

Water-soluble iridium and rhodium complexes with tris(hydroxymethyl)phosphine and their catalysis in biphasic hydrogenation and hydroformylation

Atsushi Fukuoka,^{*a†} Wataru Kosugi,^a Fumiaki Morishita,^a Masafumi Hirano,^a Louise McCaffrey,^b William Henderson^b and Sanshiro Komiya^{*a}

^a Department of Applied Chemistry, Tokyo University of Agriculture and Technology, Koganei, Tokyo, 184-8588, Japan

^b Department of Chemistry, University of Waikato, Private Bag 3105, Hamilton, New Zealand

Received (in Cambridge, UK) 28th October 1998, Accepted 5th February 1999

Novel water-soluble Ir and Rh complexes with tris(hydroxymethyl)phosphine catalyse the selective hydrogenation of the C=O bond of cinnamaldehyde and the hydroformylation of pent-1-ene both under biphasic conditions.

The use of aqueous/organic biphasic systems is attracting growing interest in catalytic reactions by transition metal complexes.¹ The biphasic systems have benefits in catalyst separation and recycling, and the reduction or elimination of organic solvents is also advantageous for the development of economical and environmentally friendly processes. The key for such biphasic catalysis is to use water-soluble phosphines as ligands. Since the launch of the commercial propylene hydroformylation process by Ruhrchemie/Rhône-Poulenc,² sulfonated derivatives of PPh₃ such as PPh₂(C₆H₄-*m*-SO₃Na) (TPPMS) and P(C₆H₄-*m*-SO₃Na)₃ (TPPTS) have been widely used as ligands in hydroformylation, hydrogenation, and related reactions catalysed by transition metals.^{1,3}

Tris(hydroxymethyl)phosphine, P(CH₂OH)₃ (THMP) is a highly water-soluble phosphine and has unique reactivity towards a number of reagents to give functionalised hydroxymethylphosphines.⁴ Although many transition metal complexes of THMP are known,⁵ there are limited examples of catalytic reactions using the THMP complexes. Chatt *et al.* reported the first examples of THMP complexes of Rh, Pd and Pt; however, these complexes showed low catalytic activities in hydrogenation and hydroformylation of olefins.^{5a} Recently, Pringle and coworkers showed high efficiency of THMP complexes of Pt, Pd and Ni in catalytic hydrophosphination of formaldehyde,⁶ and biphasic hydrogenation of sorbic acid was reported using THMP complexes of Ru.⁷ In this study, we have prepared novel THMP complexes of Ir and Rh, and their catalytic performances have been tested for hydrogenation of cinnamaldehyde and hydroformylation of pent-1-ene.

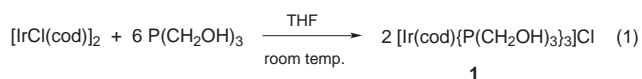
Reaction of [IrCl(cod)]₂ (cod = cycloocta-1,5-diene) with THMP^{5c} (P/Ir ratio = 3) in THF at room temperature under N₂ readily precipitated a white powder, which was purified by recrystallisation from EtOH–Et₂O to give [Ir(cod){P(CH₂OH)₃}₃]Cl **1** in 91% yield [eqn. (1)]. Complex **1** was characterised by analytical and spectroscopic methods.† Electro spray mass spectroscopy (ESMS) of **1** in MeOH at a cone voltage of 20 V gave a single peak at *m/z* 673 due to [Ir(cod)(THMP)₃]⁺ with the same isotope pattern as calculated. In the ³¹P{¹H} NMR of **1** in (CD₃)₂SO, only a singlet peak was observed at δ –17.5, which was shifted lower than free THMP at δ –25.7. A variable-temperature NMR study was performed

using CD₃OD as a solvent. Similarly, only a singlet peak was observed at δ –17.6 with a half width of 5 Hz at 20 °C. On cooling to –80 °C, the singlet peak was gradually shifted lower to δ –15.7 and slightly broadened (half width 12 Hz), and the NMR spectral change was reversible on warming again to 20 °C. The broadening of the peak suggests that **1** is fluxional in this temperature range. When THMP was added to **1**, the peaks of **1** and THMP were independently seen at 20 °C in the ³¹P{¹H} NMR, thus excluding the intermolecular exchange of the ligands. In accordance with the ³¹P{¹H} NMR, the ¹H NMR of **1** gave a doublet (*J*_{HP} 4.5 Hz) due to CH₂ of THMP at δ 4.12 and a broad peak due to OH at δ 5.53, and these peaks were shifted to lower field than those of free THMP [CH₂ at δ 3.85 (t, *J* 5.1 Hz) and OH at δ 4.68 (q, *J* 5.1 Hz)]. The ¹H NMR data including integrals and elemental analysis also support the formation of five-coordinate complex **1**.

One might expect that [IrCl(THMP)₂]₂ or [Ir(cod)(THMP)₂]Cl would also be formed in the reaction of [IrCl(cod)]₂ and THMP; however, in the presence of 3 equiv. of THMP complex **1** is exclusively formed. This type of [Ir(cod)L₃]⁺ complex is known for compact phosphines,^{8a} and [Ir(cod)(PMe₃)₃]Cl was prepared from the reaction of [IrCl(cod)]₂ with 3 equiv. of PMe₃.^{8b}

Similar reaction of [RhCl(cod)]₂ with THMP (P/Rh ratio = 3) in THF at room temperature under N₂ gave a complicated mixture, and isolation of products was unsuccessful. On the other hand, the reaction with 4 equiv. of THMP precipitated a yellow powder, and recrystallisation from EtOH–CH₂Cl₂ gave *cis*-[RhH₂{P(CH₂OH)₃}₄]Cl **2** in 74% yield based on Rh.‡ The formation of the hydride complex was unexpected; however, the presence of Rh–H was confirmed by ¹H NMR and IR. In the ¹H NMR of **2** in (CD₃)₂SO, RhH was observed at δ –11.26 with couplings to Rh and P (*J*_{RhH} 120.8 Hz, *J*_{PH} 12.9 Hz), which is characteristic for *cis*-[RhH₂(PR₃)₄]⁺.⁹ In the IR spectrum, ν_{RhH} appeared at 2007 cm^{–1}. The ³¹P{¹H} NMR gave two doublets of triplets with equal intensity at δ 21.2 (*J*_{RhP} 86, *J*_{PP} 22 Hz) and 34.9 (*J*_{RhP} 97, *J*_{PP} 22 Hz), showing the *cis* geometry of **2**. ESMS and elemental analysis also support the structure of **2**.

The hydride origin is not clear at this moment. THMP itself is a reactive agent, and the reactions of THMP such as deprotonation and elimination of formaldehyde were reported in the preparation of THMP complexes of Pt⁶ and Ru.^{5f} Other possible hydride sources are the cod ligand, the solvents (THF, EtOH, Et₂O and CH₂Cl₂), or a trace of water included in the reaction mixture.§ The possibility of cod is excluded, since a quantitative amount of free cod was observed in the reaction of [RhCl(cod)]₂ with THMP (P/Rh = 4) in (CD₃)₂SO. In the ³¹P{¹H} NMR of this reaction, the resonances of **2** and THMP oxide (δ 44) were detected, thus suggesting that a trace of water can react with Ru intermediates to give **2** and THMP oxide. When D₂O was added to **2** in (CD₃)₂SO, the Rh–H and OH peaks in ¹H NMR were significantly decreased, and the peaks completely disappeared in pure D₂O. This result shows a facile



† Present address: Catalysis Research Center, Hokkaido University, Sapporo 060-0811, Japan. E-mail: fukuoka@cat.hokudai.ac.jp

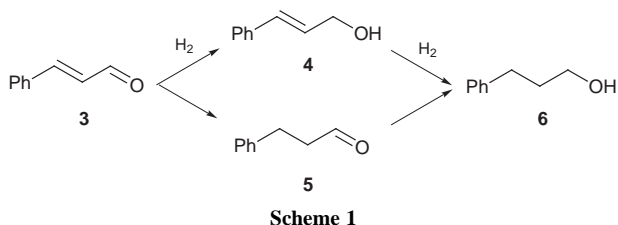


Table 1 Biphasic hydrogenation of cinnamaldehyde catalysed by [Ir(cod){P(CH₂OH)₃}₃]Cl **1**^a

Run	THMP/ 1 ^b	H ₂ ^c /atm	T/°C	Conv. of 3 (%)	Selectivity (%) ^d		
					4	5	6
1	0	30	100	90	76	2	22
2	0	100	100	99	88	2	9
3	5	90	100	20	97	3	0
4	5	90	125	97	97	2	0.3

^a Conditions: **1** 0.015 mmol, cinnamaldehyde 7.5 mmol, water/benzene = 5 ml/5 ml, reaction time 24 h. ^b Molar ratio of added THMP to **1**. ^c Initial pressure at room temperature. ^d (Mol of product)/(mol of converted **3**) × 100.

H–D exchange of Rh–H with D₂O, indicating that Rh–H has protic character.

Hydrogenation of cinnamaldehyde **3** in the biphasic water/benzene media was performed as a test reaction of the catalysis using complex **1** (Scheme 1). Selective hydrogenation of the C=O bond would give cinnamyl alcohol **4**, which is more valuable than hydrocinnamaldehyde **5** from the C=C bond hydrogenation and hydrocinnamyl alcohol **6** from the complete hydrogenation of both the C=O and C=C bonds.^{3c} Under the conditions of 100 °C and 30 atm, with complex **1**, the conversion of **3** was 90% and the proportion of **4**:**5**:**6** was 76:2:22 (Table 1, run 1). At the H₂ pressure of 100 atm, the proportion was 88:2:9, with 99% conversion (run 2). The addition of 5 equiv. of THMP to **1** at 90 atm decreased the conversion to 20%; however, the selectivity of **4** was increased to 97% (run 3). Interestingly, under the conditions of 125 °C and 90 atm in the presence of 5 equiv. of THMP, the conversion was 97% and the proportion of **4**:**5**:**6** was 97:2:0.3 (run 4). The role of added THMP in the catalytic mechanism is being studied.

Rh complex **2** catalysed the biphasic hydroformylation of pent-1-ene to give oxo aldehydes. Under the conditions of 100 °C, CO/H₂ 20 atm/20 atm, water/benzene 4 ml/4 ml, and substrate/catalyst ratio 90, pent-1-ene was quantitatively converted to hexanal (43% yield) and 2-methylpentanal (57%) in 20 h.

In all the catalytic hydrogenation and hydroformylation reactions, the substrates and products were recovered from the benzene layer, and the catalysts were present in the water layer. In order to test the catalyst stability three catalytic runs were repeated, recycling the same water layer containing **1** or **2**. No decrease was observed in the reaction rates and product selectivities, showing the reliable stability of THMP complexes **1** and **2**.

We are grateful to the Asia 2000 Foundation of New Zealand for financial support.

Notes and references

‡ *Selected data*: **1**: ¹H NMR [300 MHz, (CD₃)₂SO]: δ 2.12 and 2.41 (br, total 8H, cod CH₂), 3.90 (br, 4H, cod CH=), 4.12 [d, *J*_{PH} 4.5 Hz, 18H, P(CH₂OH)₃], 5.53 [br, 9H, P(CH₂OH)₃]. ³¹P{¹H} NMR [122 MHz, (CD₃)₂SO]: δ –17.5 (s). ESMS (20 V, MeOH) *m/z* 673 ([Ir(cod){P(CH₂OH)₃}₃]⁺). Mp 115–117 °C (decomp.). Anal. Found: C, 29.05; H, 5.41. Calc. for C₁₇H₃₉O₉P₃ClIr: C, 28.84; H, 5.55%. Molar electrical conductivity λ (MeOH, 24 °C) 9.05 S cm² mol^{–1}. Halogen check (the Beilstein test): positive. Air-stable. Soluble in water, MeOH, EtOH, 2-PrOH, and Me₂SO, but insoluble in benzene, hexane, acetone, or CH₂Cl₂. **2**: IR (KBr, cm^{–1}) 2007 (*ν*_{RhH}). ¹H NMR [300 MHz, (CD₃)₂SO]: δ –11.26 (m, *J*_{RhH} 120.8, *J*_{PH} 12.9 Hz, 2H, RhH), 3.91 and 3.99 [d, *J*_{PH} 4.5 Hz, total 24H, P(CH₂OH)₃], 5.45 and 5.51 [br, 12H, P(CH₂OH)₃]. ³¹P{¹H} NMR [122 MHz, (CD₃)₂SO]: δ 21.2 (dt, *J*_{RhP} 86, *J*_{PP} 22 Hz, 2P, *trans* to H), 34.9 (dt, *J*_{RhP} 97, *J*_{PP} 22 Hz, 2P, *trans* to P). ESMS (20 V, MeOH) *m/z* 601 ([RhH₂{P(CH₂OH)₃}₄]⁺). Mp 145–150 °C (decomp.). Anal. Found: C, 22.48; H, 5.82. Calc. for C₁₂H₃₈O₄P₄ClRh: C, 22.64; H, 6.02%. λ (MeOH, 24 °C) 8.04 S cm² mol^{–1}. Halogen check (the Beilstein test): positive. Stability and solubility are similar to those of **1**.

§ The THF solvent had no contamination of alcohols, which was confirmed by NMR. In the preparation of **2**, RhCl(THMP)₄ was not observed in the crude product but **2** was already formed in 70–80% yield with other uncharacterised species.

- B. Cornils and W. A. Herrmann, in *Applied Homogeneous Catalysis with Organometallic Compounds*, ed. B. Cornils and W. A. Herrmann, VCH, Weinheim, 1996, p. 575; W. A. Herrmann and C. W. Kohlpaintner, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1524; P. Kalcik and F. Masset, *Adv. Organomet. Chem.*, 1992, **34**, 219; I. T. Horvath, *J. Mol. Catal. A*, 1997, **117**; K. Nomura, *J. Mol. Catal. A*, 1998, **130**, 1.
- E. G. Kuntz, *CHEMTECH*, 1987, 570; B. Cornils and E. Wiebus, *CHEMTECH*, 1995, 33.
- (a) M. E. Davis, *CHEMTECH*, 1992, 498; (b) R. V. Chaudhari, B. M. Bhanage, R. M. Deshpande and H. Delmas, *Nature*, 1995, **373**, 502; (c) J. M. Gosselin, C. Mercier, G. Allmang and F. Grass, *Organometallics*, 1991, **10**, 2126; (d) E. Fache, C. Santini, F. Senocq and J. M. Basset, *J. Mol. Catal.*, 1992, **72**, 337; (e) G. Papadogianakis, L. Maat and R. A. Sheldon, *J. Chem. Soc., Chem. Commun.*, 1994, 2659.
- N. J. Goodwin, W. Henderson and J. K. Sarfo, *Chem. Commun.*, 1996, 1551; N. J. Goodwin, W. Henderson, B. K. Nicholson, J. K. Sarfo, J. Fawcett and D. R. Russell, *J. Chem. Soc., Dalton Trans.*, 1997, 4377.
- (a) J. Chatt, G. J. Leigh and R. M. Slade, *J. Chem. Soc., Dalton Trans.*, 1973, 2021; (b) D. L. Dubois and A. Miedanar, *J. Am. Chem. Soc.*, 1987, **109**, 113; (c) J. W. Ellis, K. N. Harrison, P. A. T. Hoye, A. G. Orpen, P. G. Pringle and M. B. Smith, *Inorg. Chem.*, 1992, **31**, 3026; (d) S. Komiya, H. Awata, S. Ishimatsu and A. Fukuoka, *Inorg. Chim. Acta*, 1994, **217**, 201; (e) V. S. Reddy, D. E. Berning, K. V. Katti, C. L. Barnes, W. A. Volkert and A. R. Ketring, *Inorg. Chem.*, 1996, **35**, 1753; (f) L. Higham, A. K. Powell, M. K. Whittlesey, S. Wocadlo and P. T. Wood, *Chem. Commun.*, 1998, 1107.
- P. A. T. Hoye, P. G. Pringle, M. B. Smith and K. Worboys, *J. Chem. Soc., Dalton Trans.*, 1993, 269.
- B. Drießen-Hölscher and J. Heinen, *J. Organomet. Chem.*, 1998, **570**, 141.
- (a) G. J. Leigh and R. L. Richards, in *Comprehensive Organometallic Chemistry*, ed. G. Wilkinson, F. G. A. Stone and E. W. Abel, 1982, vol. 5, p. 600; (b) J. S. Merola and R. T. Kacmarcik, *Organometallics*, 1989, **8**, 778.
- R. A. Jones, F. M. Real, G. Wilkinson, A. M. R. Galas, M. B. Hursthouse and K. M. A. Malik, *J. Chem. Soc., Dalton Trans.*, 1980, 511.

Communication 8/08350I