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Dicarbonylruthenium(II) complexes of diphosphine ligands and their catalytic activity

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ABSTRACT

The hexa-coordinated chelate complexes of the type $[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{P-P})]$ (**1a,b**) [where P-P = 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene(**a**) and bis(2-diphenylphosphinophenyl)ether(**b**)] have been synthesized by reacting the polymeric precursor $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$ with the ligands in 1:1 molar ratio. The complexes **1a,b** are characterized by elemental analyses, Mass, IR and NMR spectroscopy together with the single crystal X-ray structure determination of **1a**. The compound **1a** crystallizes in a monoclinic system with space group *C2/c* showing a slightly distorted octahedral geometry around the Ru centre. The complexes **1a** and **1b** are thermally stable up to 300 °C and exhibit high catalytic activity in transfer hydrogenation of aldehyde and ketones to corresponding alcohols. The complexes **1a** and **1b** show much higher catalytic activity for the hydrogenation of aldehyde than ketones. In general, the catalytic efficiency of **1b** is higher compared with **1a**.

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The stereo-electronic properties of phosphines and their derivatives have aroused much interest in the recent time because of their reactivity, structural novelty and catalytic activity [1–10]. A deeper insight into the catalytic systems and the relationship between ligand properties and catalytic performance will give access to more catalysts via rational design of the ligands. An important aspect to design the ligands is based on their natural bite angle, introduced by Casey and Whiteker [11] and is one of the most extensively applied parameter for diphosphines. The metal complexes containing large natural bite angle ligands such as xantphos [9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene], DPEphos [bis(2-diphenylphosphinophenyl)ether] and others with a relatively comparable backbone exhibit interesting coordination chemistry as well as catalytic activity [1,2,9,12]. Over the last decades, the ruthenium catalyzed reactions directed to organic synthesis have got much attention and a large number of highly efficient synthetic approaches are well documented in literature [13–17]. As a part of our ongoing systematic study [3,18–21], we report here the synthesis of two dicarbonylruthenium(II) complexes **1a,b** containing xantphos(**a**) and DPEphos(**b**) chelating ligands together with the X-ray crystal structure of **1a**. The catalytic activity of **1a,b** was also investigated in transfer hydrogenation reaction.

The ligands **a** and **b** react with the polymeric precursor $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$ in 1:1 molar ratio to afford hexa-coordinated com-

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plexes of the type $[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{P-P})]$ (**1a,b**) (Scheme 1), which are isolated as air-stable, light yellow solids (thermal stability: >300 °C). The synthesized compounds have been characterized by elemental analyses, Mass spectrometry, IR and NMR spectroscopy [22] together with the single crystal X-ray structure determination of **1a** (Fig. 1). The IR spectra of **1a** and **1b** show two equally intense $\nu(\text{CO})$ bands in the region 1973–2073 cm^{-1} confirming the presence of two terminal carbonyl groups cis to one another. The ¹³C NMR spectra show only one signal for the two non-equivalent carbonyl carbons as broad singlet in the region $\delta = 184$ –189 ppm for both **1a** and **1b**. ³¹P{¹H} NMR spectra of **1a** and **1b** exhibit two sharp singlets at around $\delta = 20.21$ and 14.35 ppm, respectively, for two pentavalent P-atoms, exhibiting a down field shift compared to the free ligands [$\delta = -12.3$ ppm(**a**) and -16.03 ppm(**b**)], which is in good agreement with the chelate formation in the complexes. Elemental analyses and mass spectrometric results are consistent with the proposed formula of **1a** and **1b**, which are also substantiated by the single crystal X-ray structure of **1a** (Fig. 1). Regrettably, crystals suitable for single-crystal X-ray diffraction were not obtained for **1b**, although several attempts have been made.

The complex **1a** crystallizes in a monoclinic system with space group *C2/c* where the Ru atom is situated at the centre of a distorted octahedral environment formed by two P donor, two CO and two Cl atoms. The selected bond lengths and bond angles are presented in Fig. 1. The longer bond length of Ru1–P1 (2.5492(11) Å) compared with Ru1–P2 (2.3887(11) Å) may indicate a weaker interaction in the former and is likely to be cleaved more

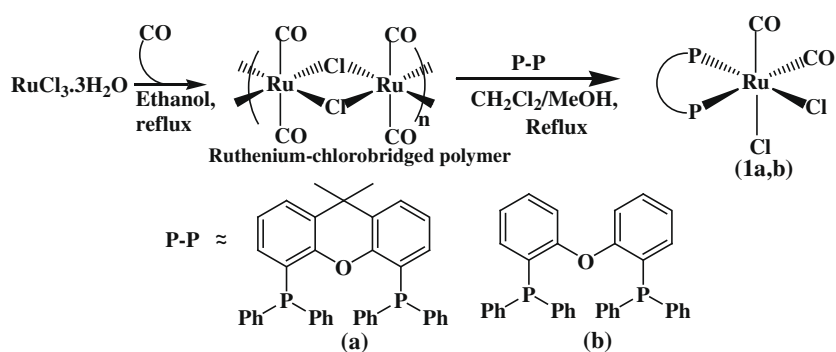
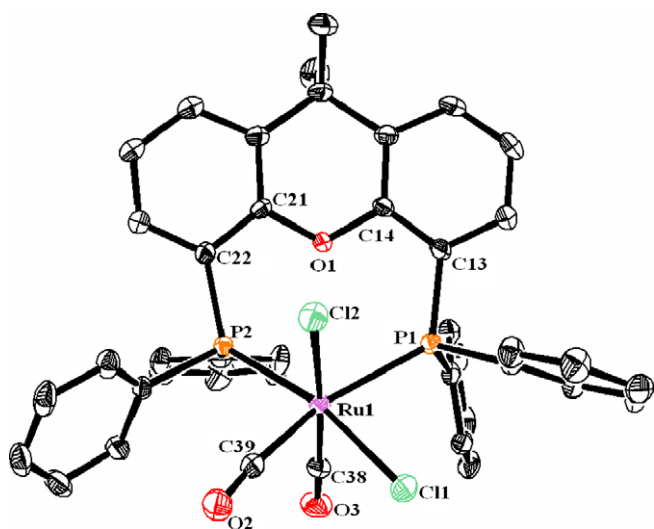
Scheme 1. Syntheses of **1a** and **1b**.

Fig. 1. ORTEP drawing (30% probability) of the complex **1a**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): P1–Ru1 2.5492(11), P2–Ru1 2.3887(11), Cl1–Ru1 2.4583(12), Cl2–Ru1 2.4308(12), C38–Ru1 1.882(5), C38–O3 1.114(6), C39–Ru1 1.926(5), C39–O2 1.100(6), P2–Ru1–P1 107.56(4), C39–Ru1–C38 89.4(2), C39–Ru1–P1 163.52(14), Cl1–Ru1–Cl2 94.66(5).

easily during catalytic reaction. The natural bite angle, 111.7° of the free xantphos ligand reduces to 107.56° (bite angle, P1–Ru1–P2) upon complexation. The P1–Ru1–P2 plane is inclined by an angle 38.48° to the plane of the backbone of xantphos ligand. The two aromatic rings of the backbone are not coplanar (the angle between the two phenyl planes is 14.74°) due to the presence of sp^3 carbon and the oxygen atom in the ring. This folded structure render the two methyl groups of the backbone locate equatorially and axially, respectively, indicated by the two different methyl signals shown in the NMR spectrum.

The complex **1a** exhibits some interesting intermolecular interactions involving shorter distances than the sum of van der Waals radii. The interactions between these molecules are presented by dotted lines and summarized in Fig. 2. The monomeric units of **1a** are held together through bifurcated [23,24] intermolecular C–H \cdots O, C–H $\cdots\pi$ and C–H \cdots Cl, C–H $\cdots\pi$ interactions (Fig. 2) which are considered as weak hydrogen bonds [24–26]. These hydrogen bondings are mainly observed between one of the H atoms of the phenyl ring of xantphos ligand and O atom of CO group or Cl atom of the adjacent molecule. Such interactions provide an additional stabilization to crystal cohesion and are essentially attributable to the supramolecular nature of most organometallic molecules.

The catalytic activities of **1a** and **1b** were investigated for transfer hydrogenation and the complexes were found to exhibit high

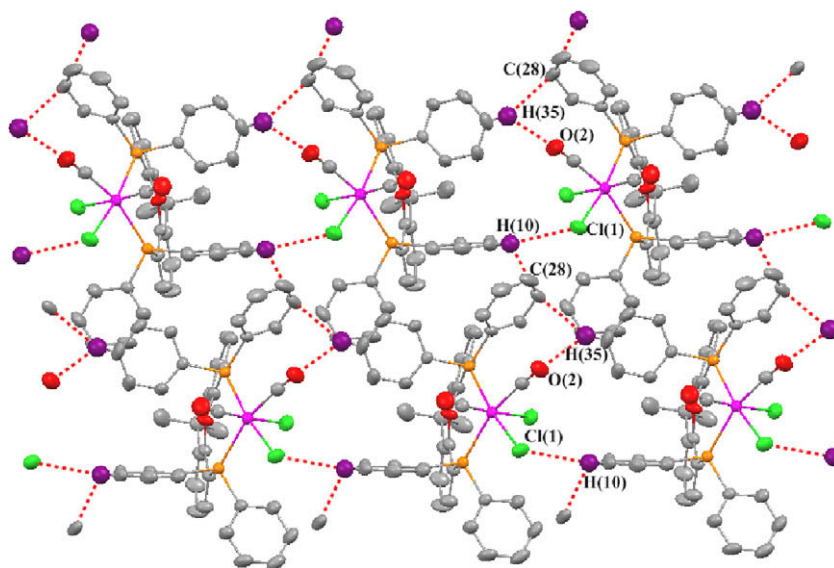


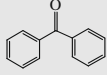


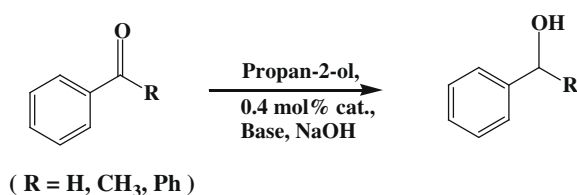
Fig. 2. Intermolecular short contacts in **1a** (when viewed along *b*-axis) through C–H \cdots O [H(35) \cdots O(2) j 2.645 Å], C–H $\cdots\pi$ [H(35) \cdots C(28) j 2.714 Å; H(10) \cdots C(28) i 2.852 Å] and C–H \cdots Cl [H(10) \cdots Cl(1) j 2.901 Å] interactions (broken lines). Symmetry codes: (i) $x, -1 + y, z$ (ii) $x, 1 - y, \frac{1}{2} + z$. All the hydrogen atoms except those involved in hydrogen bonding have been omitted for clarity.

Table 1
Catalytic transfer hydrogenation of selective substrates by complexes **1a,b**.

Entry	Substrate	Reaction time (h)	Catalysts	% Conv ^a
1		2.5	1a	98
		2	1b	99
2		24	1a	85
		18	1b	91
3		24	1a	72
		24	1b	89

Conditions: reactions were carried out at 83 °C using 0.4 mol% of substrate. Ketone/Ru/NaOH ratio: 200/1/10.

^a Conversion of the substrates were obtained from GC analyses.



Scheme 2. Reduction of aldehyde and ketones.

efficiency in the reduction of aldehyde and ketones to their corresponding alcohols (Scheme 2). Despite the large number of Ru(II) catalysts reported for this particular transformations [27–30], the use of ruthenium(II) carbonyl species (which are generally considered as sluggish catalysts for hydrogenation reaction [31]) are quite scanty [29]. However, aldehydes are difficult to reduce by catalysts commonly used for transfer hydrogenation, and controlling the chemoselectivity of the reaction presents a further challenge [32,33]. In the present study, the catalytic conversion by **1a** and **1b** for some selected aldehyde and ketones are found in the range 72–99% within the reaction time of 2–24 h (Table 1). The catalytic activity of the complexes though exhibit slightly lower efficiency for the hydrogenation of ketones (acetophenone, benzophenone), but, show higher activity in case of aldehyde (benzaldehyde) than the reported catalysts with similar configuration [29,34]. Interestingly, the rate of catalytic conversion of aldehyde is found to be about eight times faster than the analogous ketones. However, the catalytic efficacy of **1a** and **1b** decreases in presence of the bulky substituent to the substrate. This might be due to the steric hindrance caused by the bulky diphosphine ligand around the metal centre during substrate binding. In general, the catalytic activity of **1b** is higher than **1a**, which may be due to the flexible backbone of the ligand **b** [35,36].

In summary, the synthesis and characterization of two new ruthenium(II) carbonyl complexes **1a** and **1b** have been carried out. Intermolecular C–H···O, C–H···π and C–H···Cl interactions have been found to greatly stabilize the supramolecular structure of **1a** in the solid state, as determined by single crystal X-ray diffraction. **1a** and **1b** exhibit high thermal stability (>300 °C) and are found to be active in catalytic transfer hydrogenation of aldehyde and ketones. However, the complexes show much higher catalytic efficiency for the reduction of aldehyde than ketones.

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Appendix A. Supplementary material

CCDC 681434 contains the supplementary crystallographic data for **1a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2009.06.034.

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- [22] Synthesis of the complex [Ru(CO)₂Cl₂(P-P)] (**1a,b**): [Ru(CO)₂Cl₂]_n (0.439 mmol, 100 mg) in methanol (10 cm³) was refluxed with an equimolar quantity of the ligands xantphos (**a**) and DPEphos (**b**), respectively in dichloromethane to produce **1a,b**. The solvent was removed under vacuum and washed with diethyl ether. The resulting yellow compound was recrystallised from dichloromethane/*n*-hexane to give bright yellow powder. **1a**: IR (KBr, cm⁻¹): 2073, 1993 [ν(CO)]. ¹H NMR (CDCl₃, ppm): δ 7.81 (d, 2H, Ar), δ 7.69–7.44 (m, 12H, C₆H₅P), δ 6.83 (t, 2H, Ar), δ 6.58 (2H, Ar), δ 1.60 (s, 3H, CH₃), δ 1.68 (s, 3H, CH₃). ¹³C NMR (CDCl₃, ppm): δ (154.85–121.76) (Ar), δ 65.2 (Cme₂), δ 33.1, 34.8 (CH₃), δ 184.3 (CO). ³¹P{¹H} NMR (CDCl₃, ppm): δ 20.21 (s, 2P). Elemental analyses; found (Calc. for C₄₁H₃₂Cl₂O₃P₂Ru): C, 60.71 (61.00), H, 3.89 (3.97). Mass: 806.8 (m/z⁺), 779.6 (m/z⁺ – CO). **1b**: IR (KBr, cm⁻¹): 2075, 1991 [ν(CO)].

- ^1H NMR (CDCl_3 , ppm): δ 6.75–7.12 (m, 8H, Ar), δ 7.61–8.12 (m, 20H, Ar). ^{13}C NMR (CDCl_3 , ppm): δ (127.2–135.7) (m, Ar), δ 158.7 (d, O–C_{phenyl}), δ 189.3 (s, CO). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , ppm): δ 39.32 (s, 2P). Elemental analyses; found (Calc. for $\text{C}_{38}\text{H}_{28}\text{Cl}_2\text{O}_3\text{P}_2\text{Ru}$): C, 58.85 (59.49), H, 3.54 (3.65). Mass: 766.3 (m/z^+), 737.9 ($m/z^+ - \text{CO}$).
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