–Ru(1)–O(1) 86.00(15), Cl(2)–Ru(1)–O(3) 88.19(16), Cl(1)–Ru(1)–P(1) 95.11(8), Cl(1)–Ru(1)–P(2) 91.13(10), Cl(2)–Ru(1)–P(1) 92.24(8), Cl(2)–Ru(1)–P(2) 94.94(10).

Rh(I) complexes with stabilised class II and III mixed anhydride ligands

In reactions of $[\text{RhCl}(\text{PPh}_3)_3]$ with mixed anhydride ligands of the second class (Fig. 1), the desired *trans*- $[\text{RhCl}(\text{PPh}_3)_2(\text{L})]$ complexes **19** ($\text{L} = 3$) and **21** ($\text{L} = 4$) were obtained as the major products. However, similar to Rh(I) complexes of **1**, complexes **19** and **21** were prone to rearrangement and as a result product mixtures were heavily contaminated with the POP type rearrangement products **20** and **22** (Scheme 7), which could not be separated successfully. In contrast to the previously observed complex $[\text{RhCl}(\text{PPh}_3)(\text{POP})]$ (**9**), the POP type ligands in complexes **20** and **22** are coordinated in a bridging rather than chelating manner between two neighbouring Rh(I) centres. The more rigid bond angles at the phosphorus atoms, which are already constrained in a ring system, together with the increased steric demands of the biphenyl and binaphthyl containing alkoxy groups may be the cause of this observed preference. Furthermore, the concentrations of **20** and **22** are found to increase over time at the expense of **19** and **21** when product mixtures are left in solution, suggesting once again that these rearrangements are metal mediated.

In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **19**, coordinated **3** gives rise to a doublet of triplets at δ 134.5, owing to coupling to rhodium and the magnetically equivalent PPh_3 ligands ($J_{\text{P-Rh}} = 321.8$ Hz, $J_{\text{P-P}} = 46.2$ Hz). The latter resonate as a doublet of doublets at δ 36.1. The observed coupling pattern confirms the identity of **19** as the *trans*-complex, while the chemical shift of coordinated **3** is consistent with bonding only through phosphorus. Likewise, a doublet of triplets at δ 133.9 and a broad doublet of doublets at δ 35.2 are detected for complex **21** and are in agreement with the values reported for $[\text{Rh}(\text{COD})\{(\text{R})\text{-acetyl-(1,1'-binaphthyl-2,2'-diyl)phosphite}\}][\text{BF}_4]$.¹⁵

In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of partially rearranged **19**, the bridging POP type ligand of the rearrangement product, **20**, resonates as a doublet of triplets at δ 79.9 ($J_{\text{P-Rh}} = 260.5$ Hz, $J_{\text{P-P}} = 19.0$ Hz), while the magnetically equivalent PPh_3 ligands are detected as a doublet of doublets at δ 21.7



Scheme 7 Products observed for reactions of $[\text{RhCl}(\text{PPh}_3)_3]$ with the (propanoyl)phosphite ligands **3** and **4**. Conditions: (i) **3** (1 : 1), CH_2Cl_2 , R.T., 30 min; (ii) **4** (1 : 1), CH_2Cl_2 , R.T., 1 h.

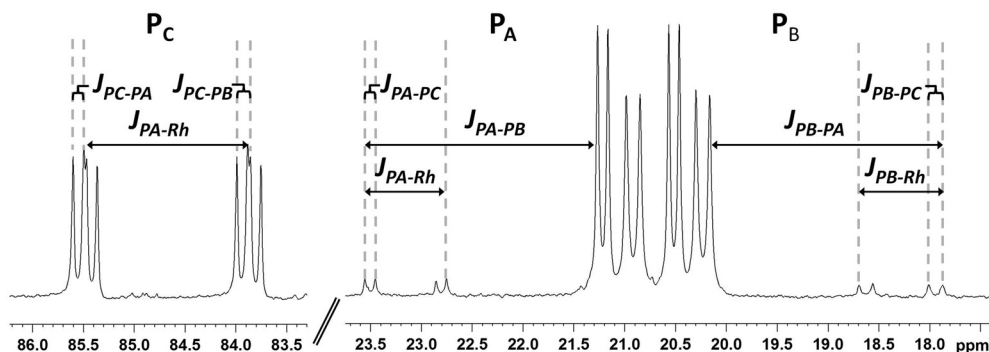
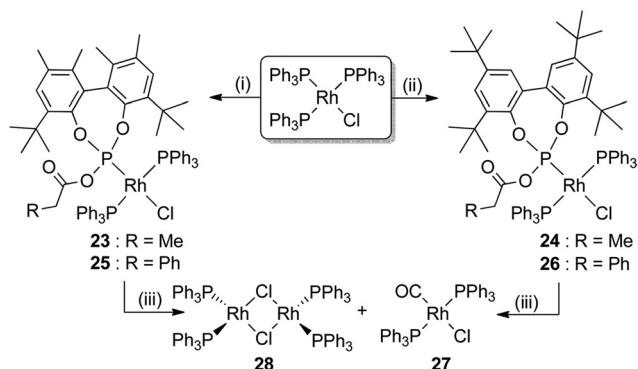


Fig. 5 Resonances corresponding to **22** in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of partially rearranged **21**. In **22** mutually *trans* PPh_3 ligands are chemically and magnetically inequivalent (indicated as P_A and P_B) resulting in the observed second order spectral effects, while the P-atoms in the POP ligand are equivalent (represented by P_C).

($J_{\text{P-Rh}} = 113.0$ Hz, $J_{\text{P-P}} = 19.0$ Hz). In contrast, the PPh_3 ligands of the rearrangement product **22** (present in the product mixture of **21**) are magnetically inequivalent, owing to the chirality of the bridging POP ligand. The chemical shifts of the PPh_3 are, however, very similar and **22** therefore represents an ABMX spin system (A and B = PPh_3 , M = POP and X = Rh) which gives rise to the more complex second order spectrum depicted in Fig. 5. For both **20** and **22**, the observed chemical shifts, coupling patterns and coupling constants are consistent with the assigned structures, where a POP type ligand is co-ordinated in a bridging fashion between two *trans*- $[\text{RhCl}(\text{PPh}_3)_2]$ entities.

For Rh(I) complexes of the more stable (propanoyl)phosphites **5–6**, and (phenylacetyl)phosphites **7–8** (which have sterically demanding *tert*-butyl groups in the vicinity of their phosphorus atoms) rearrangements of this type were not observed. The *trans*- $[\text{RhCl}(\text{PPh}_3)_2(\text{L})]$ complexes **23–26** could be prepared in high yield by reacting solutions of ligands **5**, **6**, **7** or **8** in dichloromethane with $[\text{RhCl}(\text{PPh}_3)_3]$ at room temperature for 1 h. In most cases, crude products could be successfully purified by washing with copious amounts of hexane [Scheme 8(i) and (ii)].



Scheme 8 Reaction scheme for the preparation of complexes **23–26** and their subsequent rearrangement to complexes **27** and **28**. Conditions: (i) **5** or **7**, CH_2Cl_2 , R.T., 1 h; (ii) **6** or **8**, CH_2Cl_2 , R.T., 1 h; (iii) standing in solution at R.T. for 1–2 days.

In addition, these complexes could be further purified by recrystallisation and single crystals suitable for X-ray structure determinations could be obtained for complexes **23–25** (Fig. 6 and 7). In the asymmetric unit of **23**, two molecules of **23** are co-crystallised with at least eight dichloromethane molecules, and as a result, the determined structure is heavily disordered. Owing to the poor quality of this data set, the structure of **23** is only given in the ESI (see Fig. S5†).

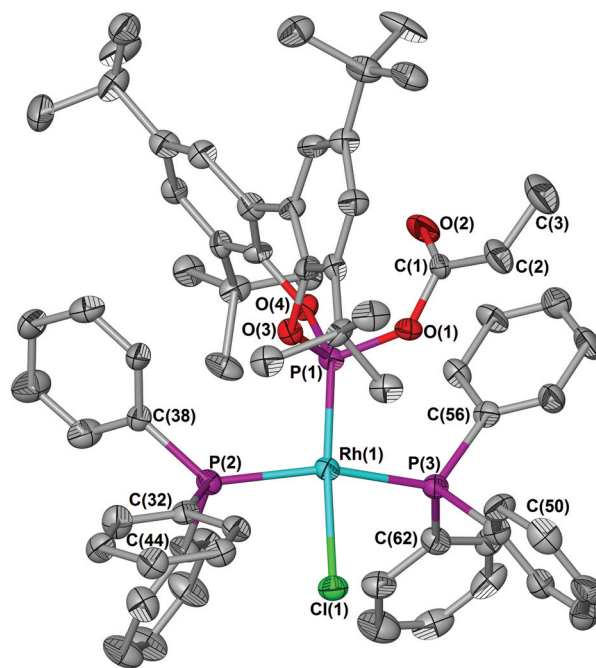


Fig. 6 Molecular structure of **24** with thermal ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths and angles: Rh(1)–P(1) 2.140(2), Rh(1)–P(2) 2.338(2), Rh(1)–P(3) 2.310(2), Rh(1)–Cl(1) 2.384(2), P(1)–O(1) 1.643(6), P(1)–O(3) 1.637(6), P(1)–O(4) 1.597(6), P(1)–Rh(1)–P(2) 97.71(8), P(1)–Rh(1)–P(3) 98.41(8), P(1)–Rh(1)–Cl(1) 161.18(9), P(2)–Rh(1)–Cl(1) 84.46(8), P(3)–Rh(1)–Cl(1) 84.13(8), P(2)–Rh(1)–P(3) 159.96(9), Rh(1)–P(1)–O(1) 113.8(2), Rh(1)–P(1)–O(3) 111.7(2), Rh(1)–P(1)–O(4) 123.9(2), O(1)–P(1)–O(3) 99.4(3), O(1)–P(1)–O(4) 102.1(3), O(3)–P(1)–O(4) 102.7(3), P(1)–O(1)–C(1) 133.0(5), O(1)–C(1)–O(2) 123.0(8), O(2)–C(1)–C(2) 127.1(8), O(1)–C(1)–C(2) 109.9(7).

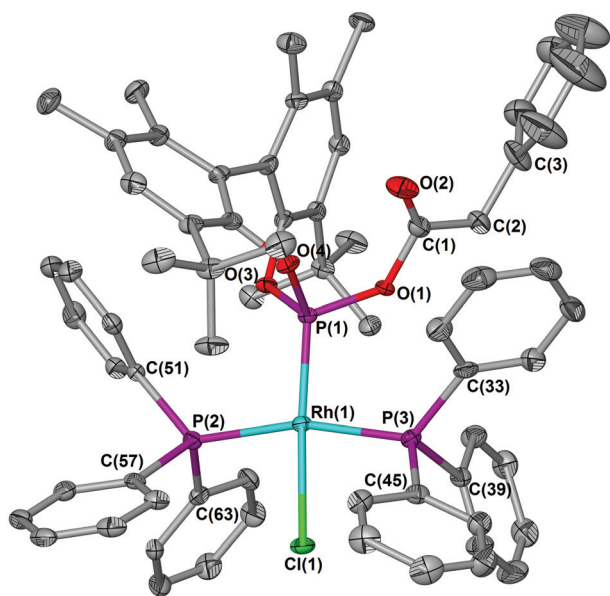


Fig. 7 Molecular structure of **25** with thermal ellipsoids set at 50% probability. Hydrogen atoms and solvent molecules are omitted for clarity. Rh(1)–P(1) 2.1412(17), Rh(1)–P(2) 2.3274(18), Rh(1)–P(3) 2.3040(18), Rh(1)–Cl(1) 2.3898(17), P(1)–O(1) 1.643(5), P(1)–O(3) 1.620(5), P(1)–O(4) 1.609(5), O(1)–C(1) 1.406(9), C(1)–O(2) 1.197(9), P(1)–Rh(1)–P(2) 98.60(6), P(1)–Rh(1)–P(3) 96.29(7), P(1)–Rh(1)–Cl(1) 173.88(7), P(2)–Rh(1)–Cl(1) 82.62(6), P(3)–Rh(1)–Cl(1) 82.30(6), P(2)–Rh(1)–P(3) 164.89(6), Rh(1)–P(1)–O(1) 113.12(17), Rh(1)–P(1)–O(3) 114.97(18), Rh(1)–P(1)–O(4) 121.55(18), O(1)–P(1)–O(3) 100.6(3), O(1)–P(1)–O(4) 99.5(3), O(3)–P(1)–O(4) 104.1(3), P(1)–O(1)–C(1) 133.2(5).

Complexes **23–25** all display very similar behaviour in solution and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra recorded for these compounds are almost identical with very little variation among the complexes in terms of their chemical shifts and coupling constants. Similar to complex **22**, the PPh_3 ligands in complexes **23–25** are chemically inequivalent with chemical shifts very close in value, once again leading to second order spectral effects.

Fig. 8 represents the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **25**; an example of the typical spectral profile associated with these complexes. Coupling constants between the coordinated (acyl)-

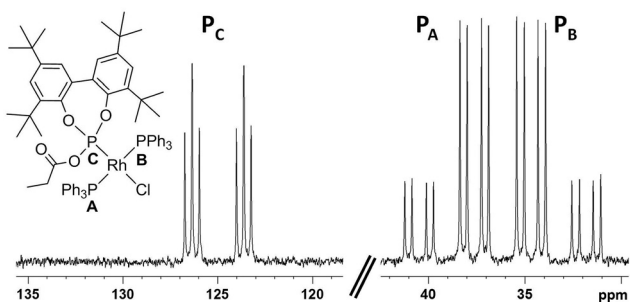
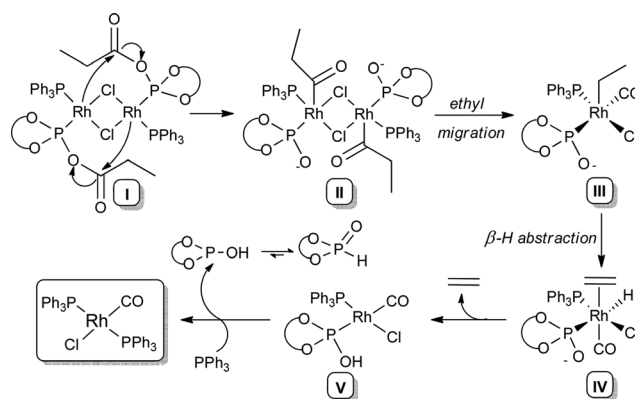


Fig. 8 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex **25**, representing an example of the typical spectral profile observed for complexes of the form $[\text{RhCl}(\text{PPh}_3)_2(\text{L})]$ where L denotes ligands **5**, **6**, **7** or **8**.

phosphite and the PPh_3 ligands are equal in magnitude and the phosphorus resonance from the (acyl)phosphite ligand (P_C) is observed as an apparent doublet of triplets at δ 124.9 ($J_{\text{P-Rh}} = 331.3$ Hz, $J_{\text{PC-PA}} = J_{\text{PC-PB}} = 48.3$ Hz). The PPh_3 ligands give rise to an ABMX pattern of doublets of doublets of doublets at δ 33.8 and δ 38.2, respectively. In addition to mutual *trans* coupling ($J_{\text{PA-PB}} = 347.9$ Hz), these ligands display equal coupling to both Rh ($J_{\text{PA-Rh}} = J_{\text{PB-Rh}} = 135.3$ Hz) and P_C ($J_{\text{PA-PC}} = J_{\text{PB-PC}} = 48.3$ Hz) and as a result the observed coupling pattern is highly symmetrical with the close proximity of their chemical shifts resulting in the pattern depicted in Fig. 8.

In solution, however, these complexes undergo complete rearrangement within 1 to 2 days *via* a mechanism different from those previously observed. Instead of POP type complexes, a variety of highly symmetrical rearrangement products is obtained with the known carbonyl complex *trans*- $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$ (**27**)²⁶ representing the major product of rearrangement. Large quantities of the latter crystallised, as either yellow prisms or yellow needles from solutions of **23–26** when left standing for a period of 1 to 2 days. The structure of known **27** could also be confirmed by X-ray crystallography. In addition to **27**, the known dimeric compound $[\{\text{RhCl}(\text{PPh}_3)_2\}_2]$ (**28**)²⁷ is also observed as a product of decay and often crystallises as burgundy prisms from solutions of **23–26** following rearrangement [Scheme 8(iii)].

Although no formal mechanistic studies were conducted, it is plausible that the formation of **27** involves decarbonylation of coordinated ligands **5–6** and **7–8** *via* a dimeric metal acyl intermediate. In the initial stages of the rearrangement, complexes **23–24** may dimerise to form mixtures of $[\{\text{RhCl}(\text{PPh}_3)_2\}_2]$ and $[\{\text{RhCl}(\text{PPh}_3)(\text{L})\}_2]$ (where L = **5–6**). While the former is very insoluble and as a consequence crystallises from solution, the latter can undergo further rearrangement to generate **27**. Scheme 9 depicts the proposed mechanism of rearrangement for (propanoyl)phosphite complexes **23** and **24** only, but it is possible that a similar mechanism exists for complexes **25–26**. Migratory deinsertion of CO is not uncommon and similar decarbonylation pathways to the one postulated here have been described in the literature.^{28–30} In addition, the detection of phosphonates in the final product



Scheme 9 Proposed mechanism for the formation of Rh(I) CO complexes by the decarbonylation of (propanoyl)phosphite ligands **5–6**.

mixtures by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy are in support of the proposed mechanism.

Experimental

General materials, methods and instruments

Reactions were carried out under dinitrogen gas (N_2 , passed through a column of Cr^{II} adsorbed on silica) using standard Schlenk, vacuum-line and cannula techniques. All glassware was flame-dried under vacuum. Triethylamine (NEt_3) and chlorodiphenylphosphine (Ph_2PCl) were purchased from Aldrich and distilled under N_2 prior to use. Before distilling, the NEt_3 was dried over potassium hydroxide (KOH) pellets. Sodium propanoate was also purchased from Aldrich and dried azeotropically with toluene before use. Cyclooctene, triphenylphosphine, paraformaldehyde, sodium tertiarybutoxide and isopropanol were purchased from Aldrich and used as received. Propanoic acid, purchased from BDH laboratories, was dried over Na_2CO_3 and distilled under N_2 prior to use. All gases were purchased from BOC gases. $[\text{RhCl}(\text{PPh}_3)_3]$ was prepared from $[\text{RhCl}_3 \cdot 3\text{H}_2\text{O}]$ and PPh_3 , while $[\text{RuCl}_2(\text{PPh}_3)_3]$ was prepared from $[\text{RuCl}_3 \cdot 3\text{H}_2\text{O}]$ and PPh_3 , using standard literature procedures.^{31,32} $[\text{RhCl}_3 \cdot 3\text{H}_2\text{O}]$ was purchased from either Engelhard or Alfa Aesar and $[\text{RuCl}_3 \cdot 3\text{H}_2\text{O}]$ from Strem Chemicals. $[\{\text{RhCl}(\text{COE})_2\}_2]$ (where COE = cyclooctene) was prepared from $[\text{RhCl}_3 \cdot 3\text{H}_2\text{O}]$ and cyclooctene using a literature procedure.³³ Ligands **1–8** were prepared using the previously described methods.¹⁷

Toluene, thf, diethyl ether and hexane, purchased from Fisher Scientific, were dried using a Braun Solvent Purification System and degassed by additional freeze–pump–thaw cycles when deemed necessary. Methanol and ethanol, purchased from Aldrich, were distilled under nitrogen from magnesium. Deuterated dichloromethane and chloroform were purchased from Aldrich and dried over phosphorus pentoxide (P_2O_5), degassed *via* three freeze–pump–thaw cycles and trap-to-trap distilled prior to use.

NMR spectra were recorded on Bruker Avance 300 FT or Bruker Avance II 400 MHz spectrometers (^1H NMR at 300/400 MHz, $^{13}\text{C}\{^1\text{H}\}$ NMR at 75/100 MHz and $^{31}\text{P}\{^1\text{H}\}$ NMR at 121/162 MHz) with chemical shifts δ reported relative to tetramethylsilane (TMS) (^1H , $^{13}\text{C}\{^1\text{H}\}$) or 85% H_3PO_4 ($^{31}\text{P}\{^1\text{H}\}$) as external reference. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were referenced internally to deuterated solvent resonances which were referenced relative to TMS.

Solid state IR spectra were recorded using pressed KBr pellets on a Perkin Elmer Spectrum GX IR spectrometer. Elemental analysis were performed by the University of St. Andrews microanalytical service using a Carlo Erba CHNS/O microanalyser. Melting points were determined on a Gallenkamp apparatus and are uncorrected. Mass spectra were recorded either by the EPSRC National Mass Spectrometry Service Centre, Swansea on a Thermofisher LTQ Orbitrap XL high resolution instrument coupled to an Advion TriVersa NanoMate electrospray infusion system or by the Mass

Spectrometry Service Centre at the University of St. Andrews using either of a Micromass GCT EI/CI or a Micromass LCT ES instrument.

Single crystal X-ray structure determinations

A summary of the crystal data collection and refinement parameters of compounds **16–18** and **23–25** can be found in the ESI.† Data sets were collected on a Rigaku Mo MM007 (dual port) high brilliance diffractometer with graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71075 \text{ \AA}$). The diffractometer is fitted with Saturn 70 and Mercury CCD detectors and two XStream LT accessories. Data were collected and processed using CrystalClear (Rigaku).³⁴ Neutral atom scattering factors were taken from Cromer and Waber.³⁵ Anomalous dispersion effects were included in Fcalc ;³⁶ the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.³⁷ The values for the mass attenuation coefficients are those of Creagh and Hubbell.³⁸ All calculations were performed using the CrystalStructure³⁹ crystallographic software package except for refinement, which was performed using SHELX-97.⁴⁰ All the structures were solved using direct, heavy-atom Patterson or conventional difference Fourier methods. All non-hydrogen atoms were refined anisotropically by full-matrix least squares calculations on F^2 using SHELX-97. The hydrogen atoms were fixed in calculated positions. Figures were generated with X-seed^{41,42} and POV Ray for Windows, with the displacement ellipsoids at 50% probability level unless stated otherwise. Further information is available on request from Prof. Alexandra M. Z. Slawin at the School of Chemistry, University of St. Andrews.

Synthetic procedures

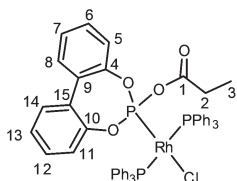
A description of all attempts to prepare and isolate compounds **10** and **13** can be found in the ESI,† together with details on the formation of the rearrangement product **16**.

$[\text{RuCl}_2(\text{Ph}_2\text{PO}_2\text{CCH}_2\text{CH}_3)_2]$, **17.** A solution of **1** (0.21 g, 0.80 mmol) in dichloromethane (5 ml) was added to a solution of $[\text{RuCl}_2(\text{PPh}_3)_3]$ (0.34 g, 0.35 mmol) in dichloromethane (10 ml) at room temperature. Upon addition the reaction mixture colour immediately became lighter until finally a bright orange solution was observed. The reaction mixture was allowed to stir at room temperature for 2 h after which the mixture was concentrated and the product precipitated by the addition of hexane (20 ml). The resulting light orange precipitate was then isolated, washed with hexane ($2 \times 20 \text{ ml}$) and dried *in vacuo* to yield the analytically pure product as a bright light orange solid (yield: 0.21 g, 87%). Single crystals in the form of orange platelets suitable for analysis by single crystal X-ray diffraction could be obtained by slow diffusion of diethyl ether into a toluene solution of **17** at room temperature. *Anal.* Calculated (%) for $\text{C}_{30}\text{H}_{30}\text{Cl}_2\text{O}_4\text{P}_2\text{Ru}$: C 52.3, H 4.4; Found C 51.9, H 4.0. ^1H NMR (400 MHz, CDCl_3): $\delta_{\text{H}} = 1.44$ (t, 3H, $^3J = 7.4 \text{ Hz}$; CH_3), 2.98 (q, 2H, $^3J = 7.4 \text{ Hz}$; CH_2), 7.20–7.42 (m, 20H; Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): $\delta_{\text{C}} = 9.6$ (s; $-\text{CH}_3$), 28.7 (s; $-\text{CH}_2-$), 127.8 (m, $J_{\text{C-P}} = 5.7 \text{ Hz}$; $\text{PPh-C}^{\text{meta}}$), 131.7 (s; $\text{PPh-C}^{\text{para}}$), 133.0 (m, $J_{\text{C-P}} = 5.7 \text{ Hz}$; $\text{PPh-C}^{\text{ortho}}$), 134.8 (d, $^1J_{\text{C-P}} = 56.0 \text{ Hz}$; $\text{PPh-C}^{\text{ipso}}$), 179.4 (s; C=O). $^{31}\text{P}\{^1\text{H}\}$ NMR (161 MHz,

CDCl_3): $\delta_{\text{P}} = 188.6$ (s; P). IR (KBr): $\tilde{\nu} = 3054$ [w, $\text{sp}^2 \nu(\text{C-H})$], 2940 [w, $\text{sp}^3 \nu(\text{C-H})$], 1649 [st, $\nu(\text{C=O})$], 1434–1364 [st, Ar $\nu(\text{C=C})$], 694 [m, $\nu(\text{P-O})$]. ES-MS: m/z (%) = 653 (100) $[\text{M} - \text{Cl}]^+$.

$[\{\text{RuCl}_2(\text{Ph}_2\text{PO}_2\text{CCH}_2\text{CH}_3)(\text{Ph}_2\text{POH})_2\}]$, **18**. Compound **17** although stable in the solid state, rearranges to the chloro-bridged Ru(II) dimer **18** when left standing in solution. Single crystals of **18** suitable for X-ray analysis were obtained as orange prisms during initial attempts to crystallise **17** by vapour diffusion of pentane into a chloroform- d_1 solution of the **17** at room temperature. ^1H NMR (300 MHz, CDCl_3): $\delta_{\text{H}} = 1.18$ (t, 3H, $^3J = 7.5$ Hz; CH_3), 2.43 (qd, 2H, $^3J = 7.5$ Hz, $^4J_{\text{H-P}} = 1.6$ Hz; CH_2), 6.51–8.09 (m, 40H; Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (161 MHz, CDCl_3): $\delta_{\text{P}} = 132.5$ (d, $^2J_{\text{PA-PB}} = 44.2$; P_A), 188.3 (d, $^2J_{\text{PB-PA}} = 44.2$; P_B).

$[\text{RhCl}(\text{PPh}_3)_2(\text{propanoyl-(1,1'-biphenyl-2,2'-diyl)phosphite})]$, **19**. A solution of ligand **3** (0.08 g, 0.27 mmol) in dichloromethane (15 ml) was added to a solution of $[\text{RhCl}(\text{PPh}_3)_3]$ (0.25 g, 0.27 mmol) in dichloromethane (10 ml) at room temperature. Upon addition the reaction mixture colour changed from burgundy to light yellow. Following a 30 minute stirring period, the reaction mixture was reduced to dryness, the residue washed with hexane (4×20 ml) and then dried *in vacuo* to furnish the product as a yellow solid. This major product was, however, contaminated with the ligand disproportionation product as well as the rearrangement product **20**. The title product could not be separated from these by-products using standard separation techniques. For complex **19** – ^1H NMR (300 MHz, CD_2Cl_2): $\delta_{\text{H}} = 0.87$ (t, 3H, $^3J = 7.5$ Hz; H^3), 1.54 (q, 2H, $^3J = 7.5$ Hz; H^2), 6.60–7.7 (m, 2H; Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CD_2Cl_2): $\delta_{\text{C}} = 8.8$ (s; C^3), 28.5 (s; C^2), 122.3 (s; C^5/C^{11}), 125.7 (s; C^7/C^{13}), 127.8 (d, $^3J_{\text{C-P}} = 4.7$ Hz; $\text{PPh-C}^{\text{meta}}$), 129.7 (s; $\text{PPh-C}^{\text{para}}$), 130.0 (s; C^6/C^{12}), 131.0 (s; C^8/C^{14}), 135.5 (d, $^2J_{\text{C-P}} = 6.0$ Hz; $\text{PPh-C}^{\text{ortho}}$), 135.9 (s; C^9/C^{15}), 137.7 (d, $^1J_{\text{C-P}} = 11.5$ Hz; $\text{PPh-C}^{\text{ipso}}$), 149.5 (d, $^2J_{\text{C-P}} = 10.6$ Hz; C^4/C^{10}), 170.2 (d; $^2J_{\text{C-P}} = 3.4$ Hz; C^1). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CD_2Cl_2): $\delta_{\text{P}} = 36.1$ (dd, $^1J_{\text{PA-Rh}} = 132.7$ Hz, $^2J_{\text{PA-PB}} = 46.6$ Hz; P_A), 134.5 (dt, $^1J_{\text{PB-Rh}} = 321.8$ Hz, $^2J_{\text{PB-PA}} = 46.6$ Hz; P_B). IR (KBr): $\tilde{\nu} = 3054$ [w, $\text{sp}^2 \nu(\text{C-H})$], 3009 [w, $\text{sp}^3 \nu(\text{C-H})$], 1761 [w, $\nu(\text{C=O})$], 1498–1434 [st, Ar $\nu(\text{C=C})$], 694 [st, $\nu(\text{P-O})$]. For complex **20** – $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CD_2Cl_2): $\delta_{\text{P}} = 21.7$ (dd, $^1J_{\text{PA-Rh}} = 113.0$ Hz, $^2J_{\text{PA-PC}} = 19.0$ Hz; P_A), 79.9 (dt, $^1J_{\text{PC-Rh}} = 260.5$ Hz, $^2J_{\text{PB-PA}} = 19.0$ Hz; P_C).

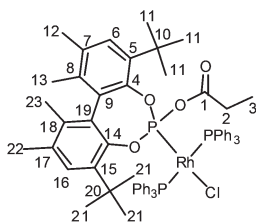


$[\text{RhCl}(\text{PPh}_3)_2\{(\text{R})\text{-propanoyl-(1,1'-binaphthyl-2,2'-diyl)phosphite}\}]$, **21**. Compound **21** was prepared using a similar method to that described for **19**, by treating a solution of $[\text{RhCl}(\text{PPh}_3)_3]$ (0.22 g, 0.24 mmol) in dichloromethane (10 ml) with a solution of **4** (0.09 g, 0.24 mmol) in dichloromethane (15 ml) at room temperature for 1 h. The title product was

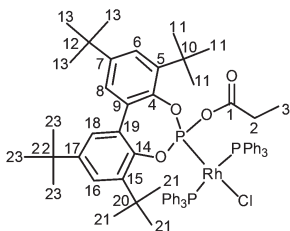
obtained as an orange solid which, despite representing the major product, was contaminated by the rearrangement product **22**. This product could not be separated from **21**, using standard purification techniques, without effecting further rearrangement. For complex **21** – ^1H NMR (300 MHz, CD_2Cl_2): $\delta_{\text{H}} = 0.91$ (t, 3H, $^3J = 6.6$ Hz; CH_3), 1.40 (m, 1H; CH_2), 1.61 (m, 1H; CH_2), 7.16–8.11 (m, 42H; Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CD_2Cl_2): $\delta_{\text{C}} = 8.8$ (s; CH_3), 28.4 (s; CH_2), 120.7 (s), 122.5 (s), 123.3 (s), 123.9 (s), 125.4 (s), 125.8 (s), 126.6 (s), 127.1 (s), 127.5 (s), 127.7 (d, $^3J_{\text{C-P}} = 4.8$ Hz; $\text{PPh-C}^{\text{meta}}$), 128.8 (s), 129.1 (s), 129.6 (s; $\text{PPh-C}^{\text{para}}$), 129.8 (s), 130.4 (s), 131.4 (s), 132.5 (s), 133.1 (s), (d, $^2J_{\text{C-P}} = 5.7$ Hz; $\text{PPh-C}^{\text{ortho}}$), 135.8 (d, $^1J_{\text{C-P}} = 22.7$ Hz; $\text{PPh-C}^{\text{ipso}}$), 147.6 (d, $^2J_{\text{C-P}} = 5.5$ Hz), 148.7 (d, $^2J_{\text{C-P}} = 12.9$ Hz), 170.2 (d, $^2J_{\text{C-P}} = 3.0$ Hz; C=O). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CD_2Cl_2): $\delta_{\text{P}} = 35.2$ (bdd, $^1J_{\text{PA-Rh}} = 132.9$ Hz, $^2J_{\text{PA-PB}} = 46.2$ Hz; P_A), 133.9 (dt, $^1J_{\text{PB-Rh}} = 322.5$ Hz, $^2J_{\text{PB-PA}} = 46.2$ Hz; P_B). IR (KBr): $\tilde{\nu} = 3049$ [m, $\text{sp}^2 \nu(\text{C-H})$], 3000–2960 [w, $\text{sp}^3 \nu(\text{C-H})$], 1751 [w, $\nu(\text{C=O})$], 1505–1432 [m, Ar $\nu(\text{C=C})$], 692 [st, $\nu(\text{P-O})$]. For complex **22** (ABMX spin system) – $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CD_2Cl_2): $\delta_{\text{P}} = 20.6$ (ddd, $^1J_{\text{PA-Rh}} = 113.3$ Hz, $^2J_{\text{PA-PB}} = 370.5$ Hz, $^2J_{\text{PA-PC}} = 17.2$ Hz; P_A), 20.5 (ddd, $^1J_{\text{PB-Rh}} = 111.3$ Hz, $^2J_{\text{PB-PA}} = 370.5$ Hz, $^2J_{\text{PB-PC}} = 21.2$ Hz; P_B), 84.7 (ddd, $^1J_{\text{PC-Rh}} = 261.1$ Hz, $^2J_{\text{PC-PA}} = 17.2$ Hz, $^2J_{\text{PC-PB}} = 21.2$ Hz; P_C).

$[\text{RhCl}(\text{PPh}_3)_2\{\text{propanoyl-(5,5',6,6'-tetramethyl-3,3'-di-tert-butyl-1,1'-biphenyl-2,2'-diyl)phosphite}\}]$, **23**. Compound **23** was prepared using a similar methodology to that which was described for the preparation of **19**. A solution of **5** (0.09 g, 0.20 mmol) in dichloromethane (15 ml) was added to a solution of $[\text{RhCl}(\text{PPh}_3)_3]$ (0.19 g, 0.20 mmol) at room temperature. The reaction mixture was stirred at this temperature for 1 h during which time the solution colour changed from burgundy to light yellow. The mixture was subsequently stripped of all volatiles under reduced pressure and the resulting residue washed with hexane (3×10 ml) to yield the product as a bright yellow solid (yield: 0.17 g, 77%). Crystals suitable for structure determination by X-ray diffraction were obtained as yellow platelets by cooling a concentrated solution of **23** in dichloromethane to -22°C . ^1H NMR (300 MHz, CD_2Cl_2): $\delta_{\text{H}} = 0.20$ (t, 3H, $^3J = 7.0$ Hz; H^3), 0.84 (q, 2H, $^3J = 7.5$ Hz; H^2), 1.37 (s, 9H; H^{11}), 1.50 (s, 3H; H^{12}), 1.55 (s, 3H; H^{22}), 1.74 (s, 9H; H^{21}), 2.09 (s, 3H; H^{13}), 2.26 (s, 3H; H^{23}), 6.91–8.31 (m, 32H; Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CD_2Cl_2): $\delta_{\text{C}} = 7.6$ (s; C^3), 16.3 (s; C^{13}), 16.9 (s; C^{23}), 20.1 (s; C^{12}), 20.5 (s; C^{22}), 27.6 (s; C^2), 31.6 (s; C^{11}), 31.9 (s; C^{21}), 34.9 (s; C^{10}), 35.1 (s; C^{20}), 127.3 (d, $^3J_{\text{C-P}} = 8.1$ Hz; $\text{PPh-C}^{\text{meta}}$), 128.0 (d, $^3J_{\text{C-P}} = 9.8$ Hz; $\text{PPh-C}^{\text{meta}}$), 129.1 (s; $\text{PPh-C}^{\text{para}}$), 129.3 (s; $\text{PPh-C}^{\text{para}}$), 131.5 (s; C^7/C^{17}), 132.2 (s; C^6), 132.4 (s; C^{16}), 132.6 (s; C^9/C^{19}), 135.0 (d, $^2J_{\text{C-P}} = 8.9$ Hz; $\text{PPh-C}^{\text{ortho}}$), 135.7 (d, $^2J_{\text{C-P}} = 8.9$ Hz; $\text{PPh-C}^{\text{ortho}}$), 136.2 (s; C^8/C^{18}), 136.6 (s; C^5/C^{15}), 136.8 (d, $^1J_{\text{C-P}} = 51$ Hz; $\text{PPh-C}^{\text{ipso}}$), 148.1 (s; C^4), 149.4 (s; C^{14}). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CD_2Cl_2): $\delta_{\text{P}} = 34.4$ (ABMX pattern, ddd, $^1J_{\text{PA-Rh}} = 138.2$ Hz, $^2J_{\text{PA-PC}} = 44.3$ Hz, $^2J_{\text{PA-PB}} = 349.5$ Hz; P_A), 37.2 (ABMX pattern, ddd, $^1J_{\text{PB-Rh}} = 138.2$ Hz, $^2J_{\text{PB-PC}} = 44.3$ Hz, $^2J_{\text{PB-PA}} = 349.5$ Hz; P_B), 129.3 (dt, $^1J_{\text{PC-Rh}} = 331.3$ Hz, $^2J_{\text{PC-PA}} = ^2J_{\text{PC-PB}} = 44.3$ Hz; P_C). IR (KBr): $\tilde{\nu} = 3054$ [w, $\text{sp}^2 \nu(\text{C-H})$], 2958–2866 [m, $\text{sp}^3 \nu(\text{C-H})$],

1780 [m, $\nu(\text{C}=\text{O})$], 1481–1393 [m, Ar $\nu(\text{C}=\text{C})$], 695 [m, $\nu(\text{P}-\text{O})$]. ES-MS: m/z (%) = 1083 (80) $[\text{M} - \text{Cl}]^+$, 821 (100) $[\text{M} - \text{Cl} - \text{PPh}_3]^+$, 627 (5) $[\text{Rh}(\text{PPh}_3)_2]^+$.

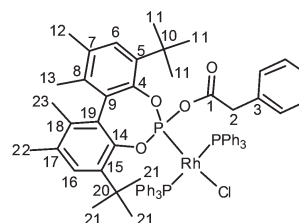


[RhCl(PPh₃)₂{propanoyl-(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl)phosphite}], 24. Using the same procedure as was described for the preparation of **19**, [RhCl(PPh₃)₃] (0.44 g, 0.48 mmol) was reacted with an excess of ligand **6** (0.39 g, 0.76 mmol) at room temperature for 1 h. After the removal of all volatiles, the orange residue was washed with copious amounts of hexane (3 × 30 ml) to furnish the analytically pure title product as a bright yellow solid (yield: 0.52 g, 92%). Crystals in the form of yellow needles suitable for analysis by X-ray diffraction were grown by slow diffusion of hexane into a concentrated solution of **24** in toluene at room temperature. Mp 220–222 °C (decomposed). Anal. Calculated (%) for C₆₇H₇₅ClO₄P₃Rh: C 68.5, H 6.4; Found C 68.5, H 6.6. ¹H NMR (300 MHz, CD₂Cl₂): δ_{H} = 0.21 (t, 3H, 3J = 7.4 Hz; H₃), 0.88 (q, 2H, 3J = 7.4 Hz; H₂), 1.32 (s, 18H; H₁₁ / H²¹), 1.53 (s, 18H; H¹³/H²³), 6.96 (d, 2H, ⁴J = 2.1 Hz; H⁶/H¹⁶), 7.10 (m, 6H), 7.21 (m, 3H), 7.33 (m, 11H), 7.63 (m, 6H), 7.81 (bt, J = 8.2 Hz, 6H). ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): δ_{C} = 7.7 (s; C³), 27.1 (s; C²), 31.6 (s; C¹¹/C²¹), 31.6 (s; C¹³/C²³), 34.8 (s; C¹⁰/C²⁰), 35.8 (s; C¹²/C²²), 124.4 (s; C⁶/C¹⁶), 127.5 (d, ³J_{C-P} = 8.8 Hz; PPh-C^{meta}), 128.1 (d, ³J_{C-P} = 9.2 Hz; PPh-C^{meta}), 128.4 (s; C⁸/C¹⁸), 129.4 (s; PPh-C^{para}), 134.9 (d, ²J_{C-P} = 10.0 Hz; PPh-C^{ortho}), 136.4 (d, ²J_{C-P} = 9.2 Hz; PPh-C^{ortho}), 136.4 (d, ¹J_{C-P} = 41.2 Hz; PPh-C^{ipso}), 139.2 (s; C⁵/C¹⁵), 146.7 (s; C⁴/C¹⁴), 145.7 (s; C⁷/C¹⁷). ³¹P{¹H} NMR (121 MHz, CD₂Cl₂): δ_{P} = 33.8 (ABMX pattern, ddd, ¹J_{PA-Rh} = 135.3 Hz, ²J_{PA-PC} = 48.3 Hz, ²J_{PA-PB} = 347.9 Hz; P_A), 38.2 (ABMX pattern, ddd, ¹J_{PB-Rh} = 135.3 Hz, ²J_{PB-PC} = 48.3 Hz, ²J_{PB-PA} = 347.9 Hz; P_B), 124.9 (dt, ¹J_{PC-Rh} = 331.8 Hz, ²J_{PC-PA} = ²J_{PC-PB} = 48.3 Hz; P_C). IR (KBr): $\tilde{\nu}$ = 3052 [m, sp² $\nu(\text{C}-\text{H})$], 2956–2869 [st, sp³ $\nu(\text{C}-\text{H})$], 1775 [st, $\nu(\text{C}=\text{O})$], 1477–1395 [m, Ar $\nu(\text{C}=\text{C})$], 694 [m, $\nu(\text{P}-\text{O})$]. ES-MS: m/z (%) = 1139 (100) $[\text{M} - \text{Cl}]^+$, 877 (35) $[\text{M} - \text{Cl} - \text{PPh}_3]^+$.



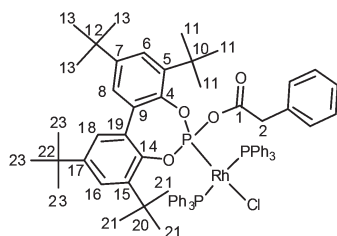
[RhCl(PPh₃)₂{phenylacetyl-(5,5',6,6'-tetramethyl-3,3'-di-tert-butyl-1,1'-biphenyl-2,2'-diyl)phosphite}], 25. Compound **25** was prepared using the same procedure described for the preparation of **19**. A solution of **7** (0.18 g, 0.35 mmol) in dichloromethane

(20 ml) was added to a solution of [RhCl(PPh₃)₃] (0.32 g, 0.35 mmol) in dichloromethane (20 ml) at room temperature. The reaction mixture was stirred at this temperature for 1 h. Removal of all volatiles under reduced pressure gave the crude product as an orange solid which could be purified by washing with hexane (3 × 20 ml) (yield: 0.32 g, 78%). Crystals suitable for X-ray structure determination were grown as yellow prisms by slowly cooling a concentrated solution of **25** in dichloromethane to –22 °C. Mp 199–204 °C (decomposed). ¹H NMR (300 MHz, CDCl₃): δ_{H} = 1.38 (s, 9H; H¹¹), 1.76 (s, 9H; H²¹), 1.49 (bs, 6H; H¹²/H²²), 2.04 (s, 3H; H¹³), 2.22 (s, 3H; H²³), 2.33 (d, 1H, ²J = 19.0 Hz; H²), 2.61 (d, 1H, ²J = 19 Hz; H²), 6.52–7.84 (m, 37H, Ph). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ_{C} = 16.5 (s; C¹³), 17.1 (s; C²³), 20.4 (s; C¹²), 20.5 (s; C²²), 31.7 (s; C¹¹), 32.0 (s; C²¹), 35.0 (s; C¹⁰/C²⁰), 40.2 (s; C²), 127.3 (d, ³J_{C-P} = 8.8 Hz; PPh-C^{meta}), 127.9 (s; Ph-C^{para}), 128.1 (s; PPh-C^{para}), 128.3 (s; PPh-C^{para}), 128.8 (s; Ph-C^{meta}), 129.5 (s; Ph-C^{ortho}), 130.0 (s; C⁶/C¹⁶), 131.5 (s; C⁹), 132.0 (s; Ph-C^{ipso}), 132.4 (s; C¹⁹), 132.8 (s; C⁷), 133.4 (s; C¹⁷), 134.8 (d, ²J_{C-P} = 9.4 Hz; PPh-C^{ortho}), 135.9 (d, ²J_{C-P} = 8.2 Hz; PPh-C^{ortho}), 136.4 (d, ¹J_{C-P} = 28.9 Hz; PPh-C^{ipso}), not observed due to overlap (C⁸/C¹⁸), 137.2 (s; C⁵/C¹⁵), 147.4 (s; C⁴/C¹⁴). ³¹P{¹H} NMR (121 MHz, CD₂Cl₂): δ_{P} = 34.9 (ABMX pattern, ddd, ¹J_{PA-Rh} = 134.9 Hz, ²J_{PA-PC} = 46.3 Hz, ²J_{PA-PB} = 344.3 Hz; P_A), 37.8 (ABMX pattern, ddd, ¹J_{PB-Rh} = 134.9 Hz, ²J_{PB-PC} = 46.3 Hz, ²J_{PB-PA} = 344.3 Hz; P_B), 131.1 (dt, ¹J_{PC-Rh} = 332.7 Hz, ²J_{PC-PA} = ²J_{PC-PB} = 46.3 Hz; P_C). IR (KBr): $\tilde{\nu}$ = 3051 [m, sp² $\nu(\text{C}-\text{H})$], 2955–2867 [m, sp³ $\nu(\text{C}-\text{H})$], 1764 [m, $\nu(\text{C}=\text{O})$], 1482–1392 [st, Ar $\nu(\text{C}=\text{C})$], 695 [m, $\nu(\text{P}-\text{O})$]. ES-MS: m/z (%) = 1145 (100) $[\text{M} - \text{Cl}]^+$, 883 (43) $[\text{M} - \text{Cl} - \text{PPh}_3]^+$, 627 (8) $[\text{Rh}(\text{PPh}_3)_2]^+$.



[RhCl(PPh₃)₂{phenylacetyl-(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl)phosphite}], 26. Using the same procedure as was described for the preparation of **19–25**, [RhCl(PPh₃)₃] (0.35 g, 0.38 mmol) was reacted with ligand **8** (0.22 g, 0.38 mmol) at room temperature for 1 h. After the removal of all volatiles, the product was extracted from the orange residue with hexane (30 ml). The hexane extract was reduced to dryness *in vacuo* to furnish the product as a bright yellow solid (yield: 0.33 g, 70%). ¹H NMR (300 MHz, CD₂Cl₂): δ_{H} = 1.29 (bs, 18H; H¹¹/H²¹), 1.54 (bs, 18H; H¹³/H²³), 2.24 (bs, 2H; H²), 7.00 (d, 2H, ⁴J = 2.7 Hz; H⁶/H¹⁶), 7.10 (d, 2H, ⁴J = 2.7 Hz; H⁸/H¹⁸), 6.51–7.88 (m, 35H, Ph). ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): δ_{C} = 31.1 (s; C¹³/C²³), 31.7 (s; C¹¹/C²¹), 34.9 (s; C¹²/C²²), 35.9 (s; C¹⁰/C²⁰), 40.0 (s; C²), 124.5 (s; C⁶/C¹⁶), 127.1 (s; C⁸/C¹⁸), 128.2 (d, ³J_{C-P} = 9.3 Hz; Ph-C^{meta}), 128.6 (s; Ph-C^{para}), 128.9 (d, ³J_{C-P} = 7.5 Hz; Ph-C^{meta}), 129.1 (s; Ph-C^{para}), 129.4 (d, ³J_{C-P} = 6.4 Hz; Ph-C^{meta}), 130.0 (s; Ph-C^{para}), 132.4 (d, ²J_{C-P} = 10.0 Hz; Ph-C^{ortho}), 132.8 (s; Ph-C^{ipso}), 134.8 (d, ²J_{C-P} = 10.4 Hz; Ph-

C^{ortho}), 135.9 (d, $^2J_{C-P} = 9.8$ Hz; Ph- C^{ortho}), 136.3 (d, $^1J_{C-P} = 38.2$ Hz; PPh- C^{ipso}), 137.7 (s; C^9), 137.8 (s; C^{19}), 132.8 (s; Ph- C^{ipso}), 139.6 (s; C^5), 139.7 (s; C^{15}), 146.7 (s; C^4/C^{14}), 147.9 (s; C^7), 148.1 (s; C^{17}), 164.4 (d, $^2J_{C-P} = 19.7$ Hz; C^1). $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): $\delta_P = 33.8$ (ABMX pattern, ddd, $^1J_{PA-Rh} = 134.9$ Hz, $^2J_{PA-PC} = 46.3$ Hz, $^2J_{PA-PB} = 346.9$ Hz; P_A), 38.7 (ABMX pattern, ddd, $^1J_{PB-Rh} = 134.9$ Hz, $^2J_{PB-PC} = 46.3$ Hz, $^2J_{PB-PB} = 346.9$ Hz; P_B), 127.0 (dt, $^1J_{PC-Rh} = 334.0$ Hz, $^2J_{PC-PA} = ^2J_{PC-PB} = 46.3$ Hz; P_C). IR (KBr): $\tilde{\nu} = 3054$ [m, $sp^2 \nu(C-H)$], 2960–2867 [st, $sp^3 \nu(C-H)$], 1776 [m, $\nu(C=O)$], 1496–1398 [st, Ar $\nu(C=C)$], 694 [m, $\nu(P-O)$]. ES-MS: m/z (%) = 1201 (100) $[M - Cl]^+$, 939 (22) $[M - Cl - PPh_3]^+$.



Conclusions

The coordination chemistry of a series of Rh(I) and Ru(II) complexes derived from mixed anhydride ligands was studied. Complexes with these ligands spontaneously rearrange in solution via a number of pathways, with the pathway of choice dependent on the mixed anhydride employed, the auxiliary ligands present as well as the nature of the metal centre. Plausible mechanisms for the formation of the observed rearrangement products could be proposed, although more advanced mechanistic studies are required to give more conclusive evidence. Although the propensity of these complexes to rearrange hampers their use in catalysis, the behaviour of these complexes are still of interest from a more fundamental point of view.

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Notes and references

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