

## Carbonylation of Methanol at Unusually Low Temperature and Pressure with *cis*-RhCl(CO)<sub>2</sub>Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>P(O)Ph<sub>2</sub>

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*cis*-RhCl(CO)<sub>2</sub>Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>P(O)Ph<sub>2</sub>, the only species observed during catalysis, formed from *cis*-RhCl(CO)Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>P(O)Ph<sub>2</sub> and CO, is the sole active species observed during catalytic studies and results in the carbonylation of methanol with catalyst turnover frequencies approaching 400 h<sup>-1</sup> at 80 °C and 50 psig CO; the crystal structure of the analogue *cis*-RhCl(CO)Ph<sub>2</sub>PCH<sub>2</sub>P(O)Ph<sub>2</sub> is reported.

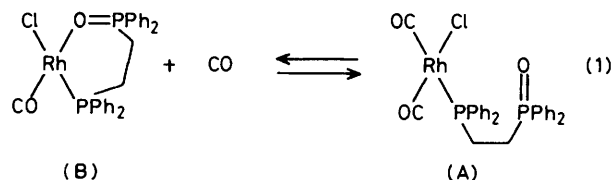
We have found that *cis*-RhCl(CO)Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>P(O)Ph<sub>2</sub> (B) is a precursor to an extremely active methanol carbonylation catalyst under very mild reaction conditions. Reaction of (B) with CO results in the displacement of the phosphine oxide-Rh bond and the formation of (A) ( $\nu_{\text{CO}}$  2096 and 2012 cm<sup>-1</sup>)<sup>1</sup> according to the equilibrium shown in equation (1).

Based on their i.r. absorbances the ratio of (A) to (B) is *ca.* 1 : 1 at 22 °C and 1 atm CO. Increasing the CO pressure to 3

atm converts (B) completely to (A). We were unable to isolate pure (A). There is no indication of co-ordinated phosphine oxide in the i.r. spectrum under reaction conditions. Reducing the pressure and purging with N<sub>2</sub> regenerates (B), indicating that the reaction is reversible. (A) rapidly reacts with MeI (22 °C) to yield (B) and acetyl iodide. The fast reaction rate precluded an accurate study of the kinetics. It is apparent from the i.r. spectra that transient Rh-Me and Rh-acyl complexes

**Table 1.**  $^{31}\text{P}$  N.m.r. ( $\delta/\text{p.p.m.}$ ;  $J/\text{Hz}$ ) and i.r. spectroscopic data ( $\nu/\text{cm}^{-1}$ ) for  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{P}(\text{O})\text{Ph}_2$  and compounds (B) ( $n = 2$ ) and (C) ( $n = 1$ ).

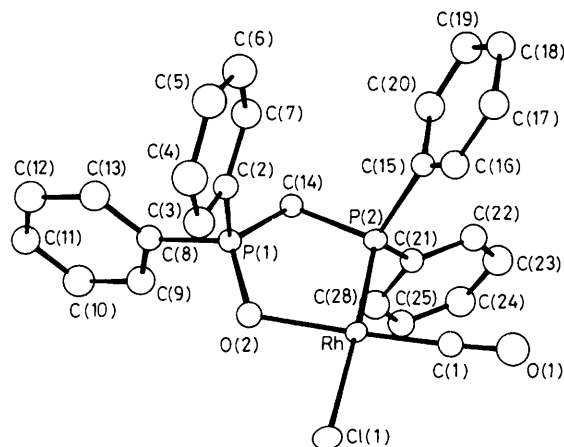
$n$	$\text{Ph}_2\text{P}(\text{CH}_2)_n\text{P}(\text{O})\text{Ph}_2$				$\text{cis-RhCl}(\text{CO})\text{Ph}_2\text{P}(\text{CH}_2)_n\text{P}(\text{O})\text{Ph}_2$						
	$\delta(\text{P})$	$\delta(\text{P}=\text{O})$	$J_{\text{PP}}$	$\nu_{\text{P}=\text{O}}$	$\delta(\text{P})$	$\delta(\text{P}=\text{O})$	$J_{\text{PP}}$	$J_{\text{RhP}}$	$J_{\text{RhOP}}$	$\nu_{\text{P}=\text{O}}$	$\nu_{\text{CO}}$
1	-28.7	27.4	49.5	1200	43.8	58.6	29.0	162.4	4.8	1065	1985
2	-12.4	34.3	48.3	1190	34.2	41.6	12.1	16.7	—	1150	1995



are formed.<sup>2</sup> Under 3 atm CO this reaction is catalytic since (B) is transformed back to (A). Methanol is readily carbonylated to acetic acid in reaction with (B), MeI, and CO. In this case, the reaction is first order in [(B)] and [MeI] and independent of [CO] from 3 to 17 atm. I.r. spectroscopic studies carried out under catalytic conditions at 80 °C and 50 psig CO (turnover frequency 400 h<sup>-1</sup>) reveal only (A). There is no indication of  $[\text{Rh}(\text{CO})_2\text{I}_2]^-$  which is the principal rhodium species present during catalysis with the Rh-I catalyst.<sup>3</sup> In addition, there is no induction period as might be expected if dissociation of  $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{P}(\text{O})\text{Ph}_2$  and subsequent formation of  $[\text{Rh}(\text{CO})_2\text{I}_2]^-$  is important.<sup>4</sup> Normal operating conditions for the Rh-I catalyst are 200 °C and 500 psig CO with catalyst turnover frequencies of 200–600 h<sup>-1</sup>.<sup>5</sup>

$\text{cis-RhCl}(\text{CO})\text{Ph}_2\text{P}(\text{CH}_2)_2\text{P}(\text{O})\text{Ph}_2$  (C) does not react with CO at 22 °C and 1 atm. Increasing the pressure to 3 atm results in the formation of a trace amount of  $\text{cis-RhCl}(\text{CO})_2\text{Ph}_2\text{P}(\text{CH}_2)_2\text{P}(\text{O})\text{Ph}_2$ . The i.r. and  $^{31}\text{P}$  n.m.r. spectroscopic data, Table 1, for (C) are consistent with the structure confirmed by X-ray crystallography shown in Figure 1.† The  $^{31}\text{P}$  phosphine oxide resonance is shifted 31 p.p.m. downfield from the corresponding resonance of the unco-ordinated ligand, indicative of electron donation from the P=O group to Rh. The 4.8 Hz coupling of the rhodium to the phosphine oxide phosphorus is an indication of oxide co-ordination. In the i.r. spectrum the P=O stretching band shifts from 1200 to 1065 cm<sup>-1</sup> upon complexation.<sup>6</sup> The 135 cm<sup>-1</sup> shift in (C) indicates a significant weakening of the P=O bond. The P–O bond length (1.514 Å) in (C) is longer than the P–O bond length in triphenylphosphine oxide (1.46 Å) or trimethylphosphine oxide (1.48 Å).<sup>7</sup> In the case of (B) the i.r. and  $^{31}\text{P}$  n.m.r. spectroscopic data are also consistent with the *cis* structure confirmed for

† Crystal data for (C):  $\text{cis-RhCl}(\text{CO})\text{Ph}_2\text{P}(\text{CH}_2)_2\text{P}(\text{O})\text{Ph}_2 \cdot \text{CH}_2\text{Cl}_2$ ,  $\text{C}_{27}\text{H}_{24}\text{Cl}_3\text{RhO}_2\text{P}_2$ , orthorhombic, space group *Pbca*,  $a = 19.564(9)$ ,  $b = 33.236(7)$ ,  $c = 8.696(4)$  Å,  $U = 5654.3$  Å<sup>3</sup>,  $Z = 8$ ,  $D_c = 1.53$  g cm<sup>-3</sup>; 5788 independent reflections with 4969 unique; 3018 with  $F^2 > 3\sigma(F)^2$  used in the refinement. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer using Mo- $K_\alpha$  radiation. Least squares refinement,  $R = 0.054$ ,  $R_w = 0.071$ . Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



**Figure 1.** Crystal structure of  $\text{cis-RhCl}(\text{CO})\text{Ph}_2\text{P}(\text{CH}_2)_2\text{P}(\text{O})\text{Ph}_2 \cdot \text{CH}_2\text{Cl}_2$  (C), showing 50% probability ellipsoids. The solvent molecule is excluded. Selected bond lengths: Rh–Cl 2.382, Rh–Cl 1.787, Rh–P(2) 2.220, Rh–O(2) 2.109, and P(1)–O(2) 1.514 Å.

(C). The smaller frequency shift (40 cm<sup>-1</sup>) of the P=O stretch and the lack of long range P–O–Rh coupling in (B) indicates that the strength of the phosphine oxide–Rh interaction varies according to (C) > (B) consistent with their observed reactivities toward CO.

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