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Trans/*cis* isomerization of [RuCl$_2${H$_2$C=C(CH$_2$PPh$_2$)$_2$)}(diamine)] complexes: Synthesis, spectral, crystal structure and DFT calculations and catalytic activity in the hydrogenation of α,β-unsaturated ketones

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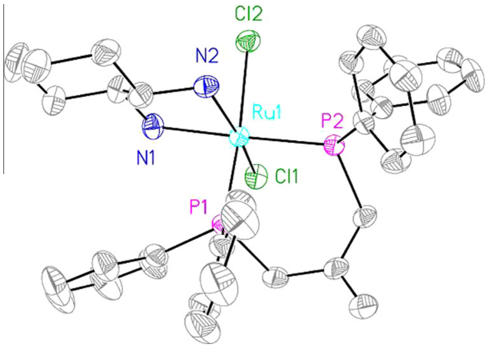
HIGHLIGHTS

- Mixed-ligands *trans*/*cis*-[Ru$^{(II)}$(P—P)(N—N)Cl$_2$] complexes are synthesized.
- The complexes have significant activity and selectivity as hydrogenation catalysts for α,ß-unsaturated ketone.
- *Trans*/*cis*-complexes was followed by using cyclic voltammetry, ^{31}P{^{1}H} NMR and UV–vis.
- The electronic spectra of *cis*/*trans*-complexes are explained by DFT and TDDFT.

GRAPHICAL ABSTRACT



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ABSTRACT

Three complexes of the general formula *trans*/*cis*-[Ru$^{(II)}$(dppme)(N—N)Cl$_2$] {dppme is H$_2$C=C(CH$_2$PPh$_2$)$_2$ and N—N is 1,2-diaminocyclohexane (*trans*/*cis*-(**1**)) and 1-methyl-1,2-diaminopropane (*trans*-(**2**)} were obtained by reacting *trans*-[RuCl$_2$(dppme)$_2$] with an excess amount of corresponding diamine in CH$_2$Cl$_2$ as a solvent. The complexes were characterized by an elemental analysis, IR, ^{1}H, ^{13}C and ^{31}P{1H} NMR, FAB-MS and UV–visible. The *trans*-(**1**) (kinetic product) readily isomerizes to the *cis*-(**1**) (thermodynamic product) and this process was followed by using ^{31}P{^{1}H} NMR, cyclic voltammetry and UV–vis spectroscopy. The electrochemical studies on complex (**1**) reveal that the Ru(III)/Ru(II) couples are sensitive to the isomer (*trans*/*cis*) formed. The *cis*-(**1**) was confirmed by X-ray structure and ^{31}P{^{1}H} NMR. Transfer-hydrogenation reactions for reduction of *trans*-4-phenyl-3-butene-2-one were conducted using complexes *trans*/*cis*-(**1**) and *trans*-(**2**). The electronic spectra of *cis*/*trans*-(**1**) in dichloromethane were calculated with the use of time-dependent DFT methods.

Introduction

The chemistry of [Ru$^{(II)}$(P—P)(N—N)] {P—P are diphosphine and N—N is diamine ligands) has been widely studied and several complexes containing this fragment (or part) have been synthesized

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[1–10]. These complexes received much attention due to their catalytic activity [4–10] mainly after the works published by Noyori [7,8] and Morris [4–6]. The diphosphine is a very versatile ligand since it can be coordinated to a transition metal as a *cis*-chelate [1–3], *trans*-spanning and bridging, leading to a great diversity of structures and properties for its complexes [11]. The catalytic reactivity and selectivity for the diphosphine complexes can be achieved through well-designed structural, electronic, and stereochemical features of these complexes [4–10]. James and coworkers [11] published a series of complexes with the general formula [$RuCl_2$(dppf)(N—N)] {dppf is 1,1′-Bis(diphenylphosphino)ferrocene and N—N are diimines (2,2-bipyridine and 1,10-phenanthroline) and diamines ligands}. They found that complexes with diamines ligands were isolated as *trans*-isomers (*trans*-dichlorides) while with the diimines were isolated as *cis*-isomers. They claimed that the formation of *trans*-isomers is due to the rigid character of the diimines while *cis*-isomers are due to the flexible character of diamines ligands. For mixed-ligands diphosphine and diamine complexes, [$Ru^{(II)}$(P—P)(N—N)Cl_2], and due to the presence of the P-donor ligand in the backbone of such coordinated complexes, the *trans*/*cis* isomerism behavior during reaction processes can be easily monitored by $^{31}P\{^1H\}$ NMR [10,12–14].

In this work we present the syntheses, characterization, and electrochemical studies of mixed-ligands *trans*/*cis*-[$Ru^{(II)}$(dppme)(N—N)Cl_2] complexes (*trans*/*cis*-(**1**)) {dppme is $H_2C{=}C(CH_2PPh_2)_2$ and N—N is 21,2-diaminocyclohexane} and *trans*-(**2**) (N—N is 1-methyl-1,2-diaminopropane) (scheme 1). In addition, we show that the *trans*-(**1**) (kinetic) readily isomerizes to the *cis*-(**1**) (thermodynamic product) and this process was followed by $^{31}P\{^1H\}$ NMR and UV–vis spectroscopy. The catalytic activity of *trans*/*cis*-(**1**) and *trans*-(**2**) complexes for hydrogenation of α,ß-unsaturated ketone was tested. Crystal structure of *cis*-(**1**) is presented and discussed. The electronic spectra of *cis*/*trans*-(**1**) in dichloromethane were calculated with the use of time-dependent DFT methods.

Experimental

Materials

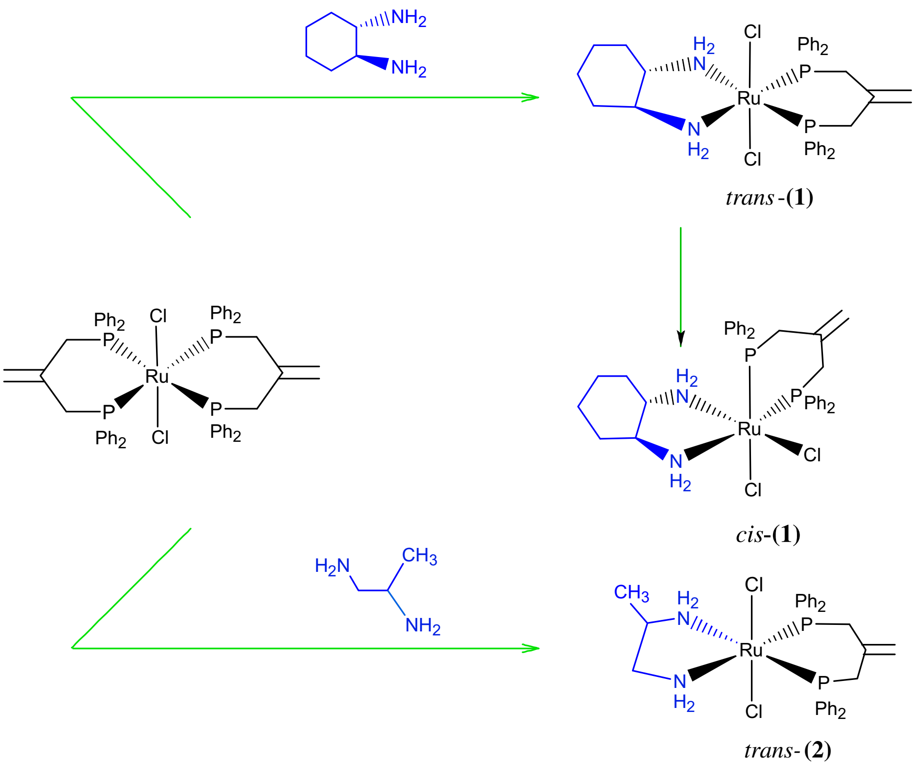
All manipulations were carried out under an argon inert atmosphere using a standard high vacuum and Schlenk-line techniques. CH_2Cl_2, *n*-hexane, and Et_2O were pre-dried, distilled from CaH_2, $LiAlH_4$, and sodium/benzophenone, respectively. The diamines, 1,2-diaminocyclohexane and 1-methyl-1,2-diaminopropane were purchased from Merck and purified by distillation before used. 3-Chloro-2-(chloromethyl)-1-propene, Ph_3P, *n*-BuLi, and $RuCl_3{\cdot}3H_2O$ were obtained from commercially available sources and used without any additional purification. *trans*-[$RuCl_2(dppme)_2$] was prepared by the procedures described in literature method [10].

Preparation of trans-[$RuCl_2$(dppme)(diamine)](**1–2**); general procedure

The corresponding diamine (10% excess, 0.55 mmol) was dissolved in 10 mL of dichloromethane and then added dropwise to a stirred solution of (0.50 g, 0.50 mmol) *trans*-[$RuCl_2(dppme)_2$] in 10 mL of dichloromethane within 5 min at room temperature. The mixture was stirred for 30 min at room temperature while the color changed from brown to yellow. After the removal of unreacted materials, the volume of the solution was concentrated to about 5 ml under reduced pressure. The product was precipitated by adding 40 mL of diethyl ether and recrystallized from dichloromethane/*n*-hexane.

Trans-[$RuCl_2$(dppme)(2-diaminocyclohexane)](trans-(**1**))

Yield (0.32 g, 92%), UV–vis in dichloromethane: λ_{max} (nm) (ε_{max}, $M^{-1}\,cm^{-1}$): 285(11.3 × 10^3), 330(9 × 10^3), 490(8.2 × 10^3). Yellow crystal, m.p. 232 °C (decomposition). IR (KBr, ν cm^{-1}): 3370(ν_{NH2}), 3150(ν_{PhCH}), 2870(ν_{PhCH}) and 315(ν_{Ru-Cl}) cm^{-1}. ^1H



Scheme 1. Synthesis of complexes *trans*/*cis*-(**1**) and *trans*-(**2**).