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Rhodium(I) carbonyl complexes of ether-phosphine ligands and their reactivity

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The reactions of dimeric complex $[Rh(CO)_2Cl]_2$ with hemilabile ether-phosphine ligands $Ph_2P(CH_2)_nOR$ [$n = 1$, $R = CH_3$ (**a**); $n = 2$, $R = C_2H_5$ (**b**)] yield *cis*-$[Rh(CO)_2Cl(P \sim O)]$ (**1**) [$P \sim O = \eta^1$-(P) coordinated]. Halide abstraction reactions of **1** with $AgClO_4$ produce *cis*-$[Rh(CO)_2(P \cap O)]ClO_4$ (**2**) [$P \cap O = \eta^2$-(P,O)chelated]. Oxidative addition reactions of **1** with CH_3I and I_2 give rhodium(III) complexes $[Rh(CO)(COCH_3)ClI(P \cap O)]$ (**3**) and $[Rh(CO)ClI_2(P \cap O)]$ (**4**) respectively. The complexes have been characterized by elemental analyses, IR, ^1H, ^{13}C and ^{31}P NMR spectroscopy. The catalytic activity of **1** for carbonylation of methanol is higher than that of the well-known $[Rh(CO)_2I_2]^-$ species. Copyright © 2002 John Wiley & Sons, Ltd.

INTRODUCTION

Platinum metal complexes containing potential bidentate ligands, particularly tertiary phosphine functionalized with oxygen, like ether,[1–7] ester[8–12] and acid[13–15] donors, have gained much interest because of their structural novelty and reactivity. Such ligands containing 'soft' phosphorus and 'hard' oxygen donors often show hemilabile behaviour,[2–10] depending on the central metal atom and its environment. When these ligands form complexes, initially a strong metal–phosphorus bond is formed and the oxygen donor of the ligands may also form a weak metal–oxygen chelate that can be cleaved reversibly in the presence of a suitable substrate molecule resulting in a 'closing and opening' mechanism.[5] The ligand backbones and different substituents on the donor atoms are known to play an important role in homogeneous catalysis by such a 'closing and opening' mechanism. Oxidative addition (OA) reactions of platinum metal complexes, particularly rhodium(I) with small molecules, being the key step in many catalytic transformation reactions, e.g. carbonylation, hydroformylation, etc., have gained much attention. Recent reports[16–19] show that rhodium(I) complexes containing different types of hemilabile phosphine ligands can be used as catalysts for carbonylation reactions. In this paper, we report the synthesis of dicarbonylrhodium(I) complexes containing ether–phosphine ligands $Ph_2P(CH_2)_nOR$ [$n = 1$, $R = CH_3$ (**a**); $n = 2$, $R = C_2H_5$ (**b**)], their reactivity towards small molecules like CH_3I and I_2, and their catalytic activity for carbonylation reaction of methanol.

EXPERIMENTAL

The complex $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$[20] and the ligands $Ph_2P(CH_2)_nOR$[21] [$n = 1$, $R = CH_3$ (**a**); $n = 2$, $R = C_2H_5$ (**b**)] were prepared according to the published procedure. All the reactions were carried out in dry solvents under nitrogen atmosphere. Elemental analyses were done by using a Perkin–Elmer 2400 elemental analyzer. IR spectra were recorded in KBr disks and in $CHCl_3$ solution using a Perkin–Elmer system 2000 FT IR spectrophotometer. NMR spectra were recorded on a Bruker DPX-300 spectrophotometer. Carbonylation of methanol was carried out in a 150 cm^3 Teflon-coated reactor (Laboratory High Pressure Reaction Vessel, HR-100, Berghof, Germany) fitted with a pressure gauge and the reaction products were analyzed by gas chromatography (Chemito 8510, F1D).

Preparation of complexes

*$[Rh(CO)_2Cl(P \sim O)]$ (**1**) [($P \sim O = \eta^1$-(P) coordinated $Ph_2P(CH_2)_nOR$, n = 1, R = CH_3 (**a**); n = 2, R = C_2H_5 (**b**)]*

To a solution of $[Rh(CO)_2Cl]_2$ (0.020 g, 0.052 mmol) in dichloromethane (10 ml), the ligand **a** (0.025 g, 0.108 mmol) or **b** (0.028 g, 0.109 mmol) was added. The reaction mixture was stirred for *ca* 0.5 h at room temperature (RT), during

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which the color of the solution changed from reddish yellow to reddish brown. The solvent was then removed under vacuum to give a reddish brown solid, which was washed with hexane–petroleum ether mixture and was recrystallized from dichloromethane–ether solution.

Data for **1a** are as follows. Yield: 91% (0.040 g). Anal. Found: C, 45.41; H, 3.50. Calc. for $C_{16}H_{15}ClO_3PRh$: C, 45.28; H, 3.53%.

Data for **1b** are as follows. Yield: 81% (0.038 g). Anal. Found: C, 48.01; H, 4.23. Calc. for $C_{18}H_{19}ClO_3PRh$: C, 47.78; H, 4.20%.

$[Rh(CO)_2(P \cap O)]ClO_4$ (2) $[(P \cap O = \eta^2\text{-}(P,O)$ chelated $Ph_2P(CH_2)_nOR$, n = 1, R = CH_3 (**a**); n = 2, R = C_2H_5 (**b**)]

To a solution of complex **1a** (0.020 g, 0.047 mmol) or **1b** (0.020 g, 0.044 mmol) in acetone (10 ml), AgClO_4 (0.010 g, 0.0485 mmol) in methanol (5 ml) was added. The reaction mixture was stirred for *ca* 3 h at RT. The white precipitate of AgCl was filtered off and the filtrate was evaporated to a deep-red solid mass, which was washed with hexane–petroleum ether mixture and recrystallized from dichloromethane–ether solution.

Data for **2a** are as follows. Yield: 87% (0.020 g). Anal. Found: C, 39.51; H, 3.10. Calc. for $C_{16}H_{15}ClO_7PRh$: C, 39.34; H, 3.07%.

Data for **2b** are as follows. Yield: 88% (0.020 g). Anal. Found: C, 41.70; H, 3.71. Calc. for $C_{18}H_{19}ClO_7PRh$: C, 41.86; H, 3.68%.

$[Rh(CO)(COCH_3)ClI(P \cap O)]$ (3) $[(P \cap O = \eta^2\text{-}(P,O)$ chelated $Ph_2P(CH_2)_nOR$, n = 1, R = CH_3 (**a**); n = 2, R = C_2H_5 (**b**)]

To a solution of complex **1a** (0.020 g, 0.047 mmol) or **1b** (0.020 g, 0.044 mmol) in dichloromethane (10 ml), CH_3I (3 ml) was added. The reaction mixture was stirred for *ca* 6 h at RT. The reddish yellow solid obtained after evaporating the solvent was washed with hexane–petroleum ether and recrystallized from dichloromethane–ether solution.

Data for **3a** are as follows. Yield: 79% (0.021 g). Anal. Found: C, 35.91; H, 3.16. Calc. for $C_{17}H_{18}ClIO_3PRh$: C, 36.04; H, 3.18%.

Data for **3b** are as follows. Yield: 80% (0.021 g). Anal. Found: C 38.51; H, 3.66. Calc. for $C_{19}H_{22}ClIO_3PRh$: C, 38.38; H, 3.70%.

$[Rh(CO)ClI_2(P \cap O)]$ (4) $[(P \cap O = \eta^2\text{-}(P,O)$ chelated $Ph_2P(CH_2)_nOR$, n = 1, R = CH_3 (**a**); n = 2, R = C_2H_5 (**b**)]

To the solution of complex **1a** (0.020 g, 0.047 mmol) or **1b** (0.020 g, 0.044 mmol) in dichloromethane (10 ml), a solution of iodine (0.020 g, 0.0787 mmol) in dichloromethane (5 ml) was added. The reaction mixture was stirred for *ca* 6 h at RT. The solution was then evaporated to dryness to get a dark-brown solid. The product was washed with hexane–

petroleum ether mixture and recrystallized from dichloromethane–ether solution.

Data for **4a** are as follows. Yield: 69% (0.021 g). Anal. Found: C, 27.56; H, 2.28. Calc. for $C_{15}H_{15}ClI_2O_2PRh$: C, 27.69; H, 2.30%.

Data for **4b** are as follows. Yield: 64% (0.019 g). Anal. Found: C, 30.22; H, 2.83. Calc. for $C_{17}H_{19}ClI_2O_2PRh$: C, 30.08; H, 2.80%.

Carbonylation of methanol

CH_3OH (3.16 ml, 0.078 mol), CH_3I (1 ml, 0.016 mol), H_2O (1 ml, 0.055 mol), $[Rh(CO)_2Cl]_2$ (0.010 g, 0.025 mmol) and the ligand **a** (0.013 g, 0.056 mmol) or **b** (0.028 g, 0.054 mmol) were placed into an autoclave. The autoclave was pressurized with CO gas (6 bar, 0.036 mol) at 25 °C. The pressure in the reactor was increased to 15 bar by increasing the temperature to 130 °C and was maintained for 1 h. Instead of generating the catalyst precursors *in situ*, the above carbonylation reactions were also performed using the complexes **1a** (0.021 g, 0.050 mmol) and **1b** (0.023 g, 0.050 mmol) directly.

RESULTS AND DISCUSSION

The complex $[Rh(CO)_2Cl]_2$ undergoes a bridge splitting reaction with two equivalents of the ether-phosphine (PO) ligands to give $[Rh(CO)_2Cl(P \sim O)]$ (**1**). The complexes **1(a,b)** show two equally intense terminal $v(CO)$ bands in $CHCl_3$ and in KBr medium in the range 1985–2065 cm^{-1} (Table 1), indicating that the two carbonyl groups are mutually *cis* to one another.[22,23] The $^{31}P\{^1H\}$ NMR spectra of the complexes **1a** and **1b** exhibit doublets due to $^{103}Rh-P$ coupling at δ 28.4 ppm and 30.4 ppm respectively (Table 1). Compared with free ligands, these values are shifted 45–50 ppm downfield, indicating coordination through the phosphorus atom.[24] The ^1H NMR spectra (Table 1) of the complexes exhibit characteristic resonances for phenyl, methylene and methyl protons of the ligands. The $^{13}C\{^1H\}$ NMR spectra (Table 1) of the complexes show characteristic signals for phenyl, methylene and methyl carbon atoms. In addition, the complexes also show a very weak signal at around δ 188 ppm attributable to the terminal carbonyl carbon, which is about 10 ppm higher than that of the carbon in $[Rh(CO)_2Cl]_2$, indicating donation of high electron density towards the carbonyl carbon from the central metal atom.[23,25]

Complexes **1(a,b)** undergo ligand substitution reactions with excess PPh_3 to form the well-known compound *trans*-$[Rh(CO)Cl(PPh_3)_2]$, indicated by elemental analysis and $v(CO)$ value at 1962 cm^{-1}.[26]

Complexes **1(a,b)**, on halide abstraction with AgClO_4, yield cationic dicarbonyl chelated complexes **2(a,b)**. Similar to the complexes **1(a,b)**, the IR spectra of **2(a,b)** in $CHCl_3$ and in KBr show two equally intense $v(CO)$ bands in the range 2000–2100 cm^{-1}, suggesting a *cis*-disposition of the two

Table 1. IR and NMR (^{1}H, ^{13}C, ^{31}P)^a data of the complexes

| Complex | IR (in KBr)^b cm^{-1} | | δ_P (ppm) | δ_H (ppm) | | | | | δ_C (ppm) | | | | | |
	ν(CO)	ν(COC)	Ph$_2$P−[J_{RhP}]	C$_6$H$_5$	PCH$_2$[J_{PH}]	CH$_2$[J_{HH}]	OCH$_2$[J_{HH}]	CH$_3$[J_{HH}]	C$_6$H$_5$	PCH$_2$[J_{PC}]	CH$_2$	OCH$_2$	CH$_3$	CO
1a	2060 1985	1110	28.4d [73.3]	7.8–7.3m	3.8d [11.2]	-	-	3.2s	132.2–128.5m	70.1d [87.5]	-	-	61.9s	187.5s
1b	2065 2000	1113	30.4d [109.6]	7.7–7.3m	2.7dt [7.5]	3.9t [4.9]	3.5q [5.8]	1.8t [2.1]	131.9–128.8m	30.9d [44.6]	71.4s	61.1s	42.5s	188.2s
2a	2070 2000	1071	36.3d [93.4]	7.8–7.2m	4.1d [8.7]	-	-	4.7s	133.1–129.2m	74.1d [64.4]	-	-	65.9s	188.3s
2b	2094 2020	1070	42.6d [101.3]	7.9–7.2m	2.9dt [6.8]	4.2t [5.6]	3.9q [4.7]	2.0t [3.1]	132.9–128.6m	31.4d [56.1]	75.3s	63.7s	42.9s	189.1s
3a	2060 1720	1075	35.1d [174.5]	7.8–7.3m	4.2d [6.2]	-	-	4.4s	132.6–128.6m	76.2 [39.0]	-	-	66.2s	185.3s 207.9s
3b	2065 1717	1082	41.7d [159.7]	7.7–7.2m	2.8dt [5.8]	4.3t [7.8]	3.8q [5.2]	2.2t [2.1]	133.1–129.2m	30.1d [27.6]	74.2s	63.9s	42.7s	180.3s 211.1s
4a	2062	1071	34.3d [181.5]	7.8–7.4m	4.3d [7.8]	-	-	4.6s	132.7–128.9m	77.6d [32.5]	-	-	67.7s	185.7s
4b	2080	1083	38.7d [133.1]	7.7–7.2m	2.9dt [5.6]	4.4t [3.0]	3.9q [6.1]	2.1t [2.1]	132.9–128.9m	29.6d [29.8]	73.1s	64.6s	43.1s	186.7s

^{a} *J* (Hz); ^{1}H (300.13 MHz), ^{13}C (75.47 MHz) and ^{31}P (121.49 MHz) NMR spectra were recorded in CDCl$_3$ using SiMe$_4$ as internal standard for ^{1}H and ^{13}C and 85% H$_3$PO$_4$ as external standard for ^{31}P nuclei; s: singlet; d: doublet; t: triplet; q: quartet; m: multiplet; dt: doublet of triplet.
^{b} In CHCl$_3$ solution ν(CO) values are: **1a**, 2062, 1987; **1b**, 2066, 2002; **2a**, 2073, 2002; **2b**, 2095, 2022.

carbonyl groups (Table 1). The $v(C-O-C)$ band occurs at around 1070 cm^{-1}, which is about 40 cm^{-1} lower than the free ligand, substantiating the formation of a rhodium–oxygen bond.[2,6] The IR spectra also show the characteristic $v(ClO_4)$ band at around 1100 cm^{-1}. Further evidence for PO chelation in 2(a,b) can also be derived from the ^{31}P{^{1}H} NMR spectra (Table 1), in which the doublets due to ^{103}Rh–P coupling are shifted characteristically downfield[24] compared with the η^1-coordinated complex 1(a,b). Further, the ^{1}H and ^{13}C{^{1}H} NMR values of the complexes 2(a,b) for methyl and methylene groups attached to the etherial oxygen are also shifted downfield significantly relative to those for non-chelated complexes 1(a,b).

Complexes 1(a,b) undergo OA with CH$_3$I to yield a six-coordinated rhodium(III) acyl species [Rh(CO)(COCH$_3$)ClI(P∩O)] (3) (Scheme 1). The IR spectra of 3(a,b) show v(CO) bands at around 2060 and 1720 cm^{-1}, attributable to terminal and acyl carbonyl group respectively, and the high value for the former indicates that the CO is *trans* to a weak *trans*-directing chloride ligand.[6] The ^{31}P{^{1}H} NMR spectra of 3(a,b) show deshielded resonances compared with the complexes 1(a,b), indicating chelation, and the high J_{RhP} values suggest that the phosphorus atom is *trans* to iodide.[6,17] The ^{1}H and ^{13}C{^{1}H} NMR data are consistent with an η^2-coordination mode of the phosphine-ether ligands. The formation of a rhodium–acyl linkage in 3(a,b) can also be evidenced from the ^{13}C{^{1}H} NMR values, which show a much more deshielded acyl carbonyl carbon resonance at around 210 ppm. The OA reactions of 1(a,b) with CH$_3$I are likely to proceed via the six-coordinated unstable alkyl intermediate[23,27] [Rh(CO)$_2$(CH$_3$)ClI(P∼O)] [3' (a,b)] (Scheme 1), which undergoes a rapid migratory insertion of CO to form the corresponding rhodium–acyl complex and thus creates a vacant coordination site for the dangling etherial oxygen to form a four- (3a) or five-membered (3b) chelate ring (Scheme 1).

Complexes 1(a,b) undergo OA with iodine to give [Rh(CO)ClI$_2$(P∩O)] (4) (Scheme 1) exhibiting only one terminal v(CO) band in the range 2060–2080 cm^{-1}, which is the characteristic region for rhodium(III) carbonyl complex.[23,27] This high v(CO) value also indicates that the CO group is *trans* to chloride. Similar to complexes 3(a,b), the IR
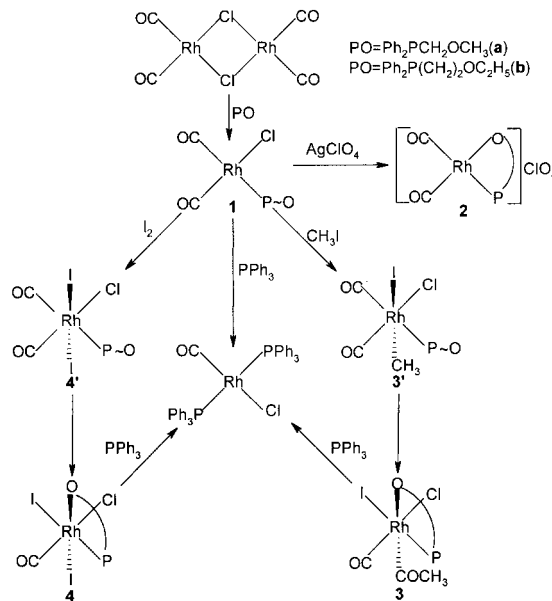
Scheme 1.

and NMR data show characteristic shifts confirming the coordination of the ether function, and the high J_{RhP} values suggest a *trans* disposition of phosphorus to the iodine atom. The formation of 4(a,b) is anticipated to occur via an unisolable intermediate [Rh(CO)$_2$ClI$_2$(P∼O)] (4') (Scheme 1) that eliminates one CO group from the complex with simultaneous chelation by the etherial oxygen donor.

The rhodium(III) complexes 3(a,b) and 4(a,b), upon treatment with excess of PPh$_3$, reduce to the rhodium(I) complex *trans*-[Rh(CO)Cl(PPh$_3$)$_2$] (Scheme 1). Similar types of reaction were also reported earlier,[23] where a rhodium(III) complex was converted to a rhodium(I) complex upon treatment with excess of PPh$_3$.

Catalytic activity of complexes 1(a,b) for carbonylation of methanol

The results of batch carbonylation of methanol to acetic acid and its ester in the presence of 1(a,b) as catalyst precursors are shown in Table 2. At 130 °C and 15 bar pressure, the precursor complex 1a, formed *in situ* from [Rh(CO)$_2$Cl]$_2$ and

Table 2. Carbonylation of methanol at 130 °C and 15 bar pressure for 1 h

Catalyst precursors	Conversion[a] (%)	AcOH[b] (%)	MeOAc[b] (%)	TON[c]
[Rh(CO)$_2$Cl]$_2$	30	2	28	216
[Rh(CO)$_2$Cl]$_2$ + **a**	37	8	29	266
1a	39	8	31	281
[Rh(CO)$_2$Cl]$_2$ + **b**	100	41	59	720
1b	99	46	53	713

[a] Conversion (%) = {[CO consumed (mol)]/[CO charged (mol)]} × 100. CO consumption was determined from analysis of the products by GC.
[b] Yields of AcOH and MeOAc were obtained from GC analyses.
[c] TON = Amount of product (mol)/[Amount of catalyst (Rh mol) × reaction time (h)].
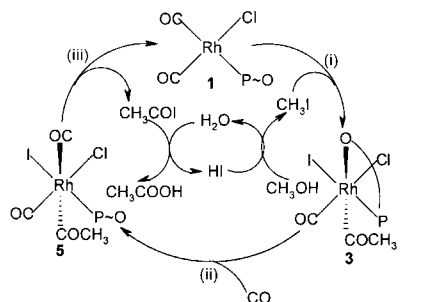
PO = Ph$_2$PCH$_2$OCH$_3$(**a**); Ph$_2$PCH$_2$CH$_2$OCH$_2$CH$_3$(**b**)

P~O = η^1-(P) coordinated PO

P⌒O = η^2-(P,O) coordinated PO

(i) Oxidative addition of CH$_3$I followed by insertion of CO

(ii) Ring opening by CO

(iii) Reductive elimination of CH$_3$COI

Scheme 2.

the ligand **a**, shows a marginally higher conversion (yield 37%; turn over number, TON = 266 h^{-1}) over the well-known species [Rh(CO)$_2$I$_2$]$^-$ (yield 30%; TON = 216 h^{-1}) generated from [Rh(CO)$_2$Cl]$_2$.[18,28] Under the same experimental condition, the precursor **1b** (generated *in situ*) shows 100% conversion, exhibiting TON = 720 h^{-1}. Instead of generating the catalyst precursors *in situ*, if the complexes **1a** and **1b** were used directly, almost the same amount of conversion was obtained (Table 2). The higher TON for precursors **1a** and **1b** compared with the [Rh(CO)$_2$I$_2$]$^-$ may be attributed to an increase of electron density at the rhodium center by the ether-phosphine ligands. Based on OA reactions of **1(a,b)** with CH$_3$I, we propose a mechanism for the carbonylation reaction (Scheme 2) in which complexes **3(a,b)** act as intermediates. Under CO pressure the PO ligands allow preferential dissociation of the weak Rh—O bond, creating a vacant coordination site for CO to form an unisolable intermediate complex **5**, which then eliminates CH$_3$COI and gives back complex **1**. Therefore, a 'closing–opening' mechanism seems to operate under the prevailing reaction condition. This reaction mechanism is similar to the catalytic cycle proposed for other reported complexes.[5,16,18] The higher activity of **1b** compared with **1a** may be attributed to the higher stability of the five-membered ring intermediate complex (**3b**) exhibiting higher basicity[29] than the four-membered ring intermediate complex (**3a**).

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