Synthesis and Evaluation of the Bonding Properties of a Potentially Tridentate Ligand: 1-(Diphenylphosphino)-2-ethoxy-1-(2-pyridyl)ethane

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The trifunctional ligand 1-(diphenylphosphino)-2-ethoxy-1-(2-pyridyl)ethane (pepye) has been prepared and its bonding properties toward Mo^0, Rh^I and Ru^{II} metallic centres evaluated. The complex *fac*-[$Mo(CO)_3$(pepye)] in which the ligand is *P,N,O* bonded in solution evolves to *cis*-[$Mo(CO)_4$(pepye)] where it is *P,N* bonded. In the complex [Rh(cod)(pepye)]ClO_4 (cod = cycloocta-1,5-diene) the ligand is *P,N* bonded. The cycloocta-1,5-diene can be displaced by carbon monoxide, and [$Rh(CO)_2$(pepye)]ClO_4 and [{Rh(CO)(pepye)}$_2$][ClO_4]$_2$ have been isolated. In the former the ligand is *P,N* bonded and in the latter the two rhodium atoms are bridged by the phosphine and ether functions of each ligand. The complex all-*cis*-[$RuCl_2$(pepye)$_2$] has been isolated in two diastereoisomeric forms in a 6:4 ratio. In polar solvents it evolves to [RuCl(pepye)$_2$]$^+$ in which one of the ligands is *P,N,O* bonded and the two diastereoisomers have been isolated as their tetraphenylborate salts. The bonded ether arm of the ligand can be displaced by carbon monoxide leading to [RuCl(CO)(pepye)$_2$]BPh_4. This reaction can be reversed in boiling acetone, more or less easily, depending upon the diastereoisomers.

The synthesis of polydentate phosphines is always a field of interest as these ligands are expected to exert more control on the co-ordination sphere of a metal with the possible consequence of new catalytic properties for the resulting complexes.[1,2]

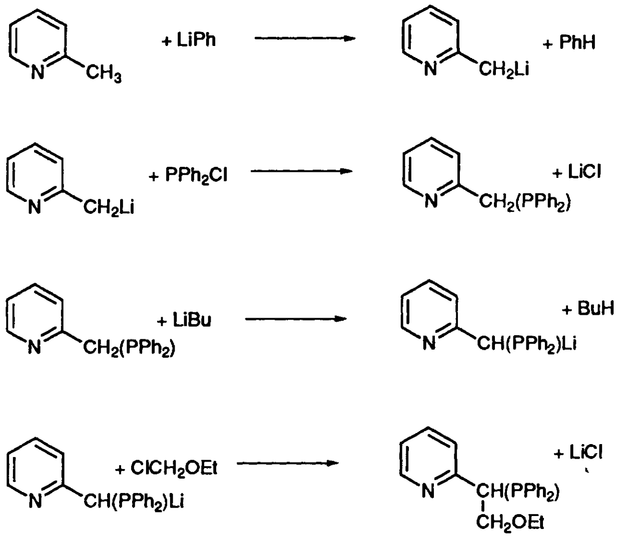
With this goal, new classes of unsymmetrical bidentate ligands were recently developed which associate phosphorus and hard donor atoms such as oxygen[3] or nitrogen.[4] Indeed it was expected, and it has often been observed,[3,4] that the hard end of the ligand is weakly co-ordinated to a soft metallic centre in solution providing, in smooth conditions, a vacant co-ordination site for an entering substrate.

The class of unsymmetrical tridentate ligands has been explored less, but some results concerning tripodal ligands associating phosphorus to oxygen or sulfur donor atoms have been published recently.[5] These studies show that the preferential order of bonding toward various metals in low-oxidation states is, as expected, $P > S \gg O$.

To extend such studies we have sought to develop tridentate ligands associating one phosphorus donor centre to nitrogen and oxygen donor centres. We therefore describe herein the synthesis of 1-(diphenylphosphino)-2-ethoxy-1-(2-pyridyl)ethane (pepye), and the study of its bonding properties toward Mo^0, Rh^I and Ru^{II} metallic centres.

Results and Discussion

Synthesis of 1-(*Diphenylphosphino*)-2-*ethoxy*-1-(2-*pyridyl*)-*ethane* (pepye).—This compound has been synthesised in four steps from 2-methylpyridine according to Scheme 1. In the first step (2-pyridylmethyl)lithium was generated by the action of phenyllithium on 2-methylpyridine in diethyl ether. In the second step, the lithium salt was added slowly to a solution of PPh_2Cl in diethyl ether; the addition must be conducted at −78 °C to avoid the formation of $(Ph_2P)_2CH(C_5H_4N)$.[6] The resulting 2-(diphenylphosphinomethyl)pyridine was purified by high vacuum distillation and isolated in 60% yield as a white solid. This compound has been synthesised previously by the action of $KPPh_2$ with 2-(chloromethyl)pyridine, and described as an oil which could not be purified by distillation.[7] Then, the successive action of butyllithium and chloromethyl ethyl ether, and final purification by crystallisation in methanol led to pepye as a white powder in 60% yield from 2-(diphenylphosphinomethyl)pyridine. The compound is air sensitive both in the solid state and in solution and has been characterised by ^1H and ^{31}P NMR spectroscopies (see Experimental section).



Scheme 1

Reaction of pepye *with* [$Mo(CO)_3(C_7H_8)$].—When a hexane solution of pepye is added to a hexane solution of 1 equivalent of [$Mo(CO)_3(C_7H_8)$] a yellow precipitate **1** quickly appears. The IR spectrum of this compound in dichloromethane solution shows two bands at 1920 and 1807 cm^{-1} in the ν(CO) stretching region, in agreement with a *fac* geometry of a $Mo(CO)_3$ fragment.[8] The ^{31}P-{^1H} NMR spectrum of a freshly prepared solution in $CDCl_3$ shows a resonance at δ 52.8 as a sharp singlet but a new resonance gradually appears at δ 45.6 and finally, the resonance at δ 52.8 totally disappears and the solution turns brown. The new compound **2** has been isolated and shows four bands at 2015, 1910, 1900 and 1852 cm^{-1} in its IR spectrum characteristic of a *cis*-Mo(CO)$_4$ group.[8] Moreover, the IR spectrum is similar to that of *cis*-[Mo(CO)$_4${PPh$_2$CH$_2$-(C$_5$H$_4$N)}] (2018, 1911, 1897, 1850 cm^{-1}).[7]

All these observations are consistent with the initial formation of *fac*-[Mo(CO)$_3$(pepye)] **1** in which pepye is tridentate but this complex is unstable in solution leading to unidentified decomposition products, and *cis*-[Mo(CO)$_4$(pepye)] **2**, in which pepye is bidentate through the P and N atoms (^{1}H NMR spectroscopy shows a doublet at δ 8.79 characteristic of the proton in position 6 of the co-ordinated pyridine ring[9]). Scheme 2 summarises these observations.

We conclude that, as could be predicted, the molybdenum–oxygen bond is labile and this result is very similar to the observations made with 2-(diphenylphosphino)-1-methoxy-2-(phenylthiomethyl)propane for which only *P*,*S*-bonded complexes have been observed with Group 6 metals.[5d]

Reactivity of pepye *toward Rhodium*(I) *Complexes*.—We chose the family of cationic complexes of Rh^I easily obtained from [Rh(cod)(acac)] (cod = cycloocta-1,5-diene, acac = acetylacetonate) as these compounds are good precursors for the synthesis of carbonyl or hydride derivatives.[10]

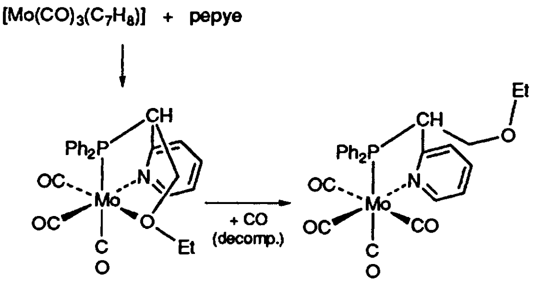
When [Rh(cod)(acac)] is treated in tetrahydrofuran (thf) solution with a slight excess of perchloric acid and then with 1 equivalent of pepye, the complex [Rh(cod)(pepye)]ClO$_4$ **3** is isolated in good yield. Its ^{31}P-{^{1}H} NMR spectrum shows a doublet at δ 47.7 with *J*(Rh–P) 153 Hz. These data are very similar to those found for [Rh(cod){PPh$_2$CH$_2$(C$_5$H$_4$N)}]ClO$_4$ [δ 41.4, *J*(Rh–P) 152 Hz][11] and are consistent with pepye bonding through the P and N atoms. In the ^{1}H NMR spectrum the resonances of the cycloocta-1,5-diene ligand deserve some comment. Indeed, due to the presence of a chiral centre in pepye, the ethylenic resonances are split into three signals of relative intensities 2:1:1, a broad resonance at δ 5.33 for the ethylenic hydrogens *trans* to the phosphorus atom,[12] and two broad resonances at δ 4.08 and 3.71 for the ethylenic hydrogen *trans* to the nitrogen atom.

When a solution of compound **3** is saturated with carbon monoxide, a rapid reaction occurs leading to a new compound [Rh(CO)$_2$(pepye)]ClO$_4$ **4**, which is stable only under a carbon monoxide atmosphere. This compound shows two IR absorptions of the same intensity at 2090 and 2027 cm^{-1}. The ^{1}H NMR spectrum of the crude solution shows the presence of free cycloocta-1,5-diene and of new resonances for the complexed pepye. In the ^{31}P-{^{1}H} NMR spectrum, a doublet is observed at δ 60.8 [*J*(Rh–P) 129.6 Hz].

When the solution is evaporated to dryness the ^{31}P-{^{1}H} NMR spectrum evolves to a broad doublet centred at δ 67 [*J*(Rh–P) 146.7 Hz], and a doublet at δ 47.7 [*J*(Rh–P) 153 Hz] characteristic of complex **3**. The IR spectrum of the solution shows the absorptions characteristic of **4** and a new band at 2005 cm^{-1}.

These first observations show that the system is complicated as there is an equilibrium between complex **3** and other carbonylated complexes, depending on the concentration of carbon monoxide.

After several cycles of carbonylation and decarbonylation under vacuum it was possible to eliminate totally the cycloocta-1,5-diene and to isolate complex [{Rh(CO)(pepye)}$_2$][ClO$_4$]$_2$ **5**, characterised by a ν(CO) absorption at 2005 cm^{-1}. A more convenient method was to separate complex **4** from free cycloocta-1,5-diene by crystallisation and to decarbonylate it in refluxing acetone. Complex **5** is characterised by a doublet at δ 76 [*J*(Rh–P) 176.5 Hz] in its ^{31}P-{H} NMR spectrum. As a tridentate ligand pepye can only accommodate a *fac* geometry and it is therefore difficult to envisage a mononuclear structure for **5**. Pignolet and co-workers[6,13] have shown that carbonylation of the closely related complex [Rh(nbd){(PPh$_2$)$_2$CH-(C$_6$H$_4$N)}]BF$_4$ (nbd = norbornadiene) leads to a binuclear compound [Rh$_2$(CO)$_2${(PPh$_2$)$_2$CH(C$_6$H$_4$N)}$_2$]BF$_4$ in which the two metals are bridged by the two phosphorus atoms of each ligand. Since the IR spectrum of this complex is very similar to that of **5** [ν(CO) at 2002 cm^{-1}] we propose the same type of structure as shown in Scheme 3. Each rhodium is bonded to a carbonyl ligand, the P and N atoms of one pepye ligand and the ether function of the other pepye ligand. This is corroborated by the high value of the *J*(Rh–P) coupling constant which is a characteristic of rhodium(I) complexes where a phosphine is *trans* to an oxygen atom.[14]



1 2

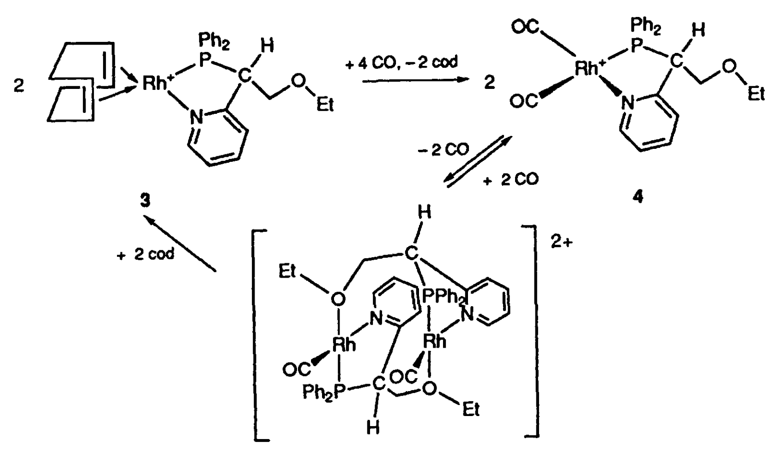
Scheme 2

We have also checked that the addition of cycloocta-1,5-diene to **5** generates complex **3**, and we propose the sequence of reactions shown in Scheme 3 for the action of carbon monoxide on complex **3**.

Complex **3** is inert toward hydrogen at atmospheric pressure but when the reaction is conducted under 10 atm of hydrogen in an NMR tube, the ^{1}H NMR spectrum shows the slow appearance of a triplet of weak intensity at δ −18.04 (*J* 20 Hz), a broad resonance centred at δ −15.5 and the formation of cyclooctane (δ 1.53). The new species formed are unstable and the solution turns brown rapidly and no product can be isolated.

Reactivity of pepye *toward Ruthenium*(II) *Complexes*.—The compound pepye reacts with [RuCl$_2$(PPh$_3$)$_3$] in a 2:1 molar ratio in toluene at room temperature giving, after several hours, a yellow precipitate **6** which analyses as [RuCl$_2$(pepye)$_2$]. The ^{31}P-{^{1}H} NMR shows two sets of two doublets at δ 78.5 and 60.2 [*J*(P–P) 32 Hz] (**6a**) and δ 75.4 and 70.1 [*J*(P–P) 33 Hz] (**6b**) in a 6:4 ratio. The values of the coupling constants show that the two phosphorus atoms are in *cis* position. The IR spectra show two Ru–Cl stretches at 302 and 251 cm^{-1} assigned to terminal chlorines in *cis* positions,[15] and a band at 1596 cm^{-1} attributable to the ring stretching vibration of the co-ordinated pyridyl group.[6] These data are consistent with the two structures shown in Fig. 1. In structure **B** the magnetic non-equivalence of the two phosphines is due to the chirality of the ligand. To investigate this ambiguity we synthesised [RuCl$_2${PPh$_2$CH$_2$(C$_5$H$_4$N)}$_2$],[11] which is characterised by two doublets at δ 62 and 56 [*J*(P–P) 34 Hz] in its ^{31}P-{^{1}H} NMR spectrum and consistent only with structure **A** with an all-*cis* geometry. This result has to be contrasted with the behaviour of the ligand 1-(diphenylphosphino)-2-(2-pyridyl)ethane which leads to *trans*,*cis*,*cis*-RuX$_2$ complexes.[4] This may be the consequence of the lengthening of the methylene chain between phosphorus and the pyridine ring.

From the preceding observations, we can conclude that the two sets of two doublets for **6** are due to the presence of a mixture of diastereoisomers. When these two diastereoisomers are dissolved in dichloromethane–methanol, a rapid change occurs in the ^{31}P-{^{1}H} NMR spectrum: two new sets of doublets {two doublets at δ 93.6 and 59.5 [*J*(P–P) 33 Hz] (**7a**), and two doublets at δ 85.5 and 73.4 [*J*(P–P) 37 Hz] (**7b**)} grow at the expense of the signals of **6**. These two sets are in the same 6:4 intensity ratio as for **6**. Comparison of the ^{31}P data of **6** and



Scheme 3

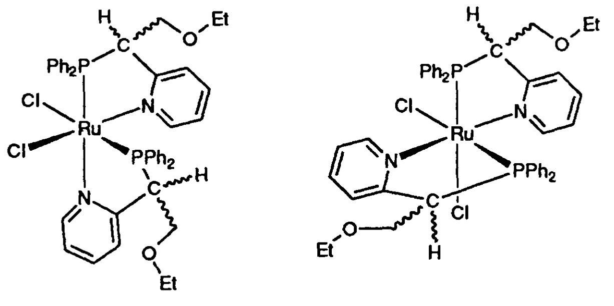
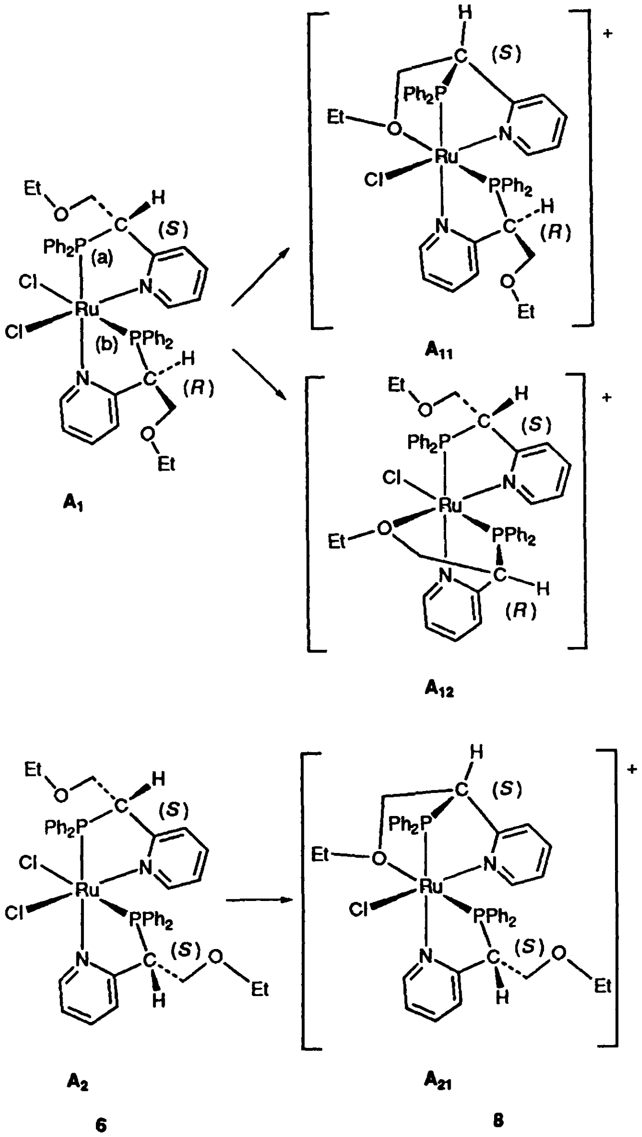


Fig. 1 Two possible structures for complex 6



Scheme 4

7 show that only one of the two resonances of each set of isomers is greatly affected. Moreover, in the two cases, this corresponds to a shift to lower field, consistent with the formation of an additional five-membered ring involving one of the phosphorus centres.[16] These results are in agreement with the formation in a polar solvent of the ionic species [RuCl(pepye-*P,N,O*)(pepye-*P,N*)]Cl in which the ether function of one of the two pepye ligands is co-ordinated. To confirm this hypothesis the exchange of Cl^- by BPh_4^- was effected and this led to the isolation of [RuCl(pepye-*P,N,O*)(pepye-*P,N*)]BPh_4 **8** which presents the same ^{31}P parameters as **7**. The two diastereoisomers **8a** and **8b** can be separated by fractional crystallisation but it was not possible to obtain crystals suitable for crystal structure determination.

Complex **8a** presents a ^1H NMR spectrum fully consistent with the presence of one pepye ligand *P,N,O* co-ordinated and one *P,N* bonded. Indeed two signals characteristic of the proton in position 6 of the co-ordinated pyridine rings are observed at δ 8.63 and 8.32 and the resonance for the hydrogen on the asymmetric carbon are well separated at δ 5.50 and 5.11 for the two pepye ligands. Selective heteronuclear $^1H-\{^{31}P\}$ decoupling experiments have shown that, as expected, the most deshielded resonance is associated with the phosphorus resonance at δ 93.6 and correspond to *P,N,O* bonded pepye. The co-ordination of the ether function is confirmed by the value of the chemical shift difference $\delta(CH_2) - \delta(CH_3)$ which is 3.11 ppm for the co-ordinated ether group and 2.34 ppm for the non-coordinated in accordance with the more electronegative character of the bonded oxygen atom.[17]

For **8b** the results are very similar: the CH resonances are observed at δ 5.69 and 5.06 and the $\delta(CH_2) - \delta(CH_3)$ values are 3.17 and 2.25 ppm respectively.

Considering the possible structures of **8a** and **8b** on the basis of structure **A** for complex **6** shown in Fig. 1, the co-ordination of the ether part of the ligand in **6** is not allowed for all the enantiomers of pepye as illustrated by the two possible diastereoisomers shown in Scheme 4. For instance for the ligand in position (a) only the *S* form allows the co-ordination of the ether function and in position (b) only the *R* form.

On this basis three possible structures for **8a** and **8b** are shown in Scheme 4. Their enantiomers also have to be considered.

To test if the co-ordinated ether was labile or not we treated a solution of **8** with carbon monoxide. A rapid reaction occurred at atmospheric pressure and the new products formed, $[RuCl(CO)(pepye)_2]BPh_4$ **9a** and **9b**, were characterised by two IR absorptions at 2005 and 2000 cm^{-1}. In the $^{31}P-\{^1H\}$ NMR spectrum two sets of two doublets are observed at δ 56.3 and 44.4 [*J*(P–P) 25.5 Hz] (**9a**) and at δ 62.2 and 31.3 [*J*(P–P) 28 Hz] (**9b**), in a 6:4 ratio. If the solution is then refluxed in boiling dichloromethane, the IR spectrum shows a decrease in intensity of the 2000 cm^{-1} absorption and the $^{31}P-\{^1H\}$ NMR spectrum shows a decrease in intensity of the signals due to **9b** and the concomitant appearance of signals for **8b**. If the reflux is conducted in boiling acetone the disappearance of **9b** and the formation of **8b** is observed rapidly, and complex **9a** disappears slowly with the simultaneous formation of **8a**.

These observations show that the co-ordinated ether is easily displaced by carbon monoxide and that this carbonylation is easily reversible for **9b** but occurs under more forcing conditions for **9a**. This reversibility also indicates that these reactions occur without modification of the positions of the other ligands around ruthenium.

The $^{13}C-\{^1H\}$ NMR spectrum of complex **9** reveals some information about the geometry of the carbonyl ligand: one doublet of doublets is observed for each isomer at δ 198.9 (*J* 107.4 and 16 Hz) (**9b**) and at δ 197.1 (*J* 107.9 and 14.7 Hz) (**9a**). These results are consistent for the two isomers with a carbonyl group *trans* to one phosphorus atom and *cis* to the other. Thus if our hypothesis about the conservation of the position of the other ligands is correct, this eliminates structure A_{12} proposed for **8** in Scheme 4 in which the ether ligand is bonded *cis* to the two phosphorus atoms.

Scheme 5 summarises our observations about the reactivity of complex **6**. The two diastereoisomers are a combination of either *R,R* (*S,S*) or *R,S* (*S,R*) configurations of pepye and considering the 6:4 ratio of these two diastereoisomers, the co-ordination of two molecules of pepye to the Ru centre has occurred with a diastereomeric excess of 20%.

In conclusion, this study has shown evidence of the hemilabile character[3] of pepye by its ether arm. It has to be noted that with the similar 1-(diphenylphosphino)-2-(2-pyridyl)ethane complexes of Ru^{II}, the action of carbon monoxide induces the rupture of the Ru–N bond,[4] a reaction which has not been observed in our case due to the greater stability of the five-membered ring formed by the pepye ligand.

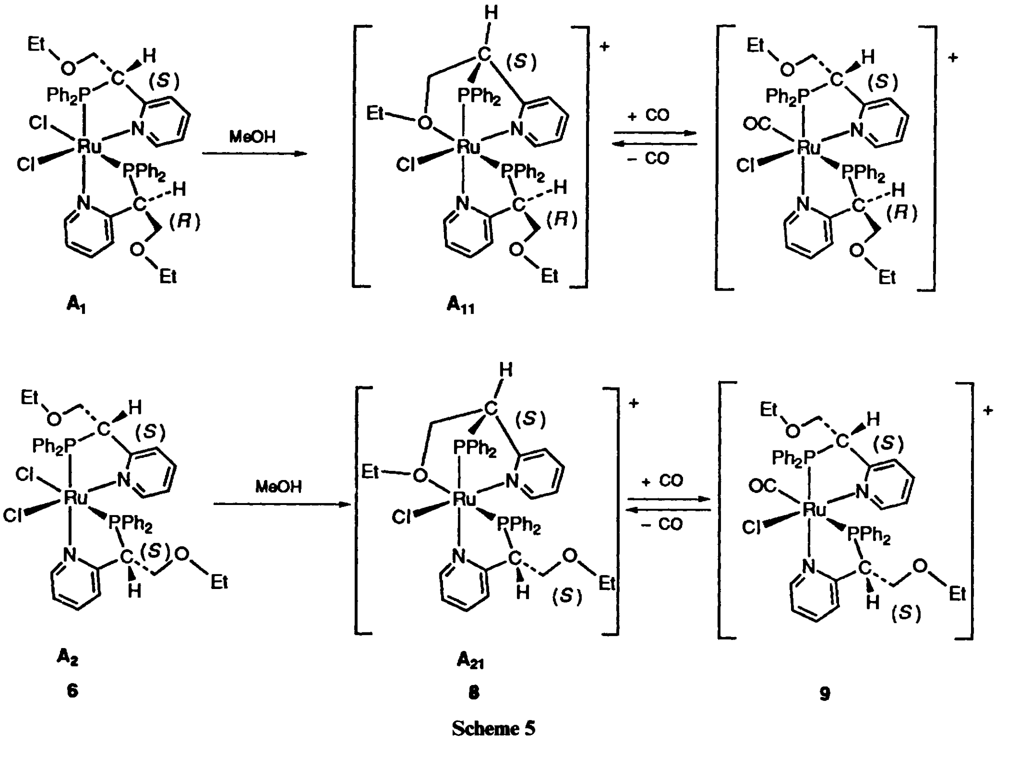
The consequent catalytic activity of these new complexes is currently being investigated.

Experimental

All reactions were performed under a nitrogen atmosphere using standard Schlenk techniques. The IR spectra were recorded on a Perkin-Elmer 225 or 983 spectrometer and NMR spectra on a Bruker AC 80, AC 200 or WM 250 instrument. Integration of ^{31}P NMR signals was carried out in inverse-gated experiments on the WM 250 machine with the smallest sweep width possible and with pulse delay of 15 or 30 s. The variations between the results obtained under the two conditions were less than 5%. Elemental analyses (C, H and N) were performed in this laboratory. The compounds $[Mo(CO)_3(C_7H_8)]$,[18] [Rh(cod)(acac)][19] and $[RuCl_2(PPh_3)_3]$[20] were prepared according to published procedures.

Synthesis of 1-(*Diphenylphosphino*)-2-*ethoxy*-1-(2-*pyridylethane* (pepye).—This compound was synthesised in four steps from 2-methylpyridine.

Preparation of 2-(*diphenylphosphinomethyl*)*pyridine*. To a stirred solution of 2 mol dm^{-3} phenyllithium (25 cm^3, 50 mmol) dissolved in diethyl ether (50 cm^3) was added dropwise at 0 °C, 2-methylpyridine (4.95 cm^3). The solution was transferred to a dropping funnel and added to a solution of PPh_2Cl (11 cm^3, 50 mmol) in diethyl ether (100 cm^3) maintained at −78 °C. To avoid the formation of $(Ph_2P)_2CH(C_5H_4N)$ the addition had to be slow and the temperature maintained at −78 °C. At the end of the addition, the temperature of the solution was increased slowly to room temperature and the solution then stirred for 1 h. After elimination of the solvents under vacuum the residue was distilled under vacuum [b.p. 192 °C (10^{-1} mm Hg)] giving 8.31 g of 2-(diphenylphosphinomethyl)pyridine as a white solid (60% yield). ^1H NMR ($CDCl_3$): δ 8.00–7.30 (14 H, $C_6H_5 + C_5H_4N$), 3.66 (s, 2 H).



Scheme 5

Synthesis of pepye. To a solution of 2-(diphenylphosphinomethyl)pyridine (8.31 g, 30 mmol) dissolved in diethyl ether (30 cm^3) was added at 0 °C, 1.6 mol dm^{-3} LiBu (18.75 cm^3, 30 mmol). The solution was stirred for 2 h at the same temperature, then chloromethyl ethyl ether (2.80 cm^3) was added at 0 °C. The solution was washed with water (3 x 30 cm^3) and dried on magnesium sulfate. It was then evaporated to dryness and the residue crystallised from methanol giving 6.03 g (60%) of pepye as white crystals. In all the following ^{1}H NMR data the protons on the alkyl chain of the pepye ligand have been denoted by Ph$_2$PC(H$_a$)(C$_5$H$_4$N)C(H$_b$)(H$_c$)OC(H$_d$)(H$_e$)C(H$_f$)$_3$. NMR (CDCl$_3$): ^{1}H, δ 8.52 (m, 1 H, C$_5$H$_4$N), 7.68–6.36 (m, 13 H, C$_6$H$_5$ + C$_5$H$_4$N), 4.03 (m, H$_b$, CH–C*H*$_2$OEt), 4.02 (s, H$_a$, C*H*-CH$_2$OEt), 3.70 (m, H$_c$, CH–C*H*$_2$OEt), 3.37 [dq, *J*(H$_d$–H$_e$) 9.6, *J*(H$_d$–H$_f$) 7, H$_d$, CH–CH$_2$OC*H*$_2$CH$_3$], 3.25 [dq, *J*(H$_d$–H$_e$) 9.6, *J*(H$_d$–H$_f$) 7, H$_e$, CH–CH$_2$OC*H*$_2$CH$_3$], 0.99 [t, *J*(H$_d$–H$_f$) = *J*(H$_e$–H$_f$) 7 Hz, 3 H$_f$, CH–CH$_2$OCH$_2$C*H*$_3$]; ^{31}P-{^{1}H}, δ −7.6 (Found: C, 75.45; H, 6.40; N, 4.95. Calc. for C$_{21}$H$_{22}$NOP: C, 75.20; H, 6.60; N, 4.20%).

Synthesis of fac-[Mo(CO)$_3$(pepye)] **1**.—To a stirred solution of [Mo(CO)$_3$(C$_7$H$_8$)] (0.735 mmol) in hexane (10 cm^3) was added pepye (0.246 g, 0.735 mmol) dissolved in hexane (10 cm^3). The solution was stirred for 2 h and a yellow precipitate appeared. The solution was filtered and the precipitate was washed with a small amount of hexane and dried under vacuum giving 0.2 g of a yellow powder (52% yield). IR (CH$_2$Cl$_2$) ν(CO): 1920s, 1807s cm^{-1}; ^{31}P-{^{1}H} NMR (CDCl$_3$): δ 52.8 (Found: C, 55.65; H, 4.50; N, 2.95. Calc. for C$_{24}$H$_{22}$MoNO$_4$P: C, 55.95; H, 4.30; N, 2.70%).

Synthesis of cis-[Mo(CO)$_4$(pepye)] **2**.—Compound **1** (0.3 g) dissolved in dichloromethane (5 cm^3) was stirred for 24 h. Filtration of the solution through Celite, addition of hexane and cooling to −20 °C led to 0.14 g of **2** as yellow crystals (44% based on pepye). IR (CH$_2$Cl$_2$) ν(CO): 2015w, 1910s, 1900s, 1852s cm^{-1}; ^{1}H NMR (C$_6$D$_6$): δ 8.79 (m, 1 H, C$_5$H$_4$N), 7.91–6.78 (m, 13 H, C$_6$H$_5$ + C$_5$H$_4$N), 4.16 [*J*(H$_b$–H$_c$) 3.9, *J*(H$_a$–H$_b$) 9.5, *J*(P–H$_b$) 10, H$_b$, CH–C*H*$_2$OEt], 3.64 [*J*(P–H$_a$) 3.9, *J*(H$_a$–H$_b$) = *J*(H$_a$–H$_c$) 9.5 Hz. H$_a$, C*H*–CH$_2$OEt], 3.36 [*J*(H$_b$–H$_c$) 3.9, *J*(H$_a$–H$_c$) 9.5, *J*(P–H$_c$) 5 Hz, H$_c$, CH–C*H*$_2$OEt], 2.82 [*J*(H$_d$–H$_e$) 10, *J*(H$_d$–H$_f$) 7, H$_d$, CH–CH$_2$OC*H*$_2$CH$_3$], 2.72 [*J*(H$_d$–H$_e$) 10, *J*(H$_e$–H$_f$) 7, H$_e$, CH–CH$_2$OC*H*$_2$CH$_3$], 0.75 [*J*(H$_d$–H$_f$) = *J*(H$_e$–H$_f$) 7 Hz, 3 H$_f$, CH–CH$_2$OCH$_2$C*H*$_3$]; ^{31}P-{^{1}H} NMR (CDCl$_3$): δ 45.6 (Found: C, 55.25; H, 4.10; N, 2.45. Calc. for C$_{25}$H$_{22}$MoNO$_5$P: C, 55.25; H, 4.10; N, 2.60%).

Synthesis of [Rh(cod)(pepye)]ClO$_4$ **3**.—This compound was synthesised according to the method of Thewissen *et al.*[21] To [Rh(cod)(acac)] (0.3 g, 1 mmol) dissolved in thf (3.5 cm^3) was added HClO$_4$ (0.99 mmol). After 15 min of stirring, pepye (0.315 g, 0.94 mmol) dissolved in thf (6 cm^3) was added and the solution stirred for 2 h. The solution was then evaporated to dryness and the residue was dissolved in acetone. Adding diethyl ether induced the precipitation of 0.48 g of **3** as yellow crystals (80%). ^{1}H NMR (CD$_2$Cl$_2$): δ 8.19 (m, 1 H, C$_5$H$_4$N), 7.99–7.43 (m, 13 H, C$_6$H$_5$ + C$_5$H$_4$N), 5.33 (m, 2 H, cod), 4.64 [*J*(P–H$_a$) 12, *J*(H$_a$–H$_b$) 4.4, *J*(H$_a$–H$_c$) 6.6, H$_a$, C*H*–CH$_2$OEt], 4.08 (m, 1 H, cod), 3.94 [*J*(H$_b$–H$_c$) 10.1, *J*(H$_a$–H$_b$) 4.4, *J*(P–H$_b$) 10, H$_b$, CH–C*H*$_2$OEt], 3.88 [*J*(H$_b$–H$_c$) 10.1, *J*(H$_c$–H$_a$) 6.6, *J*(P–H$_c$) 6.5, H$_c$, CH–C*H*$_2$OEt], 3.71 (m, 1 H, cod), 3.50 (m, 2 H, CH–CH$_2$OC*H*$_2$CH$_3$), 2.57 (m, 4 H, cod), 2.34 (m, 4 H, cod), 1.15 [t, *J*(H$_d$–H$_f$) = *J*(H$_e$–H$_f$) 7 Hz, 3 H, CH–CH$_2$OCH$_2$C*H*$_3$]; ^{31}P-{^{1}H} NMR (CDCl$_3$): δ 47.7 [d, *J*(Rh–P) 153 Hz] (Found: C, 53.75; H, 5.20; N, 2.05. Calc. for C$_{29}$H$_{34}$ClNO$_5$PRh: C, 53.95; H, 5.30; N, 2.15%).

Synthesis of [Rh(CO)$_2$(pepye)]ClO$_4$ **4**.—Carbon monoxide was bubbled for 30 min through a solution of **3** (0.25 g) in dichloromethane (10 cm^3). Addition of hexane (10 cm^3) saturated with carbon monoxide induced the crystallisation of 0.18 g of **4** as yellow crystals (80%). IR (CH$_2$Cl$_2$) ν(CO): 2090s, 2027s cm^{-1}; ^{1}H NMR [(CD$_3$)$_2$CO]: δ 8.98 (m, 1 H, C$_5$H$_4$N), 8.28–7.57 (m, 13 H, C$_6$H$_5$ + C$_5$H$_4$N), 5.33 [*J*(P–H$_a$) 14.9, *J*(H$_a$–H$_b$) = *J*(H$_a$–H$_c$) 3.5, H$_a$, C*H*–CH$_2$OEt], 3.83 [*J*(H$_b$–H$_c$) 10, *J*(H$_a$–H$_b$) 3.5, *J*(P–H$_b$) 19.9, H$_b$, CH–C*H*$_2$OEt], 3.57 [*J*(H$_b$–H$_c$) 10, *J*(H$_a$–H$_c$) 3.5, *J*(P–H$_c$) 7.8, H$_c$, CH–C*H*$_2$OEt], 3.29 (q, *J* 7, 2 H, CH–CH$_2$OC*H*$_2$CH$_3$), 1.14 (t, *J* 7 Hz, 3 H, CH–CH$_2$OCH$_2$C*H*$_3$); ^{31}P-{^{1}H} NMR (CDCl$_3$): δ 60.8 [d, *J*(Rh–P) 129.6 Hz] (Found: C, 46.70; H, 3.85; N, 2.10. Calc. for C$_{23}$H$_{22}$ClNO$_7$PRh: C, 46.55; H, 3.75; N, 2.35%)

Synthesis of [{Rh(CO)(pepye)}$_2$][ClO$_4$]$_2$ **5**.—A solution of compound **4** (0.15 g) dissolved in acetone (10 cm^3) was refluxed for 1 h. The solvent was evaporated to dryness and recrystallisation of the residue from dichloromethane–hexane led to 0.1 g of **5** as yellow crystals (70%). Bubbling CO through a solution of **5** immediately regenerated **4**; IR (CH$_2$Cl$_2$) ν(CO): 2005 cm^{-1}; ^{1}H NMR [(CD$_3$)$_2$CO]: δ 8.45 (m, 1 H, C$_5$H$_4$N), 8.20–7.55 (m, 13 H, C$_6$H$_5$ + C$_5$H$_4$N), 5.07 [*J*(P–H$_a$) 13.6, *J*(H$_a$–H$_b$) = *J*(H$_a$–H$_b$) 5, H$_a$, C*H*–CH$_2$OEt], 3.78 [*J*(H$_b$–H$_c$) 9.4, *J*(H$_a$–H$_b$) 5, *J*(P–H$_b$) 14.2, H$_b$, CH–C*H*$_2$OEt], 3.72 [*J*(H$_b$–H$_c$) 9.4, *J*(H$_a$–H$_c$) 5, *J*(P–H$_c$) 8.8, H$_c$, CH–C*H*$_2$OEt], 3.25 [*J*(H$_d$–H$_e$) 9.3, *J*(H$_d$–H$_f$) 7, H$_d$, CH–CH$_2$OC*H*$_2$CH$_3$], 3.12 [*J*(H$_d$–H$_e$) 9.3, *J*(H$_e$–H$_f$) 7, H$_e$, CH–CH$_2$OC*H*$_2$CH$_3$], 0.97 [*J*(H$_d$–H$_f$) = *J*(H$_e$–H$_f$) 7 Hz, 3 H$_f$, CH–CH$_2$OCH$_2$C*H*$_3$]; ^{31}P-{^{1}H} NMR (CDCl$_3$): δ 76.0 [d, *J*(Rh–P) 176.5 Hz] (Found: C, 46.50; H, 3.80; N, 2.65. Calc. for C$_{22}$H$_{22}$ClNO$_6$PRh: C, 46.70; H, 3.90; N, 2.50%).

Synthesis of [RuCl$_2$(pepye)$_2$] **6**.—To a stirred solution of [RuCl$_2$(PPh$_3$)$_3$] (0.5 g, 0.521 mmol) in toluene (10 cm^3) was added pepye (0.350 g, 1.042 mmol) dissolved in toluene (10 cm^3). The resulting solution was stirred for 14 h during which time it turned yellow. The solution was then evaporated to dryness. The residue was dissolved in toluene (3 cm^3) and the complex precipitated by adding hexane (6 cm^3); the procedure was repeated three times to eliminate free triphenylphosphine. The precipitate was then dissolved in dichloromethane and hexane was added to induce crystallisation. A mixture of **6a** and **6b** (0.35 g, 85%) was recovered as a yellow powder; ^{31}P-{^{1}H} NMR (CDCl$_3$): δ 78.5 [d, *J*(P–P) 32], 60.2 [d, *J*(P–P) 32] **6a**; 75.4 [d, *J*(P–P) 33], 70.1 [d, *J*(P–P) 33 Hz] **6b** (Found: C, 59.50; H, 6.05; Cl, 8.80; N, 3.15; P, 7.40; Ru, 12.10. Calc. for C$_{42}$H$_{44}$Cl$_2$N$_2$O$_2$P$_2$Ru: C, 59.85; H, 5.25; Cl, 8.40; N, 3.30; P, 7.35; Ru, 12.00%).

Synthesis of [RuCl(pepye)$_2$]BPh$_4$ **8**.—To a stirred solution of compound **6** (0.35 g, 0.415 mmol) in dichloromethane (10 cm^3) was added NaBPh$_4$ (0.142 g, 0.415 mmol) dissolved in methanol (10 cm^3). A yellow precipitate immediately appeared which was separated from the solution. This precipitate was recrystallised from acetone–methanol at −20 °C giving 0.095 g (20%) of **8a** as yellow crystals. The dichloromethane–methanol solution was evaporated to dryness and the residue dissolved in acetone. Cooling to −20 °C induced the crystallisation of 0.07 g (15%) of **8b** as yellow crystals.

For **8a**, ^{1}H NMR [(CD$_3$)$_2$CO]: δ 8.63 (m, 1 H, C$_5$H$_4$N), 8.32 (m, 1 H, C$_5$H$_4$N), 7.97–6.13 (m, 46 H, C$_6$H$_5$ + C$_5$H$_4$N), 5.50 [*J*(P–H$_a$) 18.5, *J*(H$_a$–H$_b$) 8.5, *J*(H$_a$–H$_c$) 2, H$_a$, (*P,N,O*), C*H*–CH$_2$OEt], 5.11 [*J*(P–H$_a$) 10.9, *J*(H$_a$–H$_b$) 2, *J*(H$_a$–H$_c$) 1, H$_a$, (*P,N*), C*H*–CH$_2$OEt], 4.81 [*J*(H$_b$–H$_c$) 10.9, *J*(H$_a$–H$_b$) 8.6, *J*(P–H$_b$) 2, H$_b$, (*P,N,O*), CH–C*H*$_2$OEt], 4.47 [m, 2 H, (*P,N,O*), CH–CH$_2$OC*H*$_2$CH$_3$], 4.24 [*J*(H$_b$–H$_c$) 8.6, *J*(H$_a$–H$_b$) 1, *J*(P–H$_b$) 23.6, H$_b$, (*P,N*), CH–C*H*$_2$OEt], 4.04 [*J*(H$_b$–H$_c$) 10.9, *J*(H$_a$–H$_c$) 2, *J*(P–H$_c$) 11, H$_c$, (*P,N,O*) CH–C*H*$_2$OEt], 3.84 [*J*(H$_b$–H$_c$) 8.6, *J*(H$_a$–H$_c$) 2, *J*(P–H$_c$) 4.5, H$_c$, (*P,N*), CH–C*H*$_2$OEt], 3.56 [*J*(H$_d$–H$_e$) 9.5, *J*(H$_d$–H$_f$) 7, H$_d$, (*P,N*), CH–CH$_2$OC*H*$_2$CH$_3$], 3.12 [*J*(H$_d$–H$_e$) 10, *J*(H$_d$–H$_f$) 7, H$_d$, (*P,N*), CH–CH$_2$OC*H*$_2$CH$_3$], 1.36 [*J*(H$_d$–H$_f$) = *J*(H$_e$–H$_f$) 7, 3 H$_f$, (*P,N,O*), CH–CH$_2$OCH$_2$C*H*$_3$], 1.18 [*J*(H$_d$–H$_f$) = *J*(H$_e$–H$_f$) 7 Hz, 3 H$_f$, (*P,N*), CH–CH$_2$OCH$_2$C*H*$_3$]; ^{31}P-{^{1}H} NMR (CDCl$_3$): δ 93.6

[d, *J*(P–P) 33], 59.5 [d, *J*(P–P) 33 Hz] (Found: C, 70.35; H, 5.95; N, 2.65. Calc. for $C_{66}H_{64}BClN_2O_2P_2Ru$: C, 70.35; H, 5.75; N, 2.50%).

For **8b**, ^{1}H NMR [$(CD_3)_2CO$]: δ 8.80 (m, 1 H, C_5H_4N), 8.04 (m, 1 H, C_5H_4N), 8.00–5.89 (m, 46 H, C_6H_5 + C_5H_4N), 5.69 [*J*(P–H$_a$) 13.5, *J*(H$_a$–H$_b$) 3, *J*(H$_a$–H$_c$) 6.5, H$_a$, (*P,N,O*), C*H*–CH$_2$OEt], 5.06 [*J*(P–H$_a$) 11.9, H$_a$, (*P,N*), C*H*–CH$_2$OEt], 4.35 [*J*(H$_b$–H$_c$) 9.5, *J*(P–H$_b$) 4.3, H$_b$, (*P,N*), CH–C*H*$_2$OEt], 4.06 [*J*(H$_b$–H$_c$) 9.5, H$_c$, (*P,N*), CH–C*H*$_2$OEt], 3.95 [*J*(H$_d$–H$_e$) 2, *J*(H$_d$–H$_f$) 7, H$_d$, (*P,N,O*), CH–CH$_2$OC*H*$_2$CH$_3$], 3.89 [*J*(H$_d$–H$_e$) 2, *J*(H$_e$–H$_f$) 7, H$_e$, (*P,N,O*), CH–CH$_2$OC*H*$_2$CH$_3$], 3.54 [*J*(H$_b$–H$_c$) 10.5, *J*(H$_a$–H$_b$) 3, H$_b$, (*P,N,O*), CH–C*H*$_2$OEt], 3.47 [*J*(H$_b$–H$_c$) 10.5, *J*(H$_a$–H$_c$) 6.5, *J*(P–H$_c$) 3, H$_c$, (*P,N,O*) CH–C*H*$_2$OEt], 3.37 [*J*(H$_d$–H$_e$) 2.3, *J*(H$_d$–H$_f$) 7, H$_d$, (*P,N*), CH–C*H*$_2$OEt], 3.34 [*J*(H$_d$–H$_e$) 2.3, *J*(H$_e$–H$_f$) 7, H$_f$, (*P,N*), CH–CH$_2$OC*H*$_2$CH$_3$], 1.10 [*J*(H$_d$–H$_f$) = *J*(H$_e$–H$_f$) 7, 3 H$_f$, (*P,N*), CH–CH$_2$OCH$_2$C*H*$_3$], 0.75 [*J*(H$_d$–H$_f$) = *J*(H$_e$–H$_f$) 7 Hz, 3 H$_f$, (*P,N,O*), CH–CH$_2$OCH$_2$C*H*$_3$]; ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 85.5 [d, *J*(P–P) 37], 73.4 [d, *J*(P–P) 37] (Found: C, 70.10; H, 5.65; N, 2.60. Calc. for $C_{66}H_{64}BClN_2O_2P_2Ru$: C, 70.35; H, 5.75; N, 2.50%).

Synthesis of [RuCl(CO)(pepye)$_2$]BPh$_4$ **9**.—Carbon monoxide was bubbled for 30 min through a solution of compound **8** in dichloromethane (10 cm^3). The compounds **9a** and **9b** were not isolated. For **9a**, IR (CH_2Cl_2) ν(CO): 2005 cm^{-1}; ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 56.3 [d, *J*(P–P) 25.5], 44.4 [d, *J*(P–P) 25.5 Hz]; ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 197.1 [dd, *J*(P–C) 14.7, 107.9 Hz].

For **9b**, IR (CH_2Cl_2) ν(CO): 2000 cm^{-1}; ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 62.2 [d, *J*(P–P) 28], 31.3 [d, *J*(P–P) 28 Hz]; ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 198.9 [dd, *J*(P–C) 16, 107.4 Hz].

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