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Ruthenium-catalyzed transfer hydrogenation of aromatic ketones with aminophosphine or bis(phosphino)amine ligands derived from isopropyl substituted anilines

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ABSTRACT

A series of new highly active Ru(II) complexes with two new (*N*-diphenylphosphino)isopropylanilines, having an isopropyl substituent at carbon 2- (**1**) or 2,6- (**2**) and two new bis(diphenylphosphino)isopropylanilines, having an isopropyl substituent at carbon atom 2- (**3**) or 4- (**4**), were prepared starting from the dimeric complex $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-}Cl)Cl]_2$. All the compounds have been fully characterized by microanalysis, IR, $^{31}P\{1H\}$ NMR, ^{1}H NMR and ^{13}C NMR spectroscopies. Following activation by NaOH, complexes **5**–**8** were tested in the transfer hydrogenation of acetophenone derivatives with *iso*-PrOH as the hydrogen source. Catalytic studies showed that the complexes are excellent catalytic precursors for the transfer hydrogenation of acetophenone derivatives.

1. Introduction

The chemistry of compounds containing phosphorus and nitrogen, with direct bonds between the two elements, has been known for many years, but continues to attract considerable attention, with applications in increasingly diverse fields [1,2]. Potentially this ligand family is extremely attractive since preparative routes enable access to various structural modifications via simple P–N bond formation [3]. Aminophosphines and bis(phosphine)amines, with P–NH and P–N–P skeletons respectively, have proved to be much more versatile ligands, and varying the substituents on both the P- and N centres gives rise to changes in the P–N–P angle and the conformation around the P-centres [4,5]. Small variations in these ligands can cause significant changes in their coordination behaviour and the structural features of the resulting complexes [6].

There has been recently an increasing interest in the synthesis of new and highly active transition-metal based catalysts derived from aminophosphines that can be used in different catalytic reactions including allylic alkylation [7,8], amination [9,10], Heck [11–13], Suzuki [14–16], hydroformylation [17,18], Sonogashira [19], polymerization [20] and hydrogenation reactions [21,22]. Some aminophosphines and derivatives have also found application as anticancer drugs [23], herbicides and antimicrobial agents, as well as neuroactive agents [24].

Organic synthesis needs economically and technically more benign methods that are very general. From an industrial point of view, catalytic transfer hydrogenation is an attractive alternative for high-pressure catalytic hydrogenation with molecular hydrogen [25]. Transition metal catalyzed transfer hydrogenation with 2-propanol is a convenient method to reduce ketones since there is no need for high hydrogen pressure or hazardous reducing agents [26,27]. Homogeneous ruthenium complexes are considered to be the most attractive catalysts for transfer hydrogenation reactions, though other metal complexes have also been used successfully [28,29]. Varying levels of efficiency were observed for ruthenium complexes with ligands such as diamines [30], amino alcohols [31,32], phosphanes [33] and aminophosphines [34].

In the present report, from readily available starting materials, such as isopropyl substituted anilines, two Ru(II)–aminophosphine and two Ru(II)-bis(phosphino)amine complexes have been prepared and characterized. As a part of our interest in designing new ligand systems with different spacers to control the electronic attributes at the phosphorus centers and to explore their coordination chemistry, we report here the synthesis of the Ru(II) complexes $[Ru(\eta^6\text{-}p\text{-cymene})(PPh_2NH\text{–}C_6H_4\text{-}2\text{-}CH(CH_3)_2)Cl_2]$ (**5**), $[Ru(\eta^6\text{-}p\text{-cymene})(PPh_2NH\text{–}C_6H_3\text{-}2,6\text{-}(CH(CH_3)_2)_2)Cl_2]$ (**6**), $[Ru((PPh_2)_2N\text{–}C_6H_4\text{-}2\text{-}CH(CH_3)_2)_2Cl_2]$ (**7**) and $[Ru((PPh_2)_2N\text{–}C_6H_4\text{-}4\text{-}CH(CH_3)_2)_2Cl_2]$ (**8**), and these complexes were also evaluated in the ruthenium-catalyzed transfer hydrogenation of acetophenone derivatives.

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2. Results and discussion

2.1. Synthesis and characterization of the Ru(II) complexes

Following our previous studies [35,36], we prepared a series of ruthenium complexes **5**–**8** from the reaction of $[RuCl(\mu\text{-}Cl)(p\text{-cymene})]_2$ with the monodendate **1**, **2** and chelate ligands **3**, **4** as shown in Scheme 1.

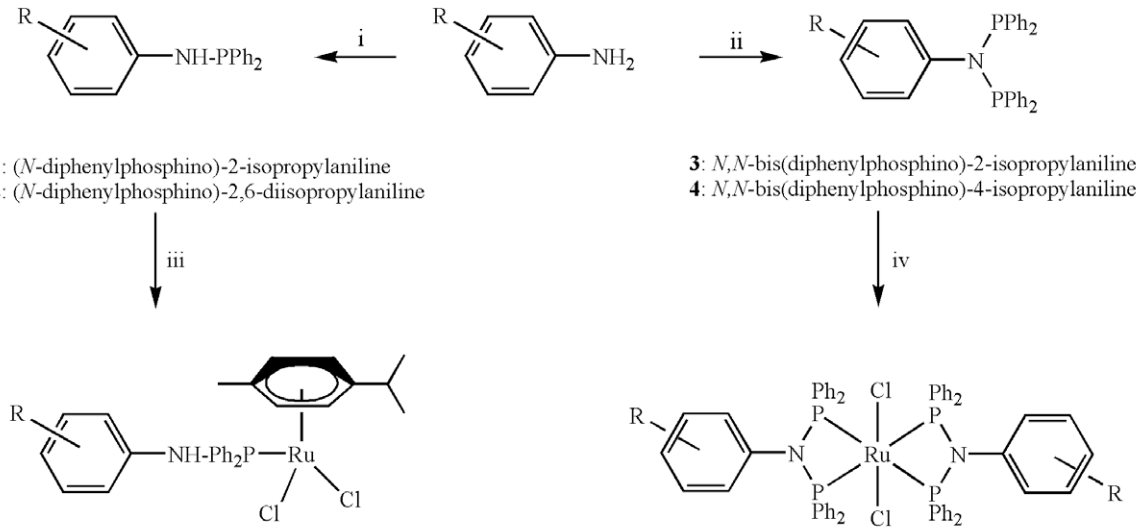
(*N*-diphenylphosphino)isopropylanilines, having an isopropyl substituent at carbon 2- (**1**) or 2,6- (**2**), were easily prepared from the aminolysis of $H_2N\text{–}C_6H_4\text{-}2\text{-}CH(CH_3)_2$ or $H_2N\text{–}C_6H_3\text{-}2,6\text{-}(CH(CH_3)_2)_2$, respectively, with one equivalent of chlorodiphenylphosphine in the presence of triethylamine at 0 °C, using thf/CH_2Cl_2 (1/2) and CH_2Cl_2 as the solvent, respectively [37]. The reactions of $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-}Cl)Cl]_2$ with $PPh_2NH\text{–}C_6H_4\text{-}2\text{-}CH(CH_3)_2$, **1** and $PPh_2NH\text{–}C_6H_3\text{-}2,6\text{-}(CH(CH_3)_2)_2$, **2** in CH_2Cl_2 in a ratio of 1/2:1 at room temperature for 3 h gave a yellow insoluble micro-crystalline precipitate of the neutral complexes **5** and **6**, respectively. The $^{31}P\{1H\}$ NMR spectra of **5** and **6** show single peaks at 51.62 and 57.69 ppm, respectively, in line with the values previously observed for similar compounds [38,39] (see Supplementary information Fig. 1). In the $^{13}C\{1H\}$ NMR spectra of **5** and **6**, $J(^{31}P\text{–}^{13}C)$ coupling constants for the carbons of the phenyl rings were recorded, which are consistent with the literature values [40–43]. The most relevant signals of the $^{13}C\{1H\}$ NMR spectra of complexes **5** and **6** are those corresponding to the arene ligands (*p*-cymene). The carbon atoms of the arene rings in the *p*-cymene ligands are observed as two singlets at 91.35 and 85.41 ppm in compound **5** and 89.53 and 86.90 ppm in compound **6**. Furthermore, ^1H NMR spectral data of **5** and **6** are consistent with the structures proposed. In the ^1H NMR spectra, **5** and **6** are characterized by the isopropyl methyl doublets of the *p*-cymene groups, at δ 0.88 and 1.25 ppm and η^6-arene doublets at δ 5.28, 5.14 and 5.06, 4.84 ppm, respectively (for details see Section 3). In addition, the structural compositions of complexes **5** and **6** have been confirmed by IR and elemental analysis.

N,N-bis(diphenylphosphino)isopropylanilines $(PPh_2)_2N\text{–}C_6H_4\text{–}CH(CH_3)_2$, having an isopropyl substituent at carbon 2- (**3**) or 4- (**4**), were easily prepared from the reaction of $H_2N\text{–}C_6H_4\text{-}2\text{-}CH(CH_3)_2$ or $H_2N\text{–}C_6H_4\text{-}4\text{-}CH(CH_3)_2$, respectively, with two equivalents of chlorodiphenylphosphine in the presence of triethylamine in thf solution at 0 °C [44]. Attempts to prepare *N,N*-bis(diphenylphosphino)-2,6-diisopropylaniline did not succeed, possibly due to the steric repulsion between the two isopropyl groups and phenyl rings of the phosphine. We also examined some simple coordination chemistry of **3** and **4** with the $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-}Cl)Cl]_2$ precursor. The complexation reactions were straightforward, with coordination to ruthenium being carried out at room temperature. Complexes **7** and **8** were formed as fine powders (Scheme 1). The reactions between the Ru(II) precursor and the bis(phosphino)amine ligands **3** and **4** were not affected by the molar ratio of $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-}Cl)Cl]_2$ nor by the steric and electronic properties of the donor phosphorus atoms. The reaction of $(PPh_2)_2N\text{–}C_6H_4\text{-}2\text{-}CH(CH_3)_2$, **3** and $(PPh_2)_2N\text{–}C_6H_4\text{-}4\text{-}CH(CH_3)_2$, **4** with $Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-}Cl)Cl]_2$ in CH_2Cl_2 solution in a molar ratio of 1:1/4 at room temperature for 4 h gives an orange/red solution. The solution was concentrated and cooled to 0 °C. The *trans* isomers of **7** and **8** were isolated as indicated by singlets in the $^{31}P\{1H\}$ NMR spectra at (δ) 79.65 and 79.25 ppm, respectively, in line with the values previously observed for similar compounds [45,46] (see Supplementary information Fig. 1), indicating that **3** and **4** act as bis(bidendate) chelating ligands. Furthermore, the ^1H and $^{13}C\{1H\}$ NMR spectroscopies are in agreement with the structures proposed, and the structural compositions of complexes **7** and **8** were further confirmed by IR spectroscopy and the microanalyses were found to be in good agreement with the theoretical values.

2.2. Catalytic transfer hydrogenation of acetophenone derivatives

The obtained complexes **5**–**8** were then examined for the ruthenium catalyzed transfer hydrogenation of arylketones to the corresponding alcohols in *iso*-PrOH solution (Scheme 2).

In a preliminary study, if the reaction was activated by an alkoxide base, the synthesized complexes **5**–**8** were evaluated as a precursor for the catalytic transfer hydrogenation of acetophenone



5: [Ru(*p*-cymene)(*N*-diphenylphosphino)-(2-isopropylaniline)Cl_2]
6: [Ru(*p*-cymene)(*N*-diphenylphosphino)-(2,6-diisopropylaniline)Cl_2]
7: [Ru(*N,N*-bis(diphenylphosphino)-(2-isopropylaniline)Cl_2]
8: [Ru(*N,N*-bis(diphenylphosphino)-(4-isopropylaniline)Cl_2]

Scheme 1. Synthesis of the complexes $[Ru(\eta^6\text{-}p\text{-cymene})(PPh_2NH\text{–}C_6H_4\text{-}2\text{-}CH(CH_3)_2)Cl_2]$ **5**, $[Ru(\eta^6\text{-}p\text{-cymene})(PPh_2NH\text{–}C_6H_3\text{-}2,6\text{-}(CH(CH_3)_2)_2)Cl_2]$ **6**, $[Ru((PPh_2)_2N\text{–}C_6H_4\text{-}2\text{-}CH(CH_3)_2)_2Cl_2]$ **7** and $[Ru((PPh_2)_2N\text{–}C_6H_4\text{-}4\text{-}CH(CH_3)_2)_2Cl_2]$ **8** (i) 1 equiv. Ph_2PCl, 1 equiv. Et_3N, thf/CH_2Cl_2 (1/2) for **1** and CH_2Cl_2 for **2**; (ii) 2 equiv. Ph_2PCl, 2 equiv. Et_3N, thf; (iii) 1/2 equiv. $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-}Cl)Cl]_2$, thf; (iv) 1/4 equiv. $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-}Cl)Cl]_2$, thf.