FULL PAPER

An alternative strategy to an electron rich phosphine based carbonylation catalyst †

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The complexes [Rh(CO)Cl(2-Ph$_2$PC$_6$H$_4$COOMe)], **1**, and *trans*-[Rh(CO)Cl(2-Ph$_2$PC$_6$H$_4$COOMe)$_2$], **2**, have been synthesized by the reaction of the dimer [Rh(CO)$_2$Cl]$_2$ with 2 and 4 molar equivalents of 2-(diphenylphosphino)-methyl benzoate. The complexes **1** and **2** show terminal ν(CO) bands at 1979 and 1949 cm^{-1} respectively indicating high electron density at the metal centre. The molecular structure of the complex **2** has been determined by single crystal X-ray diffraction. The rhodium atom is in a square planar coordination environment with the two phosphorus atoms *trans* to each other; the ester carbonyl oxygen atom of the two phosphine ligands points towards the rhodium centre above and below the vacant axial sites of the planar complex. The rhodium–oxygen distances (Rh ··· O(49) 3.18 Å; Rh ··· O(19) 3.08 Å) and the angle O(19) ··· Rh ··· O(49) 179° indicate long range intramolecular secondary Rh ··· O interactions leading to a pseudo-hexacoordinated complex. The complexes **1** and **2** undergo oxidative addition (OA) reactions with CH$_3$I to produce acyl complexes [Rh(COCH$_3$)ClI(2-Ph$_2$PC$_6$H$_4$COOMe)], **4**, and *trans*-[Rh(COCH$_3$)ClI(2-Ph$_2$PC$_6$H$_4$COO-Me)(2-Ph$_2$PC$_6$H$_4$COOMe)], **5**, and the kinetics of the reactions reveal that the complex **1** undergoes faster OA reaction than that of the complex **2**. The catalytic activity of the complexes **1** and **2** in the carbonylation of methanol were higher than that of the well known species [Rh(CO)$_2$I$_2$]$^-$ and the complex **1** shows higher activity than **2**.

Introduction

Carbonylation of methanol to ethanoic acid by Monsanto's species, [Rh(CO)$_2$I$_2$]$^-$, is one of the most successful applications of homogeneous catalysis in industry.[1–2] Considerable effort has been devoted to improve the catalyst by incorporating different ligands[3–11] in the metal complex species. In particular, hemi-labile phosphines[8–11] are of special interest because of their multifunctional behaviour, which is believed to stabilize the species through chelate formation. OA reactions are very important in respect of catalysis particularly of complexes containing tertiary phosphines functionalized with other donor groups. Because of the electronic and steric effects, such ligand can play important roles in catalysis.[12] In general, it is known that the tendency of a metal complex to undergo oxidative addition reaction increases by (i) increasing the donor capacity of the ligand *i.e.* by increasing the electron density on the central metal atom, which increases the nucleophilicity; and (ii) decreasing the bulkiness of the ligand. We have examined one ligand, 2-(diphenylphosphino)methyl benzoate, where the tertiary phosphine is functionalized with an electron with-drawing –COMe group, which should reduce the donor capacity of phosphorus and consequently reduce the electron density on the central metal of the complex. However, in our present study, we have found surprisingly high electron density on the rhodium centre of [Rh(CO)Cl(2-Ph$_2$PC$_6$H$_4$COOMe)], **1**, and [Rh(CO)Cl(2-Ph$_2$PC$_6$H$_4$COOMe)$_2$], **2**, which leads to higher catalytic activity towards the carbonylation reaction of methanol. Here we also report the OA reaction of CH$_3$I with the complexes **1** and **2** and their kinetic behaviour.

Results and discussion

The reaction of the chloro-bridged dimer [Rh(CO)$_2$Cl]$_2$ in CH$_2$Cl$_2$ with two molar equivalents of 2-(diphenylphosphino)-methyl benzoate, (2-Ph$_2$PC$_6$H$_4$COOMe), ligand proceeds rapidly with the evolution of CO gas to yield the yellow chelated monocarbonyl complex **1**. The complex **1** shows a single terminal ν(CO) band at 1979 cm^{-1}, which is the characteristic region for such a rhodium(I)–carbonyl complex and is at significantly lower frequency compared to the analogous rhodium hemilabile phosphine complexes (Table 1).[13–22] This low ν(CO) value suggests a high electron density on the rhodium centre. The ester carbonyl group of the complex **1** shows the ν(COO) band at 1638 cm^{-1}, which is about 80 cm^{-1} lower than the free ligand value (1717 cm^{-1}) indicating chelation.[23,24] The complex **1** shows a characteristic ^{31}P-{^{1}H} spectrum with a doublet at δ 45.1 (d, $^1J_{Rh–P}$ 162 Hz) and ^{1}H NMR spectra with phenylic multiplet δ 7.1–8.2 (m, 14 H, Ph) and methyl singlet δ 4.1 (s, 3 H, –COOCH$_3$). Thus, the ^{31}P-{^{1}H} NMR spectrum shows a downfield shift of about 48 ppm from that of the free ligand value (δ −3.2 ppm) indicating coordination through the phosphorus donor. On the other hand, when the dimer [Rh(CO)$_2$Cl]$_2$ in CH$_2$Cl$_2$ is allowed to react with 4 molar equivalents of 2-Ph$_2$PC$_6$H$_4$COOMe) ligand, a pale yellow complex **2** is obtained. The complex **2** surprisingly shows the terminal ν(CO) band at 1949 cm^{-1}, which is significantly lower in frequency compared to analogous rhodium hemilabile phosphine complexes (Table 1) and also than that of the well known complex *trans*-[Rh(CO)Cl(PPh$_3$)$_2$] (ν(CO) = 1964 cm^{-1}).[25] This low ν(CO) value of the complex **2** is attributable to the formation of two Rh ··· O secondary bonds (Fig. 1) by which the ester oxygen atoms donate electron density at the metal centre, which in turn donates electron density to the antibonding π* orbital of CO and consequently lowers the bond order of CO. Complex **2** shows characteristic NMR

Table 1 Comparison of $v(CO)$ of the complexes [Rh(CO)Cl(P∩X)] and [Rh(CO)Cl(P~X)$_2$] for different hemilabile phosphine ligands

[Rh(CO)Cl(P∩X)]			[Rh(CO)Cl(P~X)$_2$]		
PX (X = O, S, N)			PX (X = O, S, N)		
PX	$v(CO)$/cm$^{-1\,a}$	Ref.	PX	$v(CO)$/cm$^{-1\,a}$	Ref.
Ph$_2$P(CH$_2$)$_2$SMe	1990	13	(C$_6$H$_{11}$)$_2$PCH$_2$CH$_2$OMe	1953	19
Ph$_2$P(CH$_2$)$_2$SEt	1985	14	Ph$_2$PCH$_2$SPh	1957	15
Ph$_2$P(CH$_2$)$_2$SPh	2000^b	15	Ph$_2$P(CH$_2$)$_2$SPh	1964	15
2-Ph$_2$PC$_6$H$_4$SMe	1998^d	8	2-Ph$_2$PC$_6$H$_4$CHO	1971	20
Ph$_2$P(CH$_2$)$_2$OEt	1990^b	16	Bu^t$_2$PCH$_2$C(O)Ph	1951^c	21
Ph$_2$PCH$_2$P(S)Ph$_2$	1992^b	9	Ph$_2$P(3-C$_5$H$_4$N)	1982	22
Ph$_2$PCH$_2$P(O)Ph$_2$	1985	10	2-Ph$_2$PC$_6$H$_4$COOMe	**1949**	This work
Ph$_2$P(CH$_2$)$_2$P(O)Ph$_2$	1995	10	4-Ph$_2$PC$_6$H$_4$COOMe	**1977**	This work
Ph$_2$P(CH$_2$)$_2$P(O)(OPh)$_2$	1990^b	16			
Ph$_2$P(CH$_2$)$_2$P(O)(OiPr)$_2$	1990^b	16			
2-Ph$_2$PC$_6$H$_4$N(Me)$_2$	2005	17			
Ph$_2$P(CH$_2$)$_2$C$_5$H$_4$N	1990	18			
2-Ph$_2$PC$_6$H$_4$COOMe	**1979**	This work			

^{a} In KBr, unless otherwise stated. ^{b} In CH$_2$Cl$_2$. ^{c} In Nujol. ^{d} Medium not mentioned.
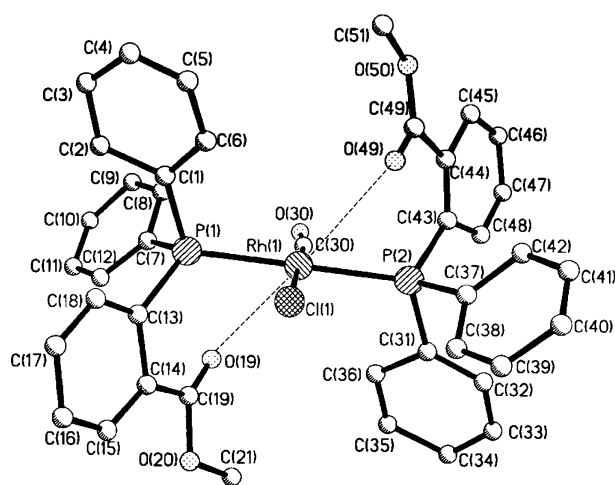
Fig. 1 Molecular structure of the complex **2** showing atomic labeling.

spectra [26,27]: ^{31}P-{^{1}H} NMR spectrum with a doublet at δ 35.9 (d, $^1J_{Rh–P}$ 136 Hz) and ^{1}H NMR with phenylic multiplet δ 7.1–8.3 (m, 14 H, Ph) and methyl singlet δ 3.7 (s, 3 H, –COOCH$_3$). Similar to complex **1**, the complex **2** shows a ^{31}P-{^{1}H} NMR spectrum with a downfield shift of about 39 ppm from that of the free ligand (δ −3.2 ppm) indicating coordination through the phosphorus donor. In order to ascertain the influence of the position of the substituted COOCH$_3$ on the phenylic ring of the triphenylphosphine ligand, we have also prepared the complex *trans*-[RhCOCl(4-Ph$_2$PC$_6$H$_4$COOMe)$_2$], **3**, which shows the terminal $v(CO)$ band at 1977 cm^{-1} and the ester $v(COO)$ band at 1717 cm^{-1} indicating non-formation of the secondary bond. Thus, the $v(CO)$ absorption of the complexes **2** and **3** clearly indicate that in the former complex the metal centre is much richer in electron density and hence expected to show higher nucleophilicity. Miller and Shaw [12] demonstrated that OA reaction of the complex *trans*-[IrClCO{PMe$_2$(2-MeOC$_6$H$_4$)}$_2$] with CH$_3$I is much faster (100-fold) compared to those complexes containing *para* or unsubstituted phosphine ligands. The higher activity is attributed to the electron donation from the methoxy oxygen by forming an Ir ⋯ O bond and thereby increasing the nucleophilicity of Ir and thus resulting in a lower activation energy for the OA reactions. Recently, Cole-Hamilton *et al.*[4] reported a few electron rich complexes of the type [Rh(CO)X(PEt$_3$)$_2$] (X = Cl, Br, I) having $v(CO)$ *ca.* 1960 cm^{-1}, which showed high catalytic activity in carbonylation of methanol, and postulated that electron rich centres play a significant role in improving the rate of the reaction.

Table 2 Crystal data and structure refinement details for complex **2**

Formula	C$_{41}$H$_{34}$ClO$_5$P$_2$Rh
Formula weight	806.98
Temperature/K	293(2)
Crystal system	Triclinic
Space group	$P1$
Z	1
a/Å	9.2330(18)
b/Å	9.5526(18)
c/Å	11.657(2)
α/°	109.932(3)
β/°	108.346(3)
γ/°	96.835(4)
μ(Mo-Kα)/mm^{-1}	0.692
Reflections collected	4406
Independent reflections [R(int)]	3566 [0.0618]
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.0476, 0.0963

The thermal stability of the complex **2** in CD$_2$Cl$_2$/D-toluene in the temperature range + 80 to −80 °C was studied by ^{31}P NMR spectroscopy. The ^{31}P NMR spectrum of the complex **2** shows a doublet at δ 35.9 ppm and the coupling constant is $^1J_{Rh–P}$ = 136.5 Hz (CD$_2$Cl$_2$) at 30 °C, which marginally lowers to $^1J_{Rh–P}$ = 131.5 Hz at 60 °C and on further lowering the temperature, the broadening is observed. With the increase of temperature to +80 °C, there is no remarkable change in the peak position and coupling constant value ($^1J_{Rh–P}$ = 138.5 Hz (D-toluene)). Thus, it indicates that the complex **2** remains stable in solution in the temperature range + 80 to −60 °C.

Single crystal X-ray structure

Some suitable crystals of the complex **2** were grown by slow diffusion of diethylether into a CH$_2$Cl$_2$ solution of the complex. The crystal structure was determined by single-crystal X-ray diffraction studies. The crystal data are given in Table 2. A perspective view of the complex molecule and numbering scheme are shown in Fig. 1. Selected bond lengths and bond angles are listed in Table 3. The rhodium atom lies in an approximately square planar environment formed by the two phosphorus donors, Rh, C (of CO) and Cl atoms. The ester carbonyl oxygen atom of the two phosphine ligands points towards the rhodium centre above and below the vacant axial sites of the planar complex. The observed rhodium–oxygen distances (Rh ⋯ O(49) 3.18 Å; Rh ⋯ O(19) 3.08 Å) and the angle O(19) ⋯ Rh ⋯ O(49) 179° indicate a long range intramolecular secondary Rh ⋯ O interactions leading to a pseudo-hexacoordinated complex. A similar type of long range interaction was earlier reported [28] for a palladium

Table 3 Selected bond lengths (Å) and angles (°) for complex **2**

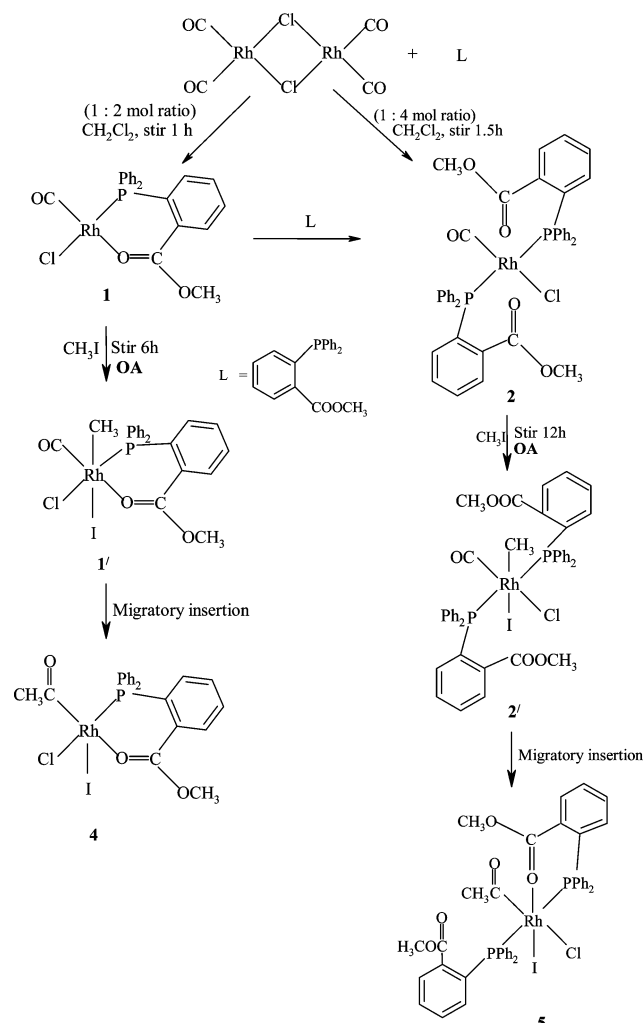|			
Rh(1)–C(30)	1.8690(11)	Rh(1)–P(2)	2.331(5)
Rh(1)–P(1)	2.327(5)	Rh(1)–Cl(1)	2.4084(11)
Rh(1)–O(19)	3.080 (12)	C(19)–O(19)	1.19(3)
Rh(1)–O(49)	3.184 (12)	C(49)–O(49)	1.18(2)
C(30)–O(30)	1.0989(11)		
C(30)–Rh(1)–P(1)	91.6(7)	C(30)–Rh(1)–P(2)	88.8(7)
P(1)–Rh(1)–P(2)	179.2(3)	C(30)–Rh(1)–Cl(1)	174.8(6)
P(1)–Rh(1)–Cl(1)	87.30(19)	P(2)–Rh(1)–Cl(1)	92.34(19)
O(30)–C(30)–Rh(1)	156(2)	C(1)–P(1)–Rh(1)	108.8(6)
C(7)–P(1)–Rh(1)	122.2(6)	C(31)–P(2)–Rh(1)	111.9(6)
C(13)–P(1)–Rh(1)	114.5(6)	C(37)–P(2)–Rh(1)	122.7(6)
C(43)–P(2)–Rh(1)	112.4(7)		

complex of 2-diphenylphosphino anisole where the Pd ⋯ O distance was 3.17 Å. Another long range interaction for the complex *trans*-[IrCOCl(PMe₂(2-MeOC₆H₄)₂] where an Ir ⋯ O secondary bond with the methoxy oxygen was reported.[12]

CCDC reference number 189598.

See http://www.rsc.org/suppdata/dt/b3/b301674a/ for crystallographic data in CIF or other electronic format.

OA reactions and their kinetics

The OA reactions of the complexes **1** and **2** with excess CH₃I yield complexes [Rh(COCH₃)ClI(2-Ph₂PC₆H₄COOMe)], **4**, and *trans*-[Rh(COCH₃)ClI(2-Ph₂PC₆H₄COO-Me)(2-Ph₂PC₆H₄-COOMe)], **5**, respectively through their corresponding unisolable alkylrhodium(III) intermediates **1′** and **2′** (Scheme 1). The ³¹P-{¹H} NMR spectrum of the complex **4** shows a doublet

centred at δ 47.0 with ¹J_{Rh–P} 172 Hz and ¹H NMR spectrum with δ 7.0–8.1 (m, 14H, Ph); 4.2 (s, 3H, COOCH₃) and 2.3 (s, 3H, COCH₃). Thus, the ³¹P-{¹H} NMR spectrum in the oxidized product shows a downfield shift by about 2 ppm compared to the parent complex **1**, which agree with previous observations.[29] The complex **5** shows a ³¹P-{¹H} NMR spectrum as doublets centred at δ 46.1 (d, ¹J_{Rh–P} 162 Hz); δ 39.5 (d, ¹J_{Rh–P} 150 Hz); ¹H NMR δ 7.1–8.3 (m, 14H, Ph), 4.0 (s, 3H, COOCH₃ chelated), 3.8 (s, 3H, COOCH₃) and 2.3 (s, 3H, COCH₃). Thus, the ³¹P-{¹H} NMR spectra in the oxidized product show a downfield shift compared to the parent complex **2**.

A kinetic study for the OA reaction of CH₃I with the complexes **1** and **2** was carried out in order to understand the steric and electronic effect of the ligand. Fig. 2a shows a plot of absorbance against time for the disappearance of the terminal *v*(CO) band of the complex **1** (1979 cm⁻¹) and formation of a new terminal *v*(CO) band at around 2061 cm⁻¹, which is a characteristic band[30,31] for Rh(III) complex **1′** (Scheme 1) along with acyl *v*(CO) band at around 1677 cm⁻¹ for the complex **4** (Scheme 1). The decay of the terminal *v*(CO) band of the complex **1** indicates that the entire course of the reaction proceeds in an exponential manner. The growth of the band at around 2061 cm⁻¹ suggests that the concentration of the intermediate (**1′**) increases up to a period of about 10 minutes and then it starts decreasing in a manner similar to that of the decaying curve of the complex **1**. The rate of growth of the band around 1677 cm⁻¹ reveals that up to a period of 10 minutes, the rate of formation of the acyl complex **4** is slow and then it increases sharply up to a period of about 25 minutes. A similar type of kinetics was also observed for the

Scheme 1 Syntheses of complexes **1** and **2** and their OA reactions with MeI.
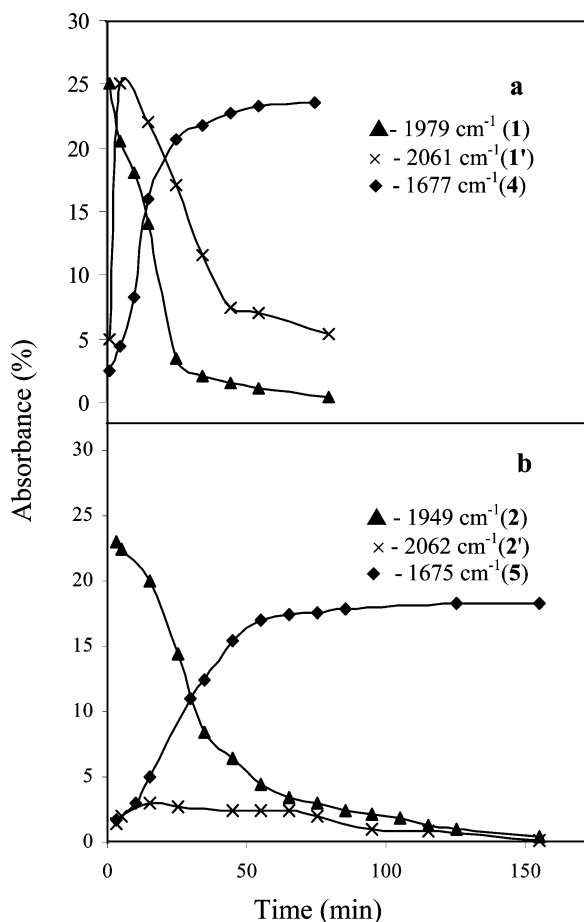
Fig. 2 The absorbance of *v*(CO) against time for the different carbonyl species: decay (▲) of the terminal *v*(CO) band for the complexes **1** and **2**; variation of intensity of terminal *v*(CO) bands (×) for the unisolable intermediates **1′** and **2′**; and the growth of the acyl *v*(CO) bands (◆) of the complexes **4** and **5**.

Table 4 Results of carbonylation reaction of methanol

Catalyst precursor	Time/h	Total conversion[a] (%)	Methyl acetate[b] (%)	Ethanoic acid[b] (%)	TON[c]
$[Rh(CO)_2I_2]^{-\ d}$	0.5	30	26.0	4.0	493
	1.0	48	38.5	9.5	790
	1.5	64	52.0	12.0	1052
1	0.5	71	32.6	37.4	1168
	1.0	77	60.8	16.2	1267
	1.5	95	28.7	65.3	1563
2	0.5	36	30.6	5.4	609
	1.0	69	59.6	9.4	1135
	1.5	82	30.9	51.1	1349
$[Rh(CO)Cl(PPh_3)_2]$	0.5	37	27.1	9.9	592
	1.0	57	34.0	23.0	938
	1.5	76	16.1	59.9	1228

[a] Conversion = {[CO consumed (mol)]/[CO charged (mol)]} × 100. CO consumption was determined from analysis of products by GC. [b] Yields of methyl acetate and acetic acid were obtained from GC analyses. [c] TON = [amount of product (mol)]/[amount of catalyst (Rh mol)]. [d] Formed from added $[Rh(CO)_2Cl]_2$ under the catalytic condition.

complex **2** (Fig. 2b) where the rate of decay of intensity of the terminal $\nu(CO)$, (1949 cm^{-1}) band is low up to a period of 10 minutes and then increases sharply till 75 minutes. The change in absorbance of the terminal $\nu(CO)$ band at around 2062 cm^{-1} shows that initial concentration of the intermediate **2′** increases up to a period of about 15 minutes and attains a maximum and then it decrease slightly followed by a steady state up to 75 minutes and thereafter declines to a minimum. This steady state may indicate an equilibrium between the unisolable intermediate **2′** and the complex **2**. During the period of 15 to 75 minutes of reaction, a sharp decrease of the terminal $\nu(CO)$ band for the complex **2** and sharp increase of acyl $\nu(CO)$ band for the complex **5** were observed. Therefore, it appears that a certain concentration (critical) of the unisolable intermediate is required to be reached for accelerating the reaction. Similar observations were also made by us in our recent work.[32]

The presence of two bulky $COOCH_3$ groups on the phosphine ligands sterically restricts the path of OA reaction of CH_3I to the Rh centre of the complex **2**. On the other hand, the secondary Rh ⋯ O interaction makes the Rh centre more nucleophilic, which facilitates the OA reaction[33] but tends to retard the migratory insertion due to a strong Rh–C bond.[34] As a result, both the OA and migratory insertion steps are slow to attain equilibrium. Such an equilibrium was not observed in case of the complex **1**, perhaps because of the absence of steric hindrance resulting in faster reaction kinetics.

Catalytic activity of complexes 1 and 2 for carbonylation of methanol

The results of batch carbonylation of methanol to acetic acid and its ester in the presence of complexes **1**, **2**, *trans*-[Rh(CO)-Cl(PPh$_3$)$_2$] and [Rh(CO)$_2$I$_2$]$^-$ as catalyst precursors are shown in Table 4. The GC analyses of the products reveal that as the reaction time increases from 0.5 to 1.5 h, the total conversion as well as Turn Over Number (TON) for the different catalyst precursors increases irrespective of the complexes. The maximum conversion of methanol with corresponding maximum TON were observed over the entire catalytic reaction period for the complex **1** and the highest conversion (95%) and TON (1563) were observed for a 1.5 h reaction period (Table 4). Under the same experimental conditions, the well-known catalyst precursor [Rh(CO)$_2$I$_2$]$^-$ generated *in-situ* [35,36] from [Rh(CO)$_2$Cl]$_2$ shows 64% conversion with a TON 1052 while that the complex **2** and *trans*-[Rh(CO)Cl(PPh$_3$)$_2$] exhibit 82% and 76% conversions respectively with corresponding TON 1349 and 1228. The data in Table 4, in general, reveal this order of efficiency of the catalytic activity: complex **1** > complex **2** > *trans*-[Rh(CO)Cl(PPh$_3$)$_2$] > [Rh(CO)$_2$I$_2$]$^-$. It therefore becomes obvious that the functionalized phosphine show higher

catalytic activity than the unfunctionalized phosphine and this higher activity may be due to higher electron density on the central metal by the chelate formation through ester oxygen donors of the ligand. From the electronic point of view (indicated by the $\nu(CO)$ value), **2** should show higher catalytic activity than **1**, but in practice, the reverse situation was observed. Similar behavior has already been observed (*vide supra*) and was attributed to steric and electronic factors. Thus the steric factor due to two bulky –COOCH$_3$ group on the two phosphine ligands in **2** sterically restrict the path of MeI addition, which is the rate determining step for carbonylation of methanol. On examining the catalytic reaction mixture by IR spectroscopy at different time intervals, and at the end of the catalytic reactions, multiple $\nu(CO)$ bands were obtained that matched well with the $\nu(CO)$ values of solution containing a mixture of the parent rhodium(I) carbonyl complexes **1** and **2** and rhodium(III) acyl complexes **4** and **5**. Thus, it may be inferred that the ligands remained bound to the metal centre throughout the entire course of the catalytic reactions.

The importance of steric effects of *ortho* substituted bidentate phosphines in polyketone catalysts has been neatly demonstrated by Pringle and co-workers.[37] We believe this work demonstrates the potential for *ortho* substituents to provide electron density to the metal centre *via* secondary coordination with effects that are as profound as those associated with major R group manipulation in phosphines.

Experimental

General procedure

The reagents were procured from Aldrich and Lancaster. All solvents were distilled under N$_2$ prior to use. All operations were carried out under oxygen-free nitrogen atmosphere using standard Schlenk technique. Microanalyses were performed by the St. Andrews University service (Chemistry Department). FT-IR spectra (4000–400 cm^{-1}) were recorded using a Perkin Elmer 2000 spectrometer in CHCl$_3$ and as KBr discs. The ^{1}H NMR (270 MHz) and ^{31}P-{^{1}H} NMR (109.36 MHz) spectra were recorded in CDCl$_3$ solution on a Jeol Delta 270 MHz Spectrometer. The carbonylation reactions of alcohol were carried out in a 100 cm^3 teflon coated high pressure reactor (HR-100 Berghof, Germany) fitted with a pressure gauge and the reaction products were analyzed by GC (Chemito 8510, FID). The X-ray crystallography data were collected at room temperature using Mo-Kα radiation with a SMART system and the structure refinements were done by full matrix least square on F^2 using SHELXTL 97 computer program. The space group was selected as $P1$ rather than $P\bar{1}$ from the distribution of intensity statistics {mean $|E \times E - 1| = 0.784$ [expected 0.968 centrosymmetric and 0.736 non-centrosymmetric]}.

Preparation

Ligands $2\text{-Ph}_2PC_6H_4COOCH_3$ and $4\text{-Ph}_2PC_6H_4COOCH_3$ were prepared by a literature method.[38] The starting complex $[Rh(CO)_2Cl]_2$ was prepared by a known method.[39]

Synthesis of the complex $[Rh(CO)Cl(2\text{-Ph}_2PC_6H_4COOMe)]$, 1

$[Rh(CO)_2Cl]_2$ 0.032 g (0.082 mmol) was dissolved in 10 cm³ CH_2Cl_2 and to this 0.053 g (0.164 mmol) of the ligand in 10 cm³ CH_2Cl_2 was added dropwise with constant stirring under nitrogen atmosphere. The reaction mixture was stirred at room temperature for about 1 h and the solvent was evaporated under reduced pressure in a rotavapor to obtain a yellow solid. The compound so obtained was washed with diethyl ether and stored over silica gel in a desiccator. Yield 0.071 g, 83.5%. [Found (calc. for $C_{21}H_{17}ClO_3PRh$): C, 51.02 (51.84), H, 3.88 (3.49).] Selected IR data (KBr): 1979 [$\nu(CO)$/cm^{-1}], 1638 [$\nu(COO)$/cm^{-1}]. NMR: $^{31}P\text{-}\{^1H\}$ NMR δ 45.1 (d, $^1J_{Rh–P}$ 162 Hz); ^1H NMR δ 7.1–8.2 (m, 14 H, Ph), 4.1 (s, 3 H, –COOCH$_3$).

Synthesis of the complex trans-$[Rh(CO)Cl(2\text{-Ph}_2PC_6H_4\text{-}COOMe)_2]$, 2

$[Rh(CO)_2Cl]_2$ 0.031 g (0.079 mmol) was dissolved in 10 cm³ CH_2Cl_2 and to this 0.102 g (0.318 mmol) of the ligand $2\text{-Ph}_2\text{-}PC_6H_4COOCH_3$ in 10 cm³ CH_2Cl_2 was added dropwise with constant stirring under nitrogen atmosphere. The reaction mixture was stirred at room temperature for about 1.5 h and the solvent was evaporated under reduced pressure in a rotavapor to obtain a light yellow solid. The compound so obtained was purified by washing with diethyl ether. Suitable crystals of the complex were developed by slow diffusion of $(C_2H_5)_2O$ into a CH_2Cl_2 solution of the complex. Yield 0.108 g, 81.2%. [Found (calc. for $C_{41}H_{34}ClO_5P_2Rh$): C, 60.55 (61.02), H, 3.98 (4.22).] Selected IR data (KBr): 1949 [$\nu(CO)$/cm^{-1}]; 1715 [$\nu(COO)$/cm^{-1}]; NMR data: $^{31}P\text{-}\{^1H\}$ δ 35.9 (d, $^1J_{Rh–P}$ = 136 Hz); ^1H NMR δ 7.1–8.3 (m, 14 H, Ph), 3.7 (s, 3H, COOCH$_3$).

Synthesis of the complex trans-$[Rh(CO)Cl(4\text{-Ph}_2PC_6H_4\text{-}COOCH_3)_2]$, 3

$[Rh(CO)_2Cl]_2$ 0.026 g (0.066 mmol) was dissolved in 10 cm³ CH_2Cl_2 and to this 0.085 g (0.264 mmol) of the ligand $4\text{-Ph}_2\text{-}PC_6H_4COOCH_3$ in 10 cm³ CH_2Cl_2 was added dropwise with constant stirring under nitrogen atmosphere. The reaction mixture was stirred at room temperature for about 90 min and the solvent was evaporated under reduced pressure in a rotavapor to obtain a light yellow solid. The compound so obtained was purified by washing with diethyl ether. Yield 0.091 g, 81.98%. [Found (calc. for $C_{41}H_{34}ClO_5P_2Rh$): C, 60.41 (61.02), H, 3.96 (4.22).] Selected IR data (KBr): 1977 [$\nu(CO)$/cm^{-1}]; 1723 [$\nu(COO)$/cm^{-1}]; NMR data: $^{31}P\text{-}\{^1H\}$ δ 30.72 (d, $^1J_{Rh–P}$ 127 Hz); ^1H NMR δ 7.2–7.9 (m, 14 H, Ph), 3.7 (s, 3H, COOCH$_3$).

Synthesis of the complex $[Rh(COCH_3)ClI(2\text{-Ph}_2PC_6H_4COOCH_3)]$, 4

The complex 1 0.105 g (0.216 mmol) was dissolved in 10 cm³ CH_2Cl_2 and to this 6 cm³ CH_3I was added. The reaction mixture was then stirred at room temperature under nitrogen atmosphere for about 6 h and the solvent was evaporated under vacuum. The yellow-reddish colored compound so obtained was washed with diethyl ether and stored over silica gel in a desiccator. Yield 0.12 g. [Found (calc. for $C_{22}H_{20}ClIO_3PRh$): C, 41.91 (42.04), H, 3.12 (3.18).] Selected IR data (KBr): 1641 [$\nu(COO)$/cm^{-1}]; 1677 [$\nu(CO)_{acyl}$/cm^{-1}]; NMR data: $^{31}P\text{-}\{^1H\}$ δ 47.9 (d, $^1J_{Rh–P}$ 172 Hz); ^1H NMR δ 7.02–8.1 (m, 14H, Ph), 4.2 (s, 3H, COOCH$_3$), 2.3 (s, 3H, COCH$_3$).

Synthesis of complex $[Rh(COMe)ClI(2\text{-Ph}_2PC_6H_4COOMe)\text{-}(2\text{-Ph}_2PC_6H_4COOMe)]$, 5

0.112 g (0.138 mmol) of complex 2 was dissolved in 10 cm³ CH_2Cl_2 and to this 6 cm³ CH_3I was added. The reaction mixture was then stirred at room temperature under nitrogen atmosphere for about 12 h and the solvent was evaporated under vacuum. The yellow-reddish colored compound so obtained was washed with diethyl ether and stored over silica gel in a desiccator. Yield 0.106 g. [Found (calc. for $C_{42}H_{37}ClIO_5P_2Rh$): C, 54.12 (53.17), H, 3.81 (3.90).] Selected IR data (KBr): 1672 [$\nu(COO)$/cm^{-1}]; 1717 [$\nu(CO)_{acyl}$/cm^{-1}]; NMR data: $^{31}P\text{-}\{^1H\}$ δ 46.1 (d, $^1J_{Rh–P}$ 162Hz); δ 39.5 (d, $^1J_{Rh–P}$ 150 Hz); ^1H NMR δ 7.1–8.3 (m, 14H, Ph), 4.0 (s, 3H, COOCH$_3$ chelated), 3.8 (s, 3H, COOCH$_3$) and 2.3 (s, 3H, COCH$_3$).

Reaction kinetics

The OA reactions of complexes 1 and 2 with CH_3I were monitored by using IR spectroscopy in a solution cell (1.0 mm path length). 10 mg (mmol) of complexes 1 and 2 were added to 1 cm³ of neat CH_3I at room temperature. An aliquot (0.5 ml) of the reaction mixture was transferred by syringe into the IR cell. Then the kinetic measurement were made by monitoring the simultaneous decay of the terminal $\nu(CO)$ of the complexes in the range 1925–2100 cm^{-1} and growth of the acyl $\nu(CO)$ of the complex 4 and 5 in the range 1600–1750 cm^{-1}. A series of spectra were taken at regular intervals. The OA reactions of CH_3I with complexes 1 and 2 were found to be concentration dependent on the complexes as well as on CH_3I. Therefore, in order to provide a pseudo-first order condition, the reaction was carried out in a large excess of CH_3I.

Carbonylation of methanol using complexes 1 and 2 as catalyst precursors

0.099 mol of CH_3OH, 0.016 mol of CH_3I, 0.055 mol of H_2O, 0.054 mmol of the complexes 1 or 2 were taken in the reactor and then pressurized with CO gas (20 bar at room temperature, 0.080 mol). The reaction vessel was then placed into the heated jacket of the autoclave and the reactions were carried out at 130 ± 5 °C (corresponding pressure 35 ± 2 bar) with variation of reaction time. The products were collected and analyzed by GC. The recycle experiments were done by maintaining the same experimental conditions as described above with the dark brown solid mass as catalyst obtained by evaporating the carbonylation reaction mixture under reduced pressure.

References

1 P. M. Maitlis, A. Haynes, G. J. Sunley and M. J. Howard, *J. Chem. Soc., Dalton Trans.*, 1996, 2187.
2 M. J. Howard, M. D. Jones, M. S. Roberts and S. A. Taylor, *Catal. Today*, 1993, **18**, 325.
3 C. A. Carraz, E. J. Ditzel, A. G. Orpen, D. D. Ellis, P. G. Pringle and G. J. Sunley, *Chem. Commun.*, 2000, 1277.
4 J. Rankin, A. D. Poole, A. C. Benyei and D. J. Cole-Hamilton, *Chem. Commun.*, 1997, 1835.
5 P. Das, M. Boruah, N. Kumari, M. Sharma, D. Konwar and D. K. Dutta, *J. Mol. Catal. A*, 2002, **178**, 283.
6 N. Kumari, M. Sharma, P. Das and D. K. Dutta, *Appl. Organomet. Chem.*, 2002, **16**, 258.
7 P. Das, P. Chutia and D. K. Dutta, *Chem. Lett.*, 2002, 766.
8 J. R. Dilworth, J. R. Miller, N. Wheatley, M. J. Baker and J. G. Sunley, *J. Chem. Soc., Chem. Commun.*, 1995, 1579.

9 M. J. Baker, M. F. Giles, A. G. Orpen, M. J. Taylor and R. J. Watt, *J. Chem. Soc., Chem. Commun.*, 1995, 197.

10 R. W. Wegman, A. G. Abatjoglou and A. M. Harrison, *J. Chem. Soc., Chem. Commun.*, 1987, 1891; A. M. Z. Slawin, M. B. Smith and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1996, 4575; P. Das, M. Sharma, Nandini Kumari, D. Konwar and D. K. Dutta, *Appl. Organomet. Chem.*, 2002, **16**, 302.

11 M. J. Baker, J. R. Dilworth, J. G. Sunley and N. Wheatley, BP Chemicals Limited (London), *US Pat.*, 5488153, 1996.

12 E. M. Miller and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1974, 480.

13 G. K. Anderson and R. Kumar, *J. Organomet. Chem.*, 1988, **342**, 263.

14 P. Das, D. Konwar and D. K. Dutta, *Indian J. Chem.*, 2001, **40A**, 626.

15 A. R. Sanger, *Can. J. Chem.*, 1983, **61**, 2214.

16 I. L. Gall, P. Laurent, E. Soulier, J-Y. Salaun and H. D. Abbayes, *J. Organomet. Chem.*, 1988, **567**, 13.

17 T. B. Rauchfuss and D. M. Roundhill, *J. Am. Chem. Soc.*, 1974, 3098.

18 M. P. Anderson, A. L. Casalnuovo, B. J. Johnson, B. M. Mattson, A. M. Mueting and L. H. Pignolet, *Inorg. Chem.*, 1988, **27**, 1649.

19 E. Lindner, Q. Wang, H. A. Mayer, R. Fawzi and M. Steimann, *Organometallics*, 1993, 1865.

20 R. E. Mail, M. A. Garrada, R. Hernandez and L. Ibralucea, *J. Organomet. Chem.*, 2002, **648**, 149.

21 H. D. Empsall, S. Johnson and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1980, 302.

22 R. H. Laitinen, J. Soininen, P. Suomalainen, T. A. Pakkanen, M. Ahlgren and J. Pursiainen, *Acta Chim. Scand.*, 1999, **53**, 335.

23 P. Braunstein, D. Matt and Y. Dusausoy, *Inorg. Chem.*, 1983, **22**, 2043; M. C. Bonnet, F. Dahan, A. Acke, W. Keim, R. P. Schulz and I. Tkatchenko, *J. Chem. Soc., Chem. Commun.*, 1994, 615.

24 M. Gonzalez, P. Crochet and P. H. Dixneuf, *J. Organomet. Chem.*, 1994, **471**, 229.

25 J. Chatt and B. L. Shaw, *J. Chem. Soc. A*, 1966, 1437.

26 A. L. Balch, R. R. Guimenyans and J. Linehow, *Inorg. Chem.*, 1985, **24**, 290.

27 J. M. Kessler, J. N. Ne'lson, J. S. Frye, A. DeCian and J. Fisher, *Inorg. Chem.*, 1993, **37**, 1048.

28 J. Blin, P. Braunstein, J. Fischer, G. Kickelbick, M. Knorr, X. Morise and T. Wirth, *J. Chem. Soc., Dalton Trans*, 1999, 2159.

29 P. Pelagatti, A. Bacchi, C. Bobbio, M. Carcell, M. Costa, C. Pelizzi and C. Vivorio, *Organometallics*, 2000, **19**, 5440.

30 A. Haynes, J. M. Pearson, P. W. Vickers, J. P. H. Charmant and P. M. Maitlis, *Inorg. Chim. Acta*, 1998, **270**, 382.

31 D. Foster, *Adv. Organomet. Chem.*, 1979, **17**, 255.

32 M. Sharma, N. Kumari, P. Das, P. Chutia and D. K. Dutta, *J. Mol. Catal. A*, 2002, **188**, 25.

33 I. C. Douek and G. Wilkinson, *J. Chem. Soc. A*, 1969, 2604.

34 L. Gonsalvi, H. Adams, G. J. Sunley, E. Ditzejl and A. Hayanes, *J. Am. Chem. Soc.*, 1999, **121**, 11233.

35 A. Haynes, B. E. Mann, G. E. Morris and P. M. Maitlis, *J. Am. Chem. Soc.*, 1993, **115**, 4090.

36 D. Forster, *J. Am. Chem. Soc.*, 1976, **98**, 846.

37 S. J. Dosset, A. Gillon, A. G. Orpen, J. S. Fleming, P. G. Pringle, D. F. Wass and M. D. Jones, *Chem. Commun.*, 2001, 699.

38 B. M. Trost, D. L. V. Vranken and C. Bingel, *J. Am. Chem. Soc.*, 1992, **114**, 9327.

39 J. A. McCleverty and G. Wilkinson, *Inorg. Synth.*, 1966, **8**, 221.