Reactions of Wilkinson's Catalyst with Pyridine; Observation of Rhodium Complexes containing both Pyridine and Phosphine Ligands†

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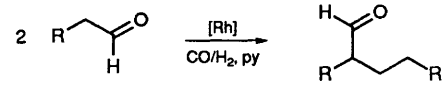
Dissolution of $[RhCl(PPh_3)_3]$, Wilkinson's catalyst, in pyridine affords an efficient catalyst for the selective reductive coupling of aldehydes. The reaction requires a close balance of the hydrogenating power and alkyl coupling ability of the catalyst. The species present in the pyridine solution of Wilkinson's catalyst have been studied in order to probe the origin of this selectivity. Pyridine has been found to replace one or more of the phosphine ligands in the precursor complex to give complexes of the type $[RhCl(py)_x(PPh_3)_{3-x}]$ (py = pyridine, $x = 1$ or 2) and $[Rh(py)_x(PPh_3)_{4-x}]Cl$ ($x = 1$, 2 or 3). The reactions of these complexes with hydrogen have been shown to give *cis*-dihydride complexes *via* oxidative addition. The complex *trans*-$[Rh(CO)(py)(PPh_3)_2]ClO_4$ has been synthesised and characterised spectroscopically and found not to react with H_2 at room temperature. Preliminary *in situ* NMR measurements have shown that under the conditions of the catalysis either phosphine or pyridine can be replaced by a CO ligand. This results in a marked decrease in the activity of the rhodium centre towards oxidative addition of hydrogen and in the stability, with respect to elimination of H_2, of the dihydride.

Nitrogen-donor ligands and solvents are commonly used in catalytic reactions.[1] However, the chemistry taking place between the N donor and the metal centre is often poorly understood. Several new aldehyde coupling reactions catalysed by cobalt[2] or rhodium complexes[3,4] have recently been described. In the presence of rhodium-based systems and in pyridine (py) as solvent, C_n enolisable aldehydes undergo reductive dimerisation to C_{2n} saturated monoaldehydes as shown in Scheme 1. Such selective aldol-type reactions are of great interest for the synthesis of intermediates for the pharmaceutical and perfume industries.

The nature of the solvent and the composition of the syngas have a profound effect on the selectivity of these reactions; nitrogen-base solvents are essential to obtain high yields of the dimer aldehyde and the ratio of $CO:H_2$ in the syngas is also crucial in the selectivity of the reaction. These observations, amongst others, led us[3] to propose that the solvent–syngas combination was essential in fine tuning the stereoelectronic properties of the active species, particularly by adjusting the relative reactivities of the enolate **A** and aldolate **B** intermediates in the catalytic cycle, Scheme 2.

Despite the frequent use of nitrogen bases as solvents/promoters in catalysis and the good ligating properties of pyridine, there are few reports in the literature describing the species present in pyridine solutions of rhodium–phosphine complexes,[5–7] although Werner and co-workers[8,9] have recently reported rhodium–pyridine complexes containing PPr^i_3. As summarised above, we believe that rhodium species containing PPh_3 and pyridine determine the activity and selectivity in the reductive dimerisation of aldehydes and have therefore begun a study to characterise the species present in the catalytic reaction solution.

† *Non-SI unit employed:* atm = 101 325 Pa.



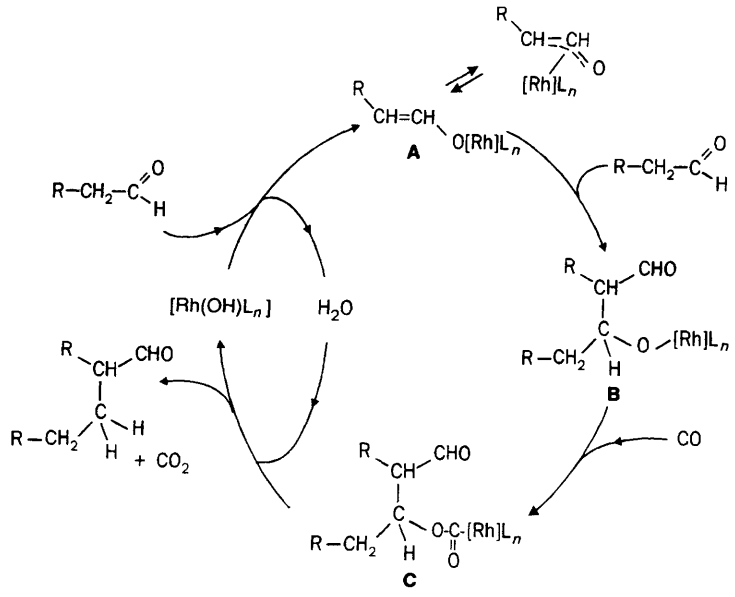
Scheme 1 Schematic reaction of the dimerisation of enolisable aldehydes catalysed by rhodium complexes; R = allyl or aryl

Experimental

The *ex situ* NMR measurements were performed on Bruker WM200B, WM250 or AMX 400 spectrometers using commercial probes. The ^{15}N-$\{^1H\}$ NMR data were obtained on the AMX 400 instrument using the INEPTRD (insensitive nuclei enhanced by polarisation transfer refocussed and decoupled) pulse sequence.[10] All spectra were recorded at −30 °C unless otherwise stated. The *in situ* NMR measurements were performed on a Bruker WM200 WB spectrometer using the high-pressure, high-resolution probes we have described elsewhere.[11,12] All solutions were prepared under a nitrogen atmosphere using standard Schlenk-line techniques and transferred to the NMR cell under nitrogen. Chemical shifts are quoted relative to $SiMe_4$ (^1H and ^{13}C), $MeNO_2$ (^{15}N) or 85% H_3PO_4 in D_2O (^{31}P). Solvents for NMR studies were distilled under N_2 after reflux over CaH_2 ($CDCl_2$ and CH_2Cl_2) or $Mg(OMe)_2$ (MeOH); both C_5H_5N and C_5D_5N were used as received after deaeration.

The complexes $[RhCl(PPh_3)_3]$,[5] $[Rh_2Cl_2(PPh_3)_4]$,[5] $[Rh_2Cl_2(C_2H_4)_4]$,[13] *trans*-$[Rh(CO)(OClO_3)(PPh_3)_2]$[14] and $[RhClH_2(py)(PPh_3)_2]$[5] were prepared by literature methods.

Preparation of the Complexes.—*cis*-$[RhCl(py)(PPh_3)_2]$ **1**. Pyridine (6.4 μl, 0.079 mmol) was added to a solution of $[Rh_2Cl_2(PPh_3)_4]$ (50 mg, 0.038 mmol) in CH_2Cl_2–CD_2Cl_2 (1:1, 2 cm^3) to give an orange solution of **1**. Red crystals of **1** could be obtained by dissolving $[Rh_2Cl_2(PPh_3)_4]$ (200 mg, 0.151 mmol) in pyridine (5 cm^3), adding diethyl ether (5 cm^3) and layering the solution with light petroleum (b.p. range



Scheme 2 Proposed catalytic cycle for the aldehyde coupling reactions

40–60 °C) (Found: C, 66.50; H, 4.75; N, 1.90. Calc. for $C_{41}H_{35}ClNP_2Rh$: C, 66.35; H, 4.75; N, 1.90%).

trans- and cis-[RhCl(py)$_2$(PPh$_3$)] **2** *and* **3**. The complex [$Rh_2Cl_2(C_2H_4)_4$] (100 mg, 0.26 mmol) and PPh_3 (120 mg, 0.46 mmol) were dissolved in pyridine (2 cm^3) to give a red solution. The species present were found to be stable only in pyridine solution and *trans*- and *cis*-[RhCl(py)$_2$(PPh$_3$)] (20 and 80% respectively) were characterised by NMR spectroscopy, Table 1.

[Rh(py)(PPh$_3$)$_3$]Cl **4**. Pyridine (8 μl, 0.1 mmol) was added to a solution of [RhCl(PPh$_3$)$_3$] (50 mg, 0.054 mmol) and PPh_3 (45 mg, 0.17 mmol) in CH_2Cl_2–CD_2Cl_2–MeOH (1:1:2; 2 cm^3) to give a solution of **4** which was characterised by NMR spectroscopy, Table 1.

cis-[Rh(py)$_2$(PPh$_3$)$_2$]Cl **5**. Pyridine (102 μl, 1.26 mmol) was added to a solution of [$Rh_2Cl_2(PPh_3)_4$] (400 mg, 0.3 mmol) in CH_2Cl_2–CD_2Cl_2–MeOH (1:1:2; 2 cm^3) to give a yellow solution of **5** which was characterised by NMR spectroscopy, Table 1.

[Rh(py)$_3$(PPh$_3$)]ClO_4 **6**. The salt $AgClO_4$ (100 mg, 0.48 mmol) was added to a solution of [$Rh_2Cl_2(C_2H_4)_4$] (100 mg, 0.25 mmol) and PPh_3 (120 mg, 0.46 mmol) in pyridine (2 cm^3) to give a green solution. The species present was found to be stable only in pyridine solution and was characterised by NMR spectroscopy, Table 1.

[RhH$_2$(py)$_2$(PPh$_3$)$_2$]Cl **8**. Hydrogen was bubbled through a solution of compound **5** at 18 °C for 15 min giving a pale yellow solution of **8** which was characterised by NMR spectroscopy, Table 1.

[RhH$_2$Cl(py)$_2$(PPh$_3$)] **9**. Hydrogen gas was bubbled through a [$^2H_5$]pyridine solution of compounds **2** and **3** at 18 °C for 15 min. Attempts to isolate **9** were unsuccessful as it converts to **3** on standing or on dilution of the pyridine solvent. Complex **9** was characterised by NMR spectroscopy, Table 1.

trans-[Rh(CO)(py)(PPh$_3$)$_2$]ClO_4 **10**. Pyridine (10.7 μl, 0.133 mmol) was added to a solution of [Rh(CO)(PPh$_3$)$_2$($OClO_3$)] (100 mg, 0.132 mmol) in CH_2Cl_2–CD_2Cl_2 (1:1, 1 cm^3) to give a yellow solution. Addition of light petroleum (b.p. 40–60 °C) gave a yellow precipitate of **10** (Found: C, 59.65; H, 4.55; N, 1.65. Calc. for $C_{42}H_{35}ClNO_5P_2Rh$: C, 60.50; H, 4.25; N, 1.70%).

Results and Discussion

Reactions of Rhodium–Phosphine Complexes with Pyridine.—Three new phosphine-containing rhodium complexes (**1**, **4** and **5**) have been identified on dissolution of Wilkinson's catalyst, [RhCl(PPh$_3$)$_3$], in pyridine by ^{31}P NMR spectroscopy (Fig. 1 and Table 1). Complex **1** is also formed, in near quantitative yield, on addition of two equivalents of pyridine to [Rh_2Cl_2-(PPh_3)$_4$] in dichloromethane solution. Thus, Fig. 2(*a*) shows a doublet of doublets due to the presence of two, inequivalent phosphine ligands in compound **1**. The nature of the other ligands within the co-ordination sphere of rhodium can be determined from ^{15}N-{^1H} INEPT measurements [Fig. 2(*b*)] which show the presence of a doublet of doublet of doublets due to coupling of the nitrogen to rhodium and two inequivalent phosphine ligands, Table 1. The co-ordination around the rhodium is then completed by a chloride ligand, hence compound **1** is *cis*-[RhCl(py)(PPh$_3$)$_2$].

In some samples, the cluster of peaks around δ 30 in Fig. 1 contained, in addition to the resonances due to Wilkinson's catalyst, traces of an additional doublet of doublets due to **4** which is obtained in near quantitative yield on addition of two equivalents of pyridine to a solution of [RhCl(PPh$_3$)$_3$] and PPh_3 in dichloromethane–methanol (1:1). This solvent system

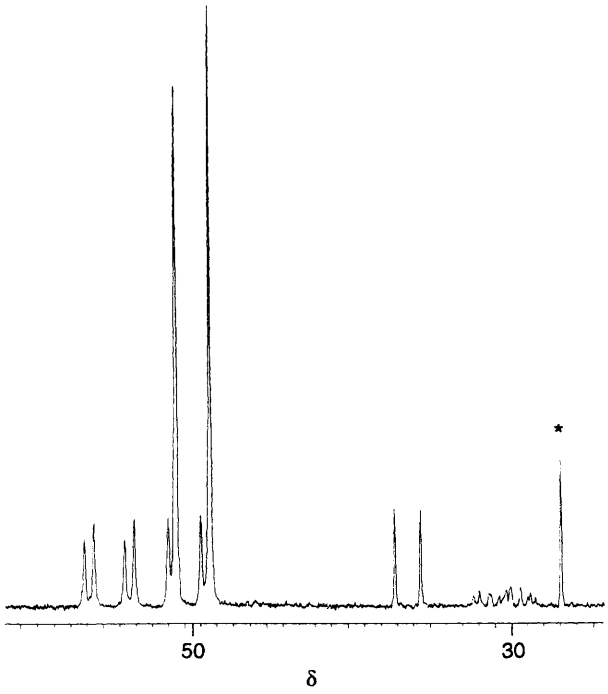


Fig. 1 Reaction of $[RhCl(PPh_3)_3]$ with pyridine; ^{31}P-$\{^1H\}$ NMR spectrum. * = PPh_3O

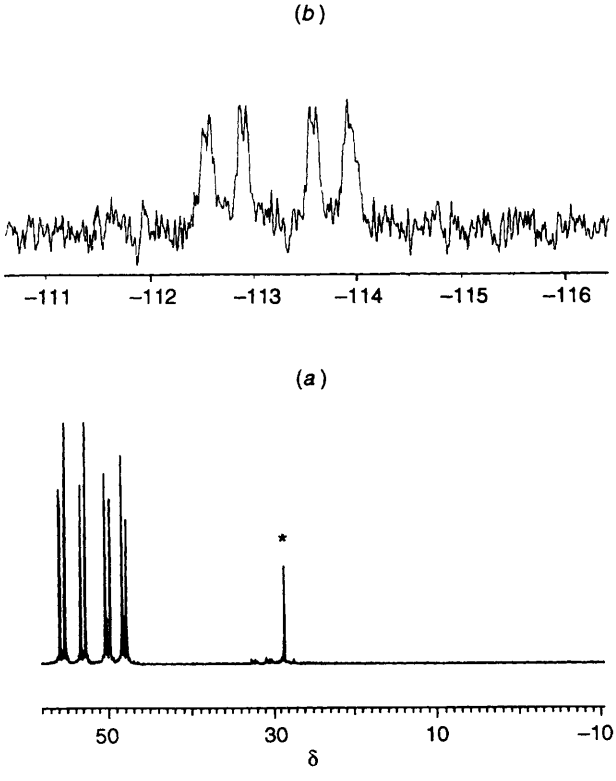


Fig. 2 Reaction of $[Rh_2Cl_2(PPh_3)_4]$ in dichloromethane with two equivalents of pyridine; (*a*) ^{31}P-$\{^1H\}$ NMR spectrum, (*b*) ^{15}N-$\{^1H\}$ INEPTRD NMR spectrum. * = PPh_3O

is known to favour ionisation of the halide ligand. A doublet of triplets at δ *ca.* 44 is now clearly visible in the ^{31}P NMR spectrum together with a doublet of doublets at δ 30.3, Fig. 3(*a*), indicating the presence of a $Rh(PPh_3)_3$ T-shaped fragment. The ^{15}N-$\{^1H\}$ INEPT NMR spectrum [Fig. 3(*b*)] reveals a poorly resolved doublet of doublet of triplets confirming that **4** is $[Rh(py)(PPh_3)_3]Cl$.

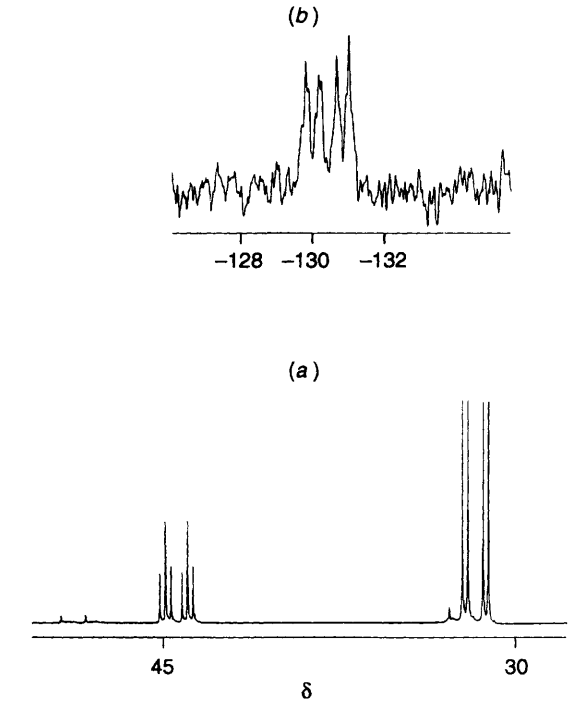


Fig. 3 Reaction of $[RhCl(PPh_3)_3]$ in dichloromethane–methanol (1:1) with two equivalents of pyridine; (*a*) ^{31}P-$\{^1H\}$ NMR spectrum, (*b*) ^{15}N-$\{^1H\}$ INEPTRD NMR spectrum

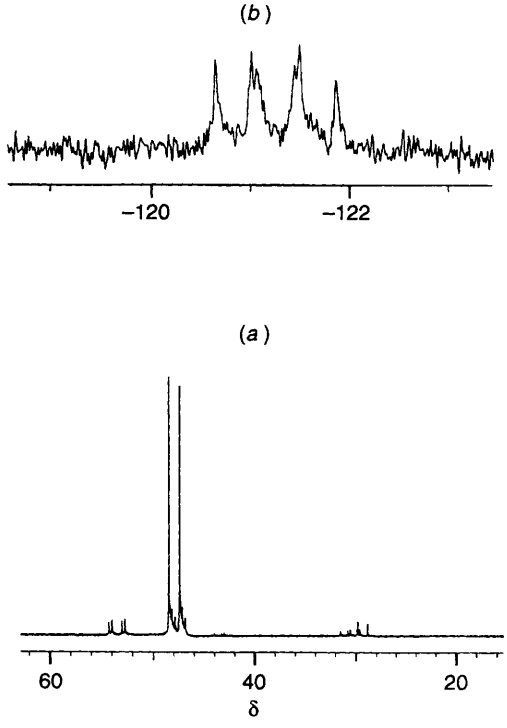


Fig. 4 Reaction of $[Rh_2Cl_2(PPh_3)_4]$ in dichloromethane–methanol (1:1) with four equivalents of pyridine; (*a*) ^{31}P-$\{^1H\}$ NMR spectrum, (*b*) ^{15}N-$\{^1H\}$ INEPTRD NMR spectrum

The ^{31}P NMR spectrum of compound **5** [Fig. 4(*a*)] consists of a doublet due to coupling to rhodium and is not particularly informative. However, we have been able to obtain near pure solutions of **5** by the addition of four equivalents of pyridine to $[Rh_2Cl_2(PPh_3)_4]$ in dichloromethane–methanol (1:1). The structure of **5** is confirmed by the ^{15}N-$\{^1H\}$ INEPT spectrum, Fig. 4(*b*), which shows a deceptively simple doublet of doublet of doublets for this second-order spin system and is thus identified as *cis*-$[Rh(py)_2(PPh_3)_2]Cl$.

Table 1 The NMR data for the complexes[a]

Compound	δ(P)	δ(N)	δ(H)	^1J(Rh–P)	^2J(P–P)	^1J(Rh–N)	^2J(*trans*-P–N)	^2J(*cis*-P–N)	^1J(Rh–H)	^2J(P–H)	^2J(H–H)
1 *cis*-[RhCl(py)$(PPh_3)_2$]	54.3 (dd)	−113.3 (ddd)		202	48	15	42	2.5			
	49.0 (dd)			163							
2 *trans*-[RhCl$(py)_2(PPh_3)$]	50.8 (d)			208							
3 *cis*-[RhCl$(py)_2(PPh_3)$]	51.8 (d)			162							
4 [Rh(py)$(PPh_3)_3$]Cl	43.6 (dt)	−130.6 (ddt)		161	40	14	35	< 3			
	30.3 (dd)			146							
5 *cis*-[Rh$(py)_2(PPh_3)_2$]Cl	48.0 (d)	−121.2 (ddd)		168	48	28	42	7			
6 [Rh$(py)_3(PPh_3)$]ClO_4	49.3 (d)			172							
7 [$RhH_2Cl(py)(PPh_3)_2$]	46.7 (d)		−16.8 (ddt)	118					13	13	13
			−17.8 (ddt)						25	11	13
8 [$RhH_2(py)_2(PPh_3)_2$]Cl	47.0 (d)		−17.5 (dt)	116					16	16	16
9 [$RhH_2Cl(py)_2(PPh_3)$]	61.4 (d)		−17.2 (m br)	150							
			−18.0 (m br)								
10 *trans*-[Rh(CO)(py)$(PPh_3)_2$]ClO_4[b]	31.5 (d)	−135.1 (d)		129		16					
X[c]	36.2 (d)			128							
Y[c]	35.7 (d)			96							
Z[c]	23.9 (m)										

[a] Coupling constants in Hz. [b] δ(C) 190.2 (dt), ^1J(Rh–C) 68, ^2J(Rh–P) 16 Hz. [c] See text.

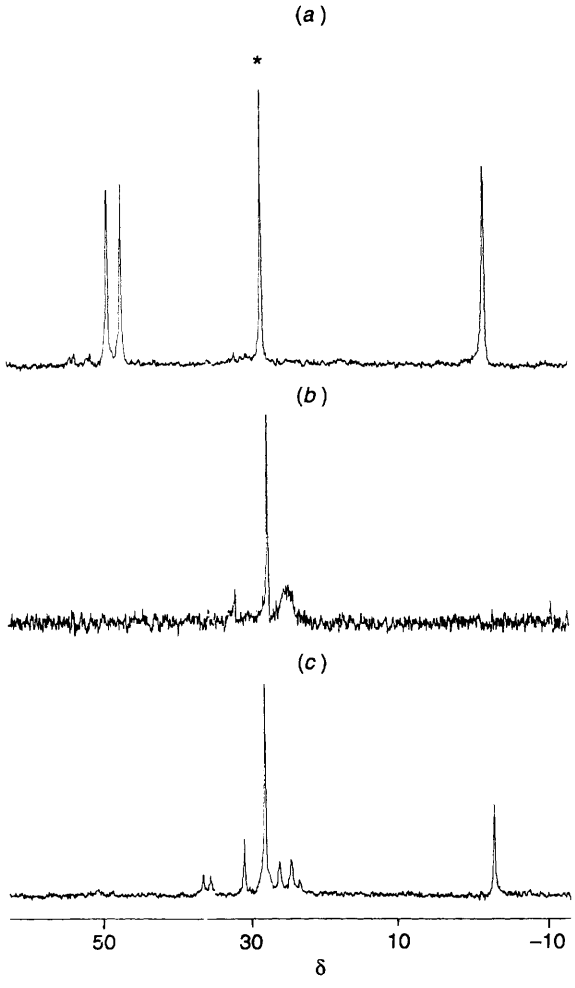


Fig. 5 The *in situ* ^{31}P NMR spectra of the catalytic reaction: (*a*) under N_2 at 253 K; (*b*) under 117 atm $CO–H_2$ (9:2) at 385 K after 16 h; (*c*) after cooling (*b*) to 253 K. * = PPh_3O

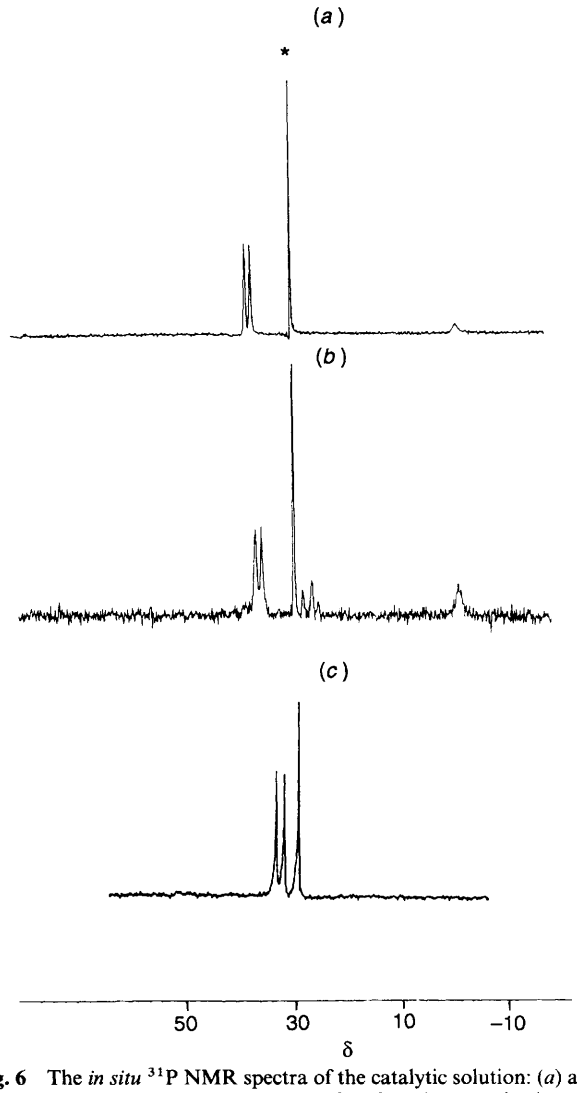


Fig. 6 The *in situ* ^{31}P NMR spectra of the catalytic solution: (*a*) after reaction with CO (47 atm, 375 K); (*b*) after depressurisation and reaction with H_2 (47 atm, 365 K); (*c*) as (*b*) after removal from the *in situ* NMR cell. Both (*a*) and (*b*) recorded at 253 K, (*c*) at 233 K. * = PPh_3O

The species responsible for the doublet around δ 36 in Fig. 1, **X**, is present in varying amounts between preparations and has not been identified conclusively. The value of ^1J(Rh–P), 128 Hz, is not inconsistent with phosphorus *trans* to phosphorus but, as shown by the variation of ^1J(Rh–P) in compounds **4**, **8** and **10**, it is necessary to know both the nature of the other ligands co-ordinated to rhodium and the oxidation state of rhodium to be confident in using ^1J(Rh–P) in assigning structure. Compound **X** has been shown not to be a rhodium–pyridine–monophosphine complex.

Dissolution of $[Rh_2Cl_2(C_2H_4)_4]$ and PPh_3 in pyridine affords a mixture of *trans*- and *cis*-$[RhCl(py)_2(PPh_3)]$ **2** and **3**, Table 1. The geometric isomerism in **2** and **3** can be determined from the ^1J(Rh–P) coupling constants. In compound **2** this is 208 Hz, a value typical for P *trans* to chlorine whilst in **3** the value, 162 Hz, is in the range typical of P *trans* to nitrogen. Complexes **2** and **3** are only stable in pyridine solution and this has precluded the determination of the ^{15}N-$\{^1H\}$ INEPT NMR spectrum which would have allowed the conclusive demonstration of the structures of these complexes. The cationic monophosphine complex $[Rh(py)_3(PPh_3)]ClO_4$ **6**, homologous with **4** and **5**, has been prepared by the addition of $AgClO_4$ to a solution of $[Rh_2Cl_2(C_2H_4)_4]$ and PPh_3 in pyridine and characterised by NMR spectroscopy, Table 1. The spectroscopic data for compounds **2**, **3** and **6** differ from those of **X** and thus it seems unlikely that **X** is a monophosphine species.

Reactions of Rhodium–Pyridine–Phosphine Complexes with H_2.—A low-resolution ^1H NMR spectrum of the complex formed on reaction of $[RhCl(PPh_3)_3]$ in pyridine with hydrogen has previously been reported[5] and suggests the formation of $[RhH_2Cl(py)(PPh_3)_2]$ **7**. This has been confirmed by high-resolution ^1H and ^{31}P NMR measurements at low temperature on the products of reaction of **1** with hydrogen, Table 1.

When H_2 is bubbled through a pyridine solution containing a mixture of **2** and **3** only complex **3** reacts to give $[RhH_2Cl(py)_2(PPh_3)]$ **9**. It has not proved possible to isolate **9**, however, its structure can be deduced from the ^1H and ^{31}P NMR spectra, Table 1. The value of ^1J(Rh–P), 150 Hz, is in the range typical for phosphorus *trans* to nitrogen; two metal–hydride resonances are seen in the ^1H NMR spectrum indicating inequivalent hydrides, presumably *trans* to nitrogen and *trans* to chlorine since the ^{31}P NMR spectrum reveals a single phosphorus site in the molecule. Therefore, complex **9** most probably has the structure shown. It is surprising that the geometric isomerism of the two complexes should have such a marked effect on the reactivity of **2** and **3** in the oxidative addition of hydrogen, however, this difference emphasises the importance of the ligand shell in modulating the activity/selectivity in organometallic catalysis.

Complex **5** in pyridine reacts with H_2, as described in the Experimental section, to give $[RhH_2(py)_2(PPh_3)_2]Cl$ **8**, which contains equivalent hydrides and equivalent triphenylphosphines, Table 1.

Reaction of trans-[Rh(CO)($OClO_3$)(PPh_3)$_2$] *with Pyridine*.—The reaction of *trans*-[Rh(CO)($OClO_3$)(PPh_3)$_2$] with one equivalent of pyridine in dichloromethane solution affords *trans*-[Rh(CO)(py)(PPh_3)$_2$]ClO_4 **10**, characterised by ^{31}P, ^{13}C and ^{15}N NMR measurements, Table 1, and by elemental analysis. This cationic complex was found not to react with H_2 under the conditions used in the previous experiments again illustrating that relatively small changes in the ligand shell can markedly affect the reactivity of the rhodium centre.

in situ *Spectroscopic Studies*.—The ^{31}P NMR spectra of the catalytic reaction mixture before and after reaction for 16 h at 385 K of 117 atm of syngas (CO–H_2, 9:2) and then quenching under the reaction gases to 235 K, are shown in Fig. 5. Before reaction the predominant species present in the solution are the cation of *cis*-[Rh(py)$_2$(PPh_3)$_2$]Cl **5**, PPh_3O and PPh_3 [Fig. 5(*a*)]. After the catalytic reaction, *cis*-[Rh(py)$_2$(PPh_3)$_2$]$^+$ is no longer present and two new groups of resonances attributed to rhodium–phosphine complexes can be seen [Fig. 5(*c*)]. The downfield doublet [δ(P) 35.7, ^1J(Rh–P) 96 Hz] can be assigned to a carbonyl complex, **Y**, on the basis of the rhodium–phosphorus coupling constant and the observation of a similar doublet in the ^{31}P NMR spectrum, Fig. 6(*a*), of the catalytic reaction solution (measured at 253 K) after pressurisation with CO (47 atm) and heating to 375 K. However the values of both δ(P) and ^1J(Rh–P) reveal this not to be the cation of **10**. The upfield resonances [δ(P) 23.9] are thought to be due to a hydride complex, **Z**, related to **Y**. Thus addition of H_2 (47 atm) to the NMR cell containing a solution of **Y** also gives **Z**, Fig. 6(*b*). Species **Z** is unstable in the absence of H_2, the ^{31}P NMR spectrum indicating conversion of **Z** to a new, possibly carbonyl-containing complex when the solution is removed from the *in situ* NMR cell, Fig. 6(*c*). The nature of these species is currently under investigation using *in situ* high-pressure Fourier-transform infrared and high-pressure NMR spectroscopies.

Conclusion

This study has resulted in the identification of 12 new rhodium-(I) and -(III)–phosphine–pyridine complexes: the structures of nine of these have been unambiguously determined by NMR measurements. The reactivity of the rhodium(I) complexes towards the oxidative addition of hydrogen is shown to be moderated by small changes to the ligand sphere around the rhodium; this may be important in modulating the selectivity of these catalysts in the reductive coupling of aldehydes. It has recently been reported that the addition of nitrogen bases, *e.g.* hydrazine, to rhodium–triphenylphosphine systems significantly improves the catalytic efficiency in certain hydrogenation reactions[1] and we have developed an extensive new chemistry of rhodium–hydrazine complexes.[15] Taken in conjunction with these results and our continuing studies it seems likely that rhodium complexes containing nitrogen- and phosphorus-donor ligands will be found to be ubiquitous in catalytic systems.

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