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Influence of phosphorus and oxygen donor diphosphine ligands on the reactivity of rhodium(I) carbonyl complexes

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ABSTRACT

The dimeric rhodium precursor $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ reacts with two molar equivalent of 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene [xantphos] (**a**), bis(2-diphenylphosphinophenyl)ether [DPEphos] (**b**) and their corresponding dioxide analogues xantphos dioxide (**c**), DPEphos dioxide (**d**) to afford the mono- and dicarbonyl complexes of the type $[\text{Rh}(\text{CO})\text{Cl}(\text{L})]$ (**1a**, **1b**) and $[\text{Rh}(\text{CO})_2\text{Cl}(\text{L})]$ (**1c**, **1d**) respectively, where $\text{L} = \mathbf{a-d}$. The complexes **1a–1d** have been characterized by elemental analyses, IR and NMR (^1H , ^{31}P and ^{13}C) spectroscopy, and the structure of the ligand **d** was determined by single crystal X-ray diffraction. **1a–1d** undergo oxidative addition (OA) reactions with different electrophiles such as CH_3I , $\text{C}_2\text{H}_5\text{I}$ and I_2 to give Rh(III) complexes of the types $[\text{Rh}(\text{CO})_y(\text{COR})\text{Cl}_2\text{L}]$ $\{\text{R} = -\text{CH}_3$ (**2a–2d**), $-\text{C}_2\text{H}_5$ (**3a–3d**); $\text{X} = \text{I}$ and $\text{y} = 0, \text{L} = \mathbf{a, b}$; $\text{y} = 1, \text{L} = \mathbf{c, d}\}$ and $[\text{Rh}(\text{CO})\text{ClI}_2\text{L}]$ (**4a–4d**) respectively. Kinetic data for the reactions of **1a–1d** with CH_3I indicate a pseudo-first-order reaction. The catalytic activity of **1a–1d** for the carbonylation of methanol to acetic acid and its ester was evaluated at different CO pressure 15, 20 and 33 bar at 130°C and a higher Turn Over Number (TON) (679–1768) were obtained compared to that of the well-known commercial species $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ (TON = 463–1000) in each case under the similar experimental conditions.

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1. Introduction

Oxidative addition to organometallic compounds is one of the key elementary steps in many catalytic processes. For this reason, the reaction has been extensively studied, and in the last few years many publications have appeared concerning its implication to ligand-promoted methanol carbonylation to acetic acid production [1–17]. The original $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ catalyst, developed at the Monsanto's laboratories [18] and studied in detail by Forster and co-workers [19,20], is largely used for the industrial production of acetic acid. It is commonly accepted that the rate determining step of this reaction is precisely the oxidative addition of MeI to a square planar d^8 complex [21] and therefore the major focus has been made on the design of catalysts for the improvement of this reaction. Ligands that increase the electron density at the metal center should facilitate the oxidative addition step and, consequently, increase the overall rate of acetic acid formation.

For this purpose, a large variety of rhodium carbonyl complexes have been synthesized by incorporating different ligands into its coordination sphere and evaluated for methanol carbonylation, giving comparable or better activities compared to the original

Monsanto's catalyst [1–17,22–24]. As a part of our continuing research activity [13–17,25–27], we have chosen two diphosphine ligands viz. 9,9-dimethyl-4,5-bis-(diphenylphosphino)xanthene (xantphos) and bis(2-diphenylphosphinophenyl)ether (DPEphos) with different ligand backbone and made them oxygen functionalized by oxidation of the phosphorus atoms. In this paper, we report the synthesis of four rhodium(I) carbonyl complexes containing the 'Soft' (phosphorus) and 'Hard' (oxygen) donor diphosphine ligands and their reactivity with different electrophiles like CH_3I , $\text{C}_2\text{H}_5\text{I}$ and I_2 . The effects of backbone and donor capacity of the ligands on catalytic carbonylation of methanol under different CO pressure have also been studied.

2. Experimental

2.1. General definition

All solvents were distilled under N_2 prior to use. $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ was purchased from M/S Arrora Matthey Ltd., Kolkata, India. The ligands xantphos and DPEphos were purchased from Across Organics, Belgium and used without further purification. H_2O_2 was obtained from Ranbaxy, New Delhi, India and estimated before use.

Elemental analyses of C and H were performed on a Perkin-Elmer 2400 elemental analyzer. The elements P, Cl and Rh were analyzed quantitatively by standard analytical techniques [28,29],

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and the quantity of O was determined by difference. IR spectra (4000–400 cm^{-1}) were recorded in KBr discs and CHCl_3 on a Perkin-Elmer system 2000 FT-IR spectrophotometer. The ^1H , ^{13}C and ^{31}P NMR spectra were recorded at room temperature in CDCl_3 solution on a Bruker DPX-300 Spectrometer and chemical shifts were reported relative to SiMe_4 and 85% H_3PO_3 as internal and external standards respectively. Mass spectra of the complexes were recorded on ESQUIRE 3000 Mass Spectrometer. The carbonylation reactions of methanol were carried out in a high pressure reactor (Parr-4592, USA) fitted with a pressure gauge and the reaction products were analyzed by GC (Chemito 8510, FID).

2.2. Synthesis of xantphos dioxide (c) and DPEphos dioxide (d)

The ligands xantphos and DPEphos dioxide were synthesized by oxidation of xantphos and DPEphos respectively by H_2O_2 following the literature protocol [25,27]

Analytical data:

Xantphos dioxide (c)

IR (KBr, cm^{-1}): 1193 [$\nu(\text{P}=\text{O})$]. ^1H NMR (CDCl_3 , ppm): δ 6.74–7.74 (m, 30H, Ph), 2.17 (s, 6H, CH_3). ^{13}C NMR (CDCl_3 , ppm): δ 153.10–124.1 (m, Ar), δ 32.3, 34.9 (s, CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , ppm): δ 30.95 [s, $\text{P}=\text{O}$]. Elemental analyses; Found (Cald. for $\text{C}_{39}\text{H}_{32}\text{O}_3\text{P}_2$): C 73.98 (74.40); H 5.02 (5.08).

DPEphos dioxide (d)

IR (KBr, cm^{-1}): 1198, 1186 [$\nu(\text{P}=\text{O})$]. ^1H NMR (DMSO- D_6 , ppm): δ 6.11–6.18, 7.2–7.69 (m, 28H, Ar), ^{13}C NMR (DMSO- D_6 , ppm): δ 122.5–134.21 (m, Ar), δ 153.4 (s, O- C_{phenyl}). $^{31}\text{P}\{^1\text{H}\}$ NMR (DMSO- D_6 , ppm): δ 26.21, 24.21 [s, $\text{P}=\text{O}$]. Elemental analyses; Found (Cald. for $\text{C}_{36}\text{H}_{28}\text{O}_3\text{P}_2$): C 75.18 (75.71); H 4.73 (4.90).

2.3. Synthesis of starting material

$[\text{Rh}(\text{CO})_2\text{Cl}]_2$ was prepared by passing CO gas over $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ at 100 °C in the presence of moisture [30].

2.4. Synthesis of the complexes $[\text{Rh}(\text{CO})_x\text{CIL}]$ (**1a–1d**), where $L = \text{xantphos}$ (**a**), DPEphos (**b**) and $x = 1$; $L = \text{xantphos dioxide}$ (**c**), DPEphos dioxide (**d**) and $x = 2$

$[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (100 mg) was dissolved in dichloromethane (10 cm^3) and to that solution, a stoichiometric quantity (Rh:L = 1:1) of the respective ligands were added. The reaction mixture was stirred at room temperature (r.t.) for about 10–60 min and the solvent was evaporated under vacuum. The yellowish red coloured compounds so obtained were washed with diethyl ether and stored over silica gel in a desiccator.

Analytical data for the complexes **1a–1d** are given as follows:

$[\text{Rh}(\text{CO})\text{Cl}(\text{xantphos})]$ (**1a**)

IR (KBr, cm^{-1}): 1974 [$\nu(\text{CO})$]. ^1H NMR (CDCl_3 , ppm): δ 6.82–7.09, 7.31–7.88 (m, Ph), δ 1.69 (s, CH_3). ^{13}C NMR (CDCl_3 , ppm): δ 152.2–126.5 (m, Ar), δ 63.8 (CMe_2), δ 32.5 (s, CH_3), δ 183.3 (s, CO). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , ppm): δ 22.55 [d, $J_{\text{P-Rh}} = 123.5$ Hz]. Elemental analyses; Found (Cald. for $\text{C}_{40}\text{H}_{32}\text{O}_2\text{P}_2\text{ClRh}$), C 63.85 (64.48); H 4.21 (4.30); P 8.45 (8.32); Cl 4.89 (4.77); Rh 13.72 (13.82); O 4.88 (4.30).

$[\text{Rh}(\text{CO})\text{Cl}(\text{DPEphos})]$ (**1b**)

IR (KBr, cm^{-1}): 1985 [$\nu(\text{CO})$]. ^1H NMR (CDCl_3 , ppm): δ 6.80–7.20, 7.30–7.37, 7.54–7.79 (m, Ph), ^{13}C NMR (CDCl_3 , ppm): δ 154.8–128.2 (m, Ar), δ 180.9 (s, CO). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , ppm): δ 27.3 [d, $J_{\text{P-Rh}} = 119.2$ Hz]. Elemental analyses; Found (Cald. for $\text{C}_{37}\text{H}_{28}\text{O}_2\text{P}_2\text{ClRh}$), C 62.91 (63.06); H 3.73 (3.97); P 8.85 (8.79); Cl 5.15 (5.04); Rh 14.23 (14.61); O 5.13 (4.54).

$[\text{Rh}(\text{CO})_2\text{Cl}(\text{xantphos dioxide})]$ (**1c**)

IR (KBr, cm^{-1}): 1983, 2058 [$\nu(\text{CO})$], 1190, 1185 [$\nu(\text{P}=\text{O})$]. ^1H NMR (CDCl_3 , ppm): δ 6.68–7.61 (m, Ph), δ 1.69 (s, CH_3). ^{13}C NMR (CDCl_3 , ppm): δ 153.8–125.2 (m, Ar), δ 34.23 (s, CH_3), δ 178.5,

180.3 (s, CO). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , ppm): δ 45.5 (d, $J_{\text{P-P}} = 69.2$ Hz), δ 48.04 (d, $J_{\text{P-P}} = 69.2$ Hz). Elemental analyses; Found (Cald. for $\text{C}_{41}\text{H}_{32}\text{O}_5\text{P}_2\text{ClRh}$), C 60.73 (61.17); H 3.78 (3.98); P 8.01 (7.70); Cl 4.59 (4.41); Rh 12.60 (12.79); O 10.29 (9.94).

$[\text{Rh}(\text{CO})_2\text{Cl}(\text{DPEphos dioxide})]$ (**1d**)

IR (KBr, cm^{-1}): 1996, 2071 [$\nu(\text{CO})$], 1189, 1186 [$\nu(\text{P}=\text{O})$]. ^1H NMR (DMSO- D_6 , ppm): δ 6.15–6.38, 7.11–7.82 (m, Ph). ^{13}C NMR (DMSO- D_6 , ppm): δ 119.2–138.5 (m, Ar), δ 153.8 (s, O- C_{phenyl}), δ 182.5, 185.9 (s, CO). $^{31}\text{P}\{^1\text{H}\}$ NMR (DMSO- D_6 , ppm): δ 35.8, 24.7 (s, $\text{P}=\text{O}$). Elemental analyses; Found (Cald. for $\text{C}_{38}\text{H}_{28}\text{O}_5\text{P}_2\text{ClRh}$), C 58.98 (59.65); H 3.51 (3.66); P 8.32 (8.10); Cl 4.41 (4.64); Rh 13.82 (13.46); O 10.96 (10.47).

2.5. Reactivity of $[\text{Rh}(\text{CO})\text{CIL}]$ (**1a,1b**) and $[\text{Rh}(\text{CO})_2\text{CIL}]$ (**1c,1d**) with CH_3I , $\text{C}_2\text{H}_5\text{I}$ and I_2

2.5.1. Synthesis of $[\text{Rh}(\text{CO})_y(\text{COR})\text{CIXL}]$ $R = \text{CH}_3$, $X = \text{I}$, $y = 0$

(**2a,2b**), $y = 1$ (**2c,2d**); $R = \text{C}_2\text{H}_5$, $X = \text{I}$, $y = 0$ (**3a,3b**), $y = 1$ (**3c,3d**)

$[\text{Rh}(\text{CO})_2\text{CIL}]$ (50 mg) was dissolved in dichloromethane (5 cm^3) and each of RX (3 cm^3) (RX = CH_3I , $\text{C}_2\text{H}_5\text{I}$) was added to it. The reaction mixture was then stirred at r.t. for about 2–10 h for CH_3I and $\text{C}_2\text{H}_5\text{I}$ respectively. The colour of the solution changed from yellowish red to dark reddish brown and the solvent was evaporated under vacuum. The compounds so obtained were washed with diethyl ether and stored over silica gel in a desiccator.

2.5.2. Synthesis of $[\text{Rh}(\text{CO})\text{CII}_2\text{L}]$ (**4a–4d**)

$[\text{Rh}(\text{CO})_2\text{CIL}]$ (50 mg) was dissolved in CH_2Cl_2 (15 cm^3) and to this solution I_2 (25 mg) was added. The reaction mixture was then stirred at r.t. for about 4 h. The solvent was evaporated under vacuum and the brown coloured compound so obtained were washed with hexane and stored over silica gel in a desiccator.

2.6. X-ray structural analysis

Single crystal of **d** was grown by slow evaporation of a saturated solution of **d** in acetone. The intensity data of the compounds were collected on Bruker Smart-CCD with Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K. The structure was solved with SHELXS-97 and refined by full-matrix least squares on F^2 using SHELXL-97 computer program [31]. Hydrogen atoms were idealized by using the riding models.

2.7. Kinetic experiment

The kinetic experiments of OA reaction of complexes **1a–1d** with CH_3I were monitored using FT-IR spectroscopy in a solution cell (CaF₂ windows, 1.0 mm path length). In order to obtain pseudo-first-order condition, excess of CH_3I relative to metal complex was used. FT-IR spectra (4.0 cm^{-1} resolution) were scanned in the $\nu(\text{CO})$ region (2200–1600 cm^{-1}) and saved at regular time interval using spectrum software. After completion of experiment, absorbance versus time data for the appropriate $\nu(\text{CO})$ frequencies were extracted by subtracting the solvent spectrum and analyzed off line using OriginPro 7.5 software. Kinetic measurements were made by following the decay of lower frequency $\nu(\text{CO})$ band of the complexes in the region 1974–1996 cm^{-1} . The pseudo-first-order rate constants were found from the gradient of the plot of $\ln(A_0/A_t)$ versus time, where A_0 is the initial absorbance and A_t is the absorbance at time t .

2.8. Carbonylation of methanol using complexes **1a–1d** as catalyst precursors

CH_3OH (0.099 mol, 4 cm^3), CH_3I (0.016 mol, 1 cm^3), H_2O (0.055 mol, 1 cm^3) and catalyst (0.0514 mmol) were placed in a

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