



Communication

Chlorocarbonyl ruthenium(II) complexes of tripodal triphos {MeC(CH₂PPh₂)₃}: Synthesis, characterization and catalytic applications in transfer hydrogenation of carbonyl compounds

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ABSTRACT

The complex [Ru(CO)₂(triphos-κ²P)Cl₂] (**1**) underwent decarbonylation in dichloromethane solution under air over a period of about two weeks to afford the chelated monocarbonyl complex [Ru(CO)(triphos-κ³P)Cl₂] (**2**). The Single Crystal X-ray structure of **2** showed a slightly distorted metal centred complex. The catalytic activity of one of the complexes [Ru(CO)(triphos-κ³P)Cl₂] (**2**) was examined in the transfer hydrogenation of aromatic carbonyl compounds and was found to be efficient with conversion up to 100% in the presence of isopropanol/NaOH.

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1. Introduction

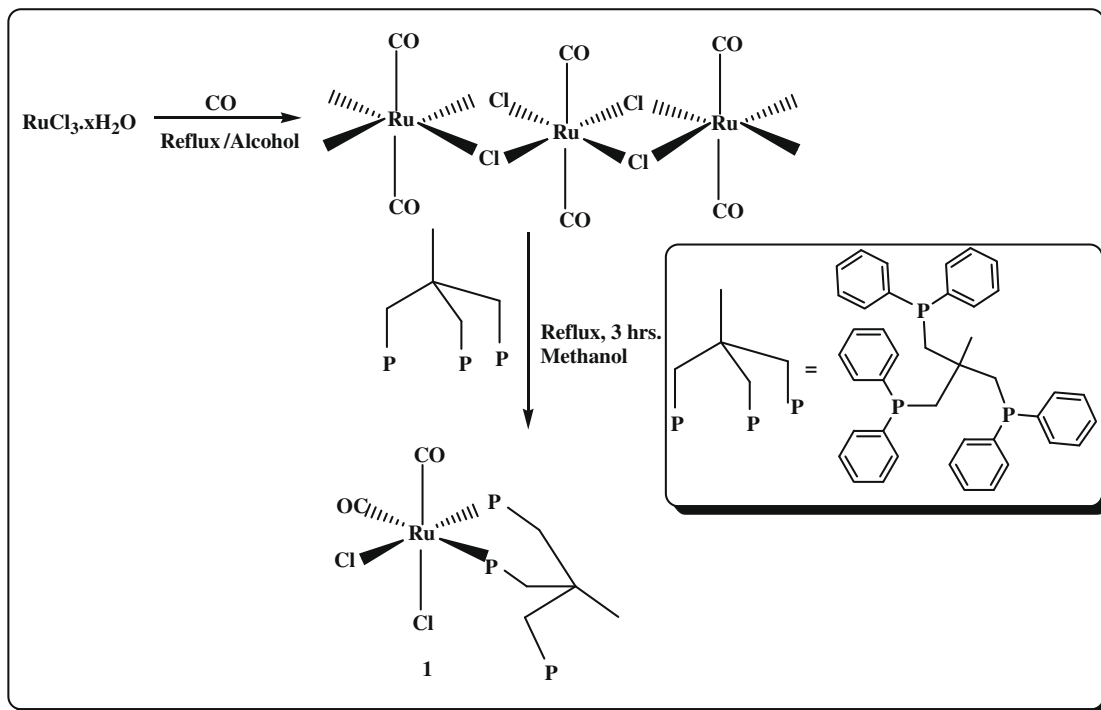
Tridentate tripodal phosphines are recognized as one of the most important classes of ligands having widespread applications in coordination chemistry [1–10]. Such ligands provide an important advantage over monodentate phosphines with respect to greater control of the coordination number, stoichiometry and stereochemistry of their complexes [11]. Moreover, polyphosphine complexes usually have two or more chelate rings which minimize the unwanted isomers, and therefore, expected to show better catalytic activities. Among these ligands, the C₃-symmetric 1,1,1-tris(diphenylphosphinomethyl)ethane (triphos){MeC(CH₂PPh₂)₃} and its derivatives are the most extensively investigated ones forming a large variety of transition metal complexes which are found to have applications in catalysis [12–22]. Bianchini and coworkers in particular, pioneering the use of this ligand in transition metal catalysis using platinum group metals for a number of processes including hydrogenation, hydroformylation, oxidation, etc. [23–30]. One preliminary report for synthesis of complexes such as [Ru(CO)₂{MeC(CH₂PPh₂)₃}Cl₂] was found in literature [31]. As a part of our continuing research activities [19,32–39], we report here the synthesis, detailed spectroscopic characterization of ruthenium(II) carbonyl complexes of the type [Ru(CO)₂(triphos-κ²P)Cl₂] (**1**) and [Ru(CO)(triphos-κ³P)Cl₂] (**2**). The molecular

structure of **2** established by Single Crystal X-ray diffraction as well as its catalytic transfer hydrogenation activities are also reported.

2. Results and discussion

The polymeric complex [Ru(CO)₂Cl₂]_n reacts with equimolar quantity of the triphos ligand by cleavage of the chloro bridge to afford **1** in good yield as a yellow crystalline solid (Scheme 1). The molecular composition of the complex is well supported by elemental analyses data. The probable molecular structure of **1** (Fig. 1) was assigned by elemental analyses, IR, NMR and mass spectrometry, where the tripodal triphos ligand attached in a bidentate manner. The bidentate coordination mode of the tripodal triphos ligand in **1** is confirmed by both the IR and ³¹P NMR spectral data. The IR spectra of **1** show two equally intense ν(CO) bands at 2054 and 1988 cm⁻¹ attributing the two terminal carbonyl groups *cis* to one another. The ¹H NMR spectra of **1** show characteristics resonance at δ = 2.58–2.67 ppm (–CH₂–) and δ = 0.98 ppm (–CH₃–), respectively, along with their phenylic protons in the range 6.61–8.05 ppm. The ³¹P NMR spectra for **1** at room temperature exhibit resonances at δ = 34.07 ppm for the coordinated phosphorus atoms and δ = –23.51 ppm due to the free dangling phosphorus atom. The free ligand, {MeC(CH₂PPh₂)₃}, has a single resonance at δ = –20.32 ppm in CDCl₃ at 25 °C is close to the free phosphorus in **1**. Both ¹H and ³¹P NMR spectra are in accordance with stereochemical rigidity of **1** in CDCl₃ solution at 25 °C. However, attempts to develop suitable single crystal of **1** for

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Scheme 1. Synthesis of $[\text{Ru}(\text{CO})_2(\text{triphos-}\kappa^2\text{P})\text{Cl}_2]$ (**1**).

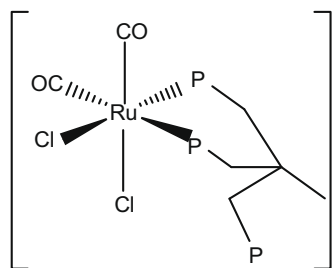
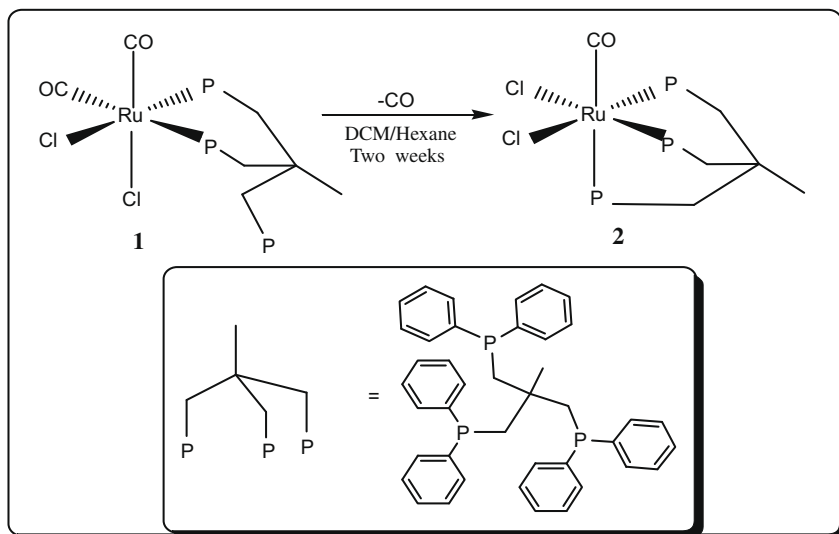


Fig. 1. Probable structure of $[\text{Ru}(\text{CO})_2(\text{triphos-}\kappa^2\text{P})\text{Cl}_2]$ (**1**).

X-ray analysis from dichloromethane solution under air led to the formation of $\kappa^3\text{-P}$ coordinated complex $[\text{Ru}(\text{CO})(\text{triphos-}\kappa^3\text{P})\text{Cl}_2]$ (**2**) over a period of about two weeks in relatively good yield (Scheme 2). The resulting monocarbonyl complex exhibits single terminal $\nu(\text{CO})$ band at 1959 cm^{-1} . Such decarbonylation reaction was also observed in ruthenium complexes of the type $[\text{Ru}(\text{CO})_2(\text{Ph}_2\text{PCH}_2\text{P}(\text{S})\text{Ph}_2)_2\text{Cl}_2]$ [36]. The dangling P atom in **1** underwent chelation which is substantiated by a single ^{31}P NMR resonance data. In order to obtain an unambiguous characterization of **2**, an X-ray diffraction study was undertaken. The arrangement of the atoms in the crystal is shown in Fig. 2. Ru(II) is situated in the centre of a slightly distorted octahedral coordination environment. Crystal data and structure refinement as well as some selected bond lengths (\AA) and bond angles ($^\circ$) for the complex **2** are



Scheme 2. Decarbonylation reaction of **1**.

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