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Influence of arene dissociation and phosphine coordination on the catalytic activity of [RuCl(κ^2-triphos)(*p*-cymene)]PF_6

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ABSTRACT

The catalytic activity of a ruthenium(II)-*p*-cymene complex containing a partially coordinated triphosphine ligand, [RuCl(κ^2-triphos)(*p*-cymene)]PF_6 **1**, has been investigated in the hydrogenation of styrene to ethylbenzene. The influence of arene dissociation and coordination of the free phosphine donor group on the catalytic activity have been probed directly and indirectly by comparison to structural analogues. Analogues of **1** containing in a diphosphine ligand, [RuCl(κ^2-dppp)(*p*-cymene)]PF_6 **2**, or a labile arene ligand, [RuCl(κ^2-triphos)(η^6-$PhCO_2Et$)]PF_6 **3**, show significantly enhanced catalytic activity – demonstrating the importance of ligand coordination/dissociation dynamics in ruthenium(II)-arene compounds during catalysis. These observations are supported by thermolysis reactions of **1** in DMSO. In addition, improved syntheses of **1** and **2** are reported together with the solid-state structures of *syn*-**1**, *syn*-**3** and [Ru(η^3-C_8H_{13})(κ^3-triphos)]PF_6.

1. Introduction

Tripodal triphosphine ligands continue to find widespread application in coordination chemistry and catalysis [1,2]. Among these ligands, the C_3 symmetric phosphine 1,1,1-tris(diphenylphosphinomethyl)-ethane (triphos) and it's derivatives are the most extensively investigated, forming a large variety of transition metal complexes, many of which have been evaluated as catalysts [1–3]. While predominately forming complexes adopting a κ^3-coordinaton mode [2], triphos is also known to partially bind to metal centres in a κ^2-manner [4]. The interconversion between these two coordination modes, by 'arm-off, arm-on' dissociation/association of one of the phosphine centres, has significant consequences for the reactivity of the complex [5]. Examples of dynamic coordination include reversible arm-off triphos dissociation and concomitant addition of CO to [Rh(CO)H(κ^3-triphos)], under hydroformylation conditions [6], and equilibration between κ^3 and μ:κ^2,κ^1- coordination modes in [Rh(COD)(κ^3-triphos)]PF_6 on addition of $[RuCl_2(p\text{-cymene})]_2$ [7].

Ruthenium(II)-arene complexes have been used extensively as catalyst precursors in many different reactions. Complexes of this type bearing chiral amino-amido ligands are especially notable as catalysts for the asymmetric transfer hydrogenation of carbonyl compounds [8]. Other transformations mediated by ruthenium(II)-arene pre-catalysts include alkyne oxidation [9], C–C bond formation [10], olefin metathesis [11], Diels–Alder reactions [12], and free-radical polymerization [13]. As part of our on-going investigations on the catalytic activity of ruthenium(II)-arene complexes [14,15], we report here further on a complex containing a κ^2-coordinated triphos ligand, [RuCl(κ^2-triphos)(*p*-cymene)]PF_6 **1**. Isolation and characterisation of two isomers of this complex together with a study of their catalytic activity is described. The role of arene and phosphine coordination on the catalytic activity has been probed by comparison to structural analogues and thermolysis reactions.

2. Results and discussion

The κ^2-triphos complex [RuCl(κ^2-triphos)(*p*-cymene)]PF_6 **1** is readily prepared by reaction of triphos with the activated ruthenium arene precursor, $[Ru_2(\mu\text{-}Cl)_3(p\text{-cymene})_2]PF_6$ and $[NH_4]PF_6$ in refluxing methanol [16]. Two isomers of **1**, differing by the orientation of the pendant arm of the triphos ligand with respect to the metallocyclic ring, are formed in a 1:1 ratio. Separation was achieved by selective precipitation of the less soluble *anti*-**1** from methanol and subsequent recrystallisation, allowing the definitive characterisation of both isomers – absent in the initial communication [16]. The κ^2-coordination of the triphos ligand is readily apparent from the ^1H and $^{31}P\{^1H\}$ NMR spectra of **1**, the later showing two ^{31}P environments (integral 2:1 ratio) for each of the isomers. The resonances of the two phosphorous centres are observed at 26.9 and 25.2 ppm for the *syn*- and *anti*-isomers,

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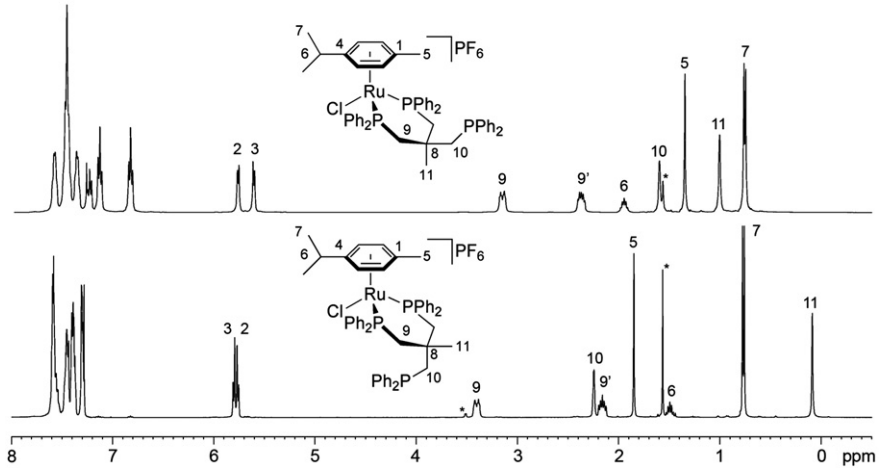


Fig. 1. ^{1}H NMR spectra of *syn*-**1** (top) and *anti*-**1** (bottom) ($CDCl_3$, 293 K).

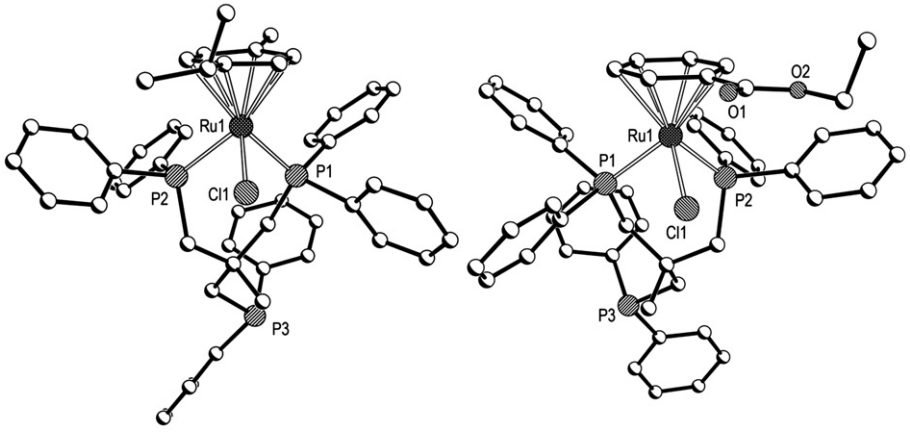
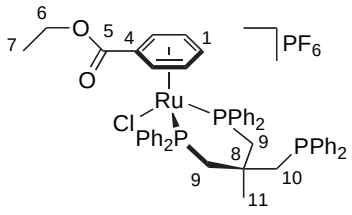


Fig. 2. Ball and stick representations of *syn*-**1** (left) and *syn*-**3** (right). Counter anions, solvent molecules and hydrogen atoms are omitted for clarity. Selected bond lengths (Å): *syn*-**1**: Ru1-P1, 2.3278(14); Ru1-P2, 2.3295(14); Ru1-Cl1, 2.4038(12), Ru1-C, 2.223(5) – 2.324(5). *syn*-**3**: Ru1-P1, 2.328(2); Ru1-P2, 2.330(2); Ru1-Cl1, 2.401(2); Ru1-C, 2.216(6) – 2.276(6).

respectively. Both are similar to that observed for [RuCl(κ^2-dppp)(*p*-cymene)]PF_6 **2** (25.5 ppm) [17]. The chemical shifts of the uncoordinated phosphorus centres (*syn*-**1**, −29.1; *anti*-**1**, −27.6 ppm) are similar to that of free triphos (−25.8 ppm). Inequivalent hydrogen environments on C^9 and large differences in the chemical shift values of H^{10} and H^{11} between the isomers ($\Delta\delta$ = 0.65 and 0.93 ppm, respectively) are observed by ^{1}H NMR spectroscopy (Fig. 1). Both structural assignments are supported by solid-state structures determined by X-ray diffraction; that of *syn*-**1** is depicted Fig. 2 and that of *anti*-**1** was reported earlier [16]. Both structures exhibit comparable structural metrics to related ruthenium(II)-arene phosphine complexes [15,17,18]. The triphos configuration assignments are consistent with those observed in *fac*-[ReX(CO)$_3$(κ^2-triphos)] (X = Cl, Br) [4c]. No interconversion between the isomers was observed on prolonged heating in MeOH.

Structural analogues of **1** containing a diphosphine ligand, [RuCl(κ^2-dppp)(*p*-cymene)]PF_6 **2**, or a labile arene ligand, [RuCl(κ^2-triphos)(η^6-$PhCO_2Et$)]PF_6 **3**, where chosen to investigate the role of the free phosphine donor and arene dissociation in the catalytic activity of **1**, respectively. Complex **2** was prepared via a new procedure from [RuCl(PPh_3)(κ^1-dppp)(*p*-cymene)]PF_6 by intramolecular substitution of PPh_3 in almost quantitative yield [18b]. Complex **3** is new and was isolated as the *syn*-isomer in modest yield from the reaction between [$RuCl_2$(η^6-$PhCO_2Et$)]$_2$, triphos and $TlPF_6$ in CH_2Cl_2 at room temperature (Chart 1) [19]. The solid-state structure of *syn*-**3** is depicted in Fig. 2. The structure demonstrates the η^6-coordination of the arene ligand [Ru1-C = 2.216(6)–2.276(6) Å] and the adoption of a "piano-stool" geometry about the ruthenium centre. In solution the structure observed in the solid-state is retained; notably the ^{1}H NMR spectrum of *syn*-**3** exhibits chemical shifts for H^9, H^{10} and H^{11} that are similar to those in *syn*-**1**. The ^{31}P resonances for the triphos ligand are observed at 25.5 and −30.7 in a 2:1 ratio, comparable to **1**.

To establish the relative binding strength of the arene ligands, thermolysis reactions were carried by heating solutions of **1**–**3** in DMSO (Scheme 1). These reactions were monitored in situ using ^{31}P



syn-**3**

Chart 1.