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The application of tunable tridendate P-based ligands for the Ru(II)-catalysed transfer hydrogenation of various ketones

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Two novel versatile tridendate aminophosphine–phosphinite and phosphinite ligands were prepared and their trinuclear neutral ruthenium(II) dichloro complexes were found to be effective catalysts for the transfer hydrogenation of various ketones in excellent conversions up to 99% in the presence of 2-propanol/NaOH in 0.1 M isopropanol solution. Particularly, [Ru_3($PPh_2OC_2H_4$)$_2$ N–PPh_2(η^6-*p*-cymene)$_3Cl_6$] acts as an excellent catalyst giving the corresponding alcohols in excellent conversion up to 99% (turnover frequency $\leq 1176\ h^{-1}$). A comparison of the catalytic properties of the complexes is also discussed briefly. Furthermore, the structures of these ligands and their corresponding complexes have also been clarified using a combination of multinuclear NMR spectroscopy, infrared spectroscopy and elemental analysis. ^1H–^{13}C HETCOR or ^1H–^1H COSY correlation experiments were used to confirm the spectral assignments. Copyright © 2014 John Wiley & Sons, Ltd.

Keywords: AMPP; phosphinite; ruthenium; catalysis; transfer hydrogenation; ketone

Introduction

Catalytic transfer hydrogenation with the support of a stable hydrogen donor is a useful alternative method for catalytic hydrogenation by molecular hydrogen for the reduction of ketones.[1–3] In transfer hydrogenation, organic compounds such as primary and secondary alcohols[4] or formic acid and its salts[5] have been employed as the hydrogen source. The use of a hydrogen donor has a lot of advantages over the use of molecular hydrogen since it avoids the risks and constraints associated with hydrogen gas as well as the necessity for pressure vessels and other equipment. It is well known that a variety of transition metal complexes are strikingly active for the hydrogenation of ketones.[6] Particularly, over the last three decades, most effort on hydrogenation has been focused on the use of ruthenium catalysts. One reason is that ruthenium catalysts have admirable performances.[7,8] Another is that ruthenium has a cost advantage over other hydrogenation metals such as rhodium and iridium.[9]

The chemistry of aminophosphine–phosphinite (AMPP), aminophosphines, phosphines and phosphinites has also been much explored in recent years.[10–13] These compounds are extremely attractive as potential ligands since various structural modifications are accessible via simple P–N, P–C and P–O bond formation.[14,15] Many modified phosphine ligands and a variety of AMPP ligands have important applications in organometallic chemistry and catalysis, giving selective catalysts for hydroformylation, hydrosilylation, transfer hydrogenation, etc.[16–18] While much effort has been devoted to the synthesis of aminophosphines and phosphines, similar studies of the analogous phosphinites are less extensive,[19,20] although phosphinites have different chemical, electronic and structural advantages compared to phosphines and aminophosphines.[21–23] Phosphinites are versatile ligands which allow effective catalytic transformations.[24] The metal–phosphorus bond is often stronger for phosphinites compared to the related phosphines due to the presence of electron-withdrawing P–OR groups. In addition, the empty σ*-orbital of the phosphinite P(OR)R_2 is stabilized, making the phosphinite a better acceptor, and another advantage is the easy preparation of phosphinites.[25]

We have recently reported many phosphinite ligands, and have employed them successfully as ligands in transition metal-promoted transfer hydrogenation of ketones.[26,27] Furthermore, it is well known that many modified phosphine ligands[28–30] and a variety of chiral AMPP ligands have important applications in organometallic chemistry and catalysis.[31–33] Taking into consideration the mentioned factors and as a part of our interest in designing new ligand systems with various spacers to control the electronic attributes at phosphorus centres and to explore their coordination chemistry, we report here the synthesis of novel tridendate phosphinite and AMPP ligands and their catalytic evaluation in the transfer hydrogenation of various ketones.

Experimental

Materials and Methods

Unless otherwise stated, all reactions were carried out under an atmosphere of argon using conventional Schlenk glassware. Solvents were dried using established procedures and distilled under argon immediately prior to use. Analytical-grade and deuterated solvents were purchased from Merck. PPh_2Cl, diethanolamine and

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triethanolamine are purchased from Fluka and were used as received. The starting material $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$ was prepared according to literature procedures.[34,35] FT-IR spectra were recorded with a Mattson 1000 ATI UNICAM FT-IR spectrometer. ^{1}H NMR (400.1 MHz), ^{13}C NMR (100.6 MHz) and ^{31}P-{^{1}H} NMR (162.0 MHz) spectra were recorded using a Bruker AV400 spectrometer, with δ referenced to external tetramethylsilane and 85% H_3PO_4, respectively. Elemental analysis was carried out with a Fisons EA 1108 CHNS-O instrument. Melting points were recorded using Gallenkamp Model apparatus with open capillaries.

Transfer Hydrogenation of Ketones

A typical procedure for the catalytic hydrogen transfer reaction was as follows. A solution of complex $[Ru_3(PPh_2OC_2H_4)_2N\text{–}PPh_2(\eta^6\text{-}p\text{-cymene})_3Cl_6]$ (**3**) or $[(RuPPh_2OC_2H_4)_3N(\eta^6\text{-}p\text{-cymene})_3Cl_6]$ (**4**) (0.005 mmol), NaOH (0.025 mmol) and the corresponding ketone (0.5 mmol) in degassed 2-propanol (5 ml) were refluxed until the reactions were completed. Then, a sample of the reaction mixture was taken off, diluted with acetone and analysed immediately using GC. The conversions were related to the residual unreacted ketone. GC analyses were performed using a Shimadzu 2010 Plus gas chromatograph equipped with a capillary column (5% biphenyl, 95% dimethylsiloxane; 30 m × 0.32 mm × 0.25 μm). The GC parameters for transfer hydrogenation of ketones were as follows: initial temperature, 50°C; initial time, hold minimum 1 min; solvent delay, 4.48 min; temperature ramp, 15°C min^{-1}; final temperature, 270°C, hold minimum 5 min; final time, 20.67 min; injector port temperature, 200°C; detector temperature, 200°C, injection volume, 2.0 μl.

Synthesis of Ligands and Their Ruthenium(II) Complexes

*Synthesis of 2-[(diphenylphosphanyl)({2-[(diphenylphosphanyl)oxy]ethyl})amino]-ethyldiphenylphosphinite (**1**)*

Chlorodiphenylphosphine (0.66 g, 2.85 mmol) was added dropwise over a period of 10 min to a solution of diethanolamine (0.10 g, 0.95 mmol) and triethylamine (0.29 g, 2.85 mmol) in THF (30 ml) at room temperature with vigorous stirring. The mixture was stirred at room temperature for 4 h, and then the white precipitate (triethylammonium chloride) was filtered under argon, the solvent was removed and the remaining part was dried vacuum to produce a viscous oil of compound **1** (yield: 0.59 g, 94.3%). ^{1}H NMR ($CDCl_3$, δ, ppm): 7.29–7.50 (m, 30H, *o*-, *m*- and *p*-protons of phenyls), 3.96 (t, J = 6.5 Hz, 2H, $NCH_2CH_2OPPh_2$), 3.40 (t, J = 6.5 Hz, 2H, $NCH_2CH_2OPPh_2$). ^{13}C-{^{1}H} NMR ($CDCl_3$, δ, ppm): 141.87, 141.68 (*i*-carbons of phenyls), 132.12, 131.92 (*o*-carbons of phenyls), 130.52, 130.31 (*p*-carbons of phenyls), 129.27, 128.33 (*m*-carbons of phenyls), 68.0 ($NCH_2CH_2OPPh_2$), 50.1 ($NCH_2CH_2OPPh_2$), assignment was based on the ^{1}H–^{13}C HETCOR spectrum. ^{31}P-{^{1}H} NMR ($CDCl_3$, δ, ppm): 111.10 (s, O–PPh_2), 60.71 (s, N–PPh_2). Selected FT-IR (cm^{-1}): 804 (P–N), 1023 (—P-O), 1434 (P–Ph). Anal. Calcd for $C_{40}H_{38}O_2P_3N$ (%): C, 72.94; H, 5.37; N, 2.13. Found (%): C, 72.83; H, 5.46; N, 2.76.

*Synthesis of 2-[bis({2-[(diphenylphosphanyl)oxy]ethyl})amino]ethyldiphenyl-phosphinite (**2**)*

Chlorodiphenylphosphine (0.44 g, 1.98 mmol) was added dropwise over a period of 10 min to a solution of triethanolamine (0.10 g (98%), 0.66 mmol) and triethylamine (0.20 g, 1.98 mmol) in THF (30 ml) at room temperature with vigorous stirring. The mixture was stirred at room temperature for 1 h, and then the white precipitate (triethylammonium chloride) was filtered under argon, the solvent was removed and the remaining part was dried in vacuum to produce a yellow viscous oil of compound **2** (yield: 0.43 g, 93.3%). ^{1}H NMR ($CDCl_3$, δ, ppm): 7.46–7.49 (m, 12H, *o*-protons of phenyls), 7.27–7.39 (m, 18H, *m*- and *p*-protons of phenyls), 3.89 (t, 6H, $^3J_{H\text{-}H}$ = 6.9 Hz, $NCH_2CH_2OPPh_2$), 2.89 (t, 6H, $^3J_{H\text{-}H}$ = 6.9 Hz, $NCH_2CH_2OPPh_2$). ^{13}C-{^{1}H} NMR ($CDCl_3$, δ, ppm): 142.1 (d, $^1J_{31P\text{-}13C}$ = 18.3 Hz, *i*-carbons of phenyls), 130.4 (d, $^2J_{31P\text{-}13C}$ = 22.1 Hz, *o*-carbons of phenyls), 129.2 (s, *p*-carbons of phenyls), 128.3 (d, $^3J_{31P\text{-}13C}$ = 7.0 Hz, *m*-carbons of phenyls), 68.4 ($NCH_2CH_2OPPh_2$), 56.0 ($NCH_2CH_2OPPh_2$), assignment was based on the ^{1}H–^{13}C HETCOR spectrum. ^{31}P-{^{1}H} NMR ($CDCl_3$, δ, ppm): 113.93 (s, O–PPh_2). Selected FT-IR (cm^{-1}): 1026 (P–O), 1435 (P–Ph). Anal. Calcd for $C_{42}H_{42}O_3P_3N$ (%): C, 71.89; H, 6.03; N, 2.00. Found (%): C, 71.51; H, 5.85; N, 1.77.

*Synthesis of **3***

To a solution of $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$ (0.874 g, 1.43 mmol) in THF, a solution (THF, 30 ml) of **1** (0.627 g, 0.95 mmol) was added. The resulting reaction was allowed to proceed with stirring at room temperature for 2 h. Then, the solution was filtered and the solvent evaporated under vacuum. The solid residue thus obtained was washed with diethyl ether (3 × 10 ml) and then dried under vacuum. Following recrystallization from diethyl ether–CH_2Cl_2, a red crystalline powder was obtained. Yield 1.32 g, 88.1%; m.p. 168–170°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.77–7.81 (m, 12H, *o*-protons of O- and N-phenyls), 7.47 (br, 6H, *m*- and *p*-protons of N-phenyls), 7.28–7.34 (m, 12H, *m*- and *p*-protons of O-phenyls), 5.23–5.30 (m, 12H, aromatic protons of *p*-cymene), 3.69 (br, 4H, NCH_2CH_2OPPh), 3.32 (m, 4H, NCH_2CH_2OPPh), 2.55 (m, 3H, C*H*– of *p*-cymene), 1.73 (s, 9H, CH_3–Ph of *p*-cymene), 1.02 (d, 18H, ^3J = 6.3 Hz, $(CH_3)_2CHPh$ of *p*-cymene). ^{13}C NMR ($CDCl_3$, δ, ppm): 141.36, 141.54 (*i*-carbons of phenyls), 132.76, 132.65 (*o*-carbons of phenyls), 130.77, 130.32 (*p*-carbons of phenyls), 128.34, 127.93 (*m*-carbons of phenyls), 110.40, 95.93 (quaternary carbons of *p*-cymene), 90.41, 87.72 (aromatic carbons of *p*-cymene), 64.73 ($NCH_2CH_2OPPh_2$), 48.05 ($NCH_2CH_2OPPh_2$), 30.07 (CH– of *p*-cymene), 21.75 ($(CH_3)_2CHPh$ of *p*-cymene), 17.43 (CH_3Ph of *p*-cymene), assignment was based on the ^{1}H–^{13}C HETCOR, DEPT and ^{1}H–^{1}H COSY spectra. ^{31}P-{^{1}H} NMR ($CDCl_3$, δ, ppm): 114.4 (s, O–PPh_2), 74.56 (s, N–PPh_2). FT-IR (KBr, cm^{-1}): 953 (P–N), 1030 (P–O), 1436 (P–Ph). Anal. Calcd for $C_{70}H_{80}NP_3O_2Ru_3Cl_6$ (1577.3 g mol^{-1}) (%): C, 53.31; H, 5.11; N, 0.89. Found (%): C, 53.25; H, 5.04; N, 0.86.

*Synthesis of **4***

To a solution of $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$ (0.603 g, 0.99 mmol) in THF, a solution (THF, 30 ml) of **2** (0.461 g, 0.66 mmol) was added. The resulting reaction was allowed to proceed with stirring at room temperature for 2 h. Then, the solution was filtered and the solvent evaporated under vacuum. The solid residue thus obtained was washed with diethyl ether (3 × 10 ml) and then dried under vacuum. Following recrystallization from diethyl ether–CH_2Cl_2, a red crystalline powder was obtained. Yield 0.95 g, 89.5%; m.p. 132–134°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.81–7.85 (m, 12H, *o*-protons of phenyls), 7.28–7.43 (m, 18H, *m*- and *p*-protons of phenyls), 5.22–5.27 (m, 12H, aromatic protons of *p*-cymene), 3.78 (br, 6H, NCH_2CH_2OPPh), 2.63 (br, 9H, NCH_2CH_2OPPh and –C*H*– of *p*-cymene), 1.83 (s, 9H, CH_3–Ph of *p*-cymene), 1.07 (d, 18H, ^3J = 6.1 Hz, $(CH_3)_2CHPh$ of *p*-cymene). ^{13}C NMR ($CDCl_3$, δ, ppm): 141.8 (d, $^1J_{31P\text{-}13C}$ = 16.2 Hz, *i*-carbons of phenyls), 132.60 (d, $^1J_{31P\text{-}13C}$ = 11.0 Hz, *o*-carbons of phenyls), 130.85 (s, *p*-carbons of phenyls), 128.05 (d, $^3J_{31P\text{-}13C}$ = 10.1 Hz, *m*-carbons of phenyls), 111.42, 110.42 (quaternary carbons

of *p*-cymene), 90.54, 87.75 (aromatic carbons of *p*-cymene), 65.06 ($NCH_2CH_2OPPh_2$), 54.55 ($NCH_2CH_2OPPh_2$), 30.10 (*C*H– of *p*-cymene), 21.81 ($(CH_3)_2CHPh$ of *p*-cymene), 17.58 (CH_3Ph of *p*-cymene), assignment was based on the ^1H–^{13}C HETCOR, DEPT and ^1H–^1H COSY spectra. ^{31}P-{^1H} NMR ($CDCl_3$, δ, ppm): 112.49 (s, O–PPh_2). FT-IR (KBr, cm^{-1}): 1030 (P–O), 1436 (P–Ph). Anal. Calcd for $C_{72}H_{84}NP_3O_3Ru_3Cl_6$ (1620.3 g mol^{-1}) (%): C, 53.37; H, 5.23; N, 0.86. Found (%): C, 53.26; H, 5.19; N, 0.81.

Results and Discussion

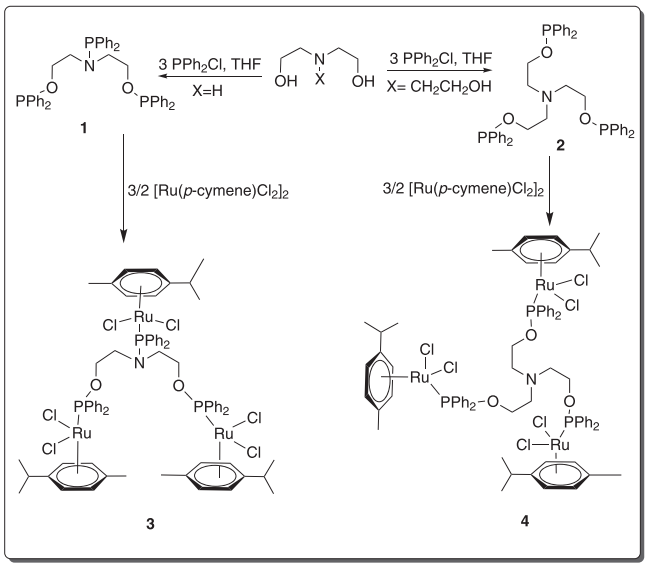
Synthesis and Characterization of Ruthenium(II) Complexes

The synthetic procedure for the preparation of the P-based ligands is shown in Scheme 1. Ligands **1** and **2** were synthesized via hydrogen abstraction by a base (Et_3N) and the subsequent reaction with three equivalents of Ph_2PCl in anhydrous THF under argon atmosphere. The ammonium salt was separated by filtration and the ligands were obtained by extracting the solvent *in vacuo* in excellent yields. The progress of this reaction was conveniently followed using ^{31}P-{^1H} NMR spectroscopy. The ^{31}P-{^1H} NMR spectra of compounds **1** and **2** show single resonances due to AMPP at 111.10 ppm (s, O–PPh_2) and 60.71 ppm (s, N–PPh_2) and phosphinite at 113.93 ppm, respectively,[36–39] in line with the values previously observed for similar compounds.[40–44] Typical ^{31}P-{^1H} NMR spectra of these ligands are illustrated in the supporting information (SI, spectra 1.1–1.4). The structures of these compounds are consistent with the data obtained from a combination of multinuclear NMR spectroscopy, FT-IR spectroscopy and elemental analysis (for details, see the experimental section).

The reactions of [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ with AMPP and phosphinite ligands are shown in Scheme 1. The ability of dimers [Ru(arene)(μ-Cl)Cl]$_2$ to form complexes of general formula [Ru(η^6-arene)Cl_2L] is well known.[45] We examined simple coordination chemistry of **1** and **2** with [Ru(*p*-cymene)Cl_2]$_2$. The starting ruthenium(II) complex, [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$, was synthesized from the reaction of the commercially available α-phellandrene (5-isopropyl-2-methylcyclohexa-1,3-diene) with $RuCl_3$.[46] As expected, complexation reaction was straightforward, with coordination to ruthenium being carried out at room temperature. Both of the ruthenium complexes were readily synthesized in good yields. The initial colour change, i.e. from clear orange to deep red,[47] is attributed to the dimer cleavage, most probably by the AMPP or phosphinite ligands. The reaction of **1** or **2** with 3/2 equivalent of [Ru(*p*-cymene)Cl_2]$_2$ affords the corresponding **3** and **4**, respectively, as the main products. The ^{31}P-{^1H} NMR spectra are quite consistent with the structure, namely the spectra of **3** and **4** show resonances at 114.41 (s, O–PPh_2), 74.56 ppm (s, N–PPh_2) and 112.49 ppm (s, O–PPh_2), respectively (SI, Figs. 3a and 4a).[48,49] In the ^{13}C NMR spectra, through-space P–C coupling is observed. Furthermore, the ^1H NMR spectral data of the complexes are consistent with the proposed structures. The structural composition of the complexes is also confirmed from FT-IR and elemental analyses (see experimental section). Although single crystals of the complexes can be obtained by slow diffusion of diethyl ether into a solution of the compound in dichloromethane over several days, unfortunately we were not able to keep the crystals from rapid decomposition in air.

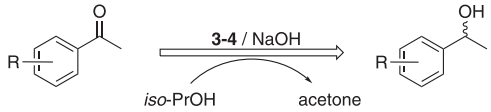
Catalytic Transfer Hydrogenation of Ketones

We have reported that Ru(II)–arene complexes, based on ligands with P–N, P–O and P–N–P backbones, are active catalysts in the reduction of various ketones.[50] The excellent catalytic performance and the higher structural variability of phosphinite-based transition metal catalysts[51–53] prompted us to develop new Ru(II) catalyst systems with well-shaped phosphinite ligands.[54–59] The most important advantage of phosphinite ligands over the corresponding phosphine ligands is the ease of preparation, and by taking into consideration this feature and the marked versatility of phosphines, we also modified the tridendate phosphinite ligands to analogous AMPP ligands. From a practical standpoint, it is of substantial interest to develop highly efficient AMPP ligands for



Scheme 1. Synthesis of the 2-[(diphenylphosphanyl)({2-[(diphenylphosphanyl)oxy]ethyl})amino]ethyldiphenylphosphinite (**1**) and 2-[bis({2-[(diphenylphosphanyl)oxy]ethyl})amino]ethyldiphenylphosphinite (**2**) ligands and their [$Ru_3(Ph_2POC_2H_4)_2NPPh_2(\eta^6$-*p*-cymene)$_3Cl_6$] (**3**) and [$(RuPh_2POC_2H_4)_3N(\eta^6$-*p*-cymene)$_3Cl_6$] (**4**) complexes.

Table 1. Transfer hydrogenation of acetophenone with isopropanol catalysed by **3** and **4**



Entry	Catalyst	Substrate/cat./NaOH	Time	Conversion (%)[a]	TOF (h^{-1})[b]
1	**3**[c]	100:1:5	1 h	Trace	—
2	**4**[c]	100:1:5	1 h	Trace	—
3	**3**[d]	100:1	2 h	<5	—
4	**4**[d]	100:1	2 h	<5	—
5	**3**[e]	100:1:5	10 min	99	594
6	**4**[e]	100:1:5	25 min	98	392

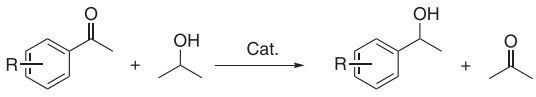
[a]Determined by GC (three independent catalytic experiments).
[b]Referred to the reaction time indicated in column; TOF = (mol product/mol catalyst) × h^{-1}.
[c]At room temperature.
[d]Refluxing in isopropanol, in the absence of base.
[e]Refluxing in isopropanol.

transfer hydrogenation reactions.[60] Therefore, the catalytic activity of complexes **3** and **4** in the transfer hydrogenation of aromatic ketones by isopropanol was investigated. In a typical experiment, 0.005 mmol of the complex and 0.5 mmol of acetophenone were added to a solution of NaOH in isopropanol (0.005 mmol of NaOH in 5 ml of isopropanol) and refluxed at 82°C, while the reaction was monitored using GC.

The complexes were tested as precursors for the catalytic transfer hydrogenation of acetophenone using isopropanol/NaOH as a reducing system. The results are summarized in Table 1. At room temperature no appreciable formation of 1-phenylethanol is observed (Table 1, entries 1 and 2) and also the catalytic activity of $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$ under the applied experimental conditions is insignificant. In addition, as can be inferred from Table 1 (entries 3 and 4), the precatalysts as well as the presence of NaOH are necessary to observe appreciable conversions. The base facilitates the formation of ruthenium alkoxide by abstracting a proton of the alcohol and subsequently alkoxide undergoes β-elimination to give ruthenium hydride, which is an active species in this reaction. This is the mechanism proposed by several research groups studying ruthenium(II)-catalysed transfer hydrogenation reaction by metal hydride intermediates.[61–67] Specifically, the role of the base is to generate a more nucleophilic alkoxide ion which would quickly attack the ruthenium complex responsible for dehydrogenation of isopropanol. As Table 1 shows, high conversions can be achieved with these catalytic systems. The results obtained from optimization studies demonstrate clearly that excellent conversions are achieved in the reduction of acetophenone to 1-phenylethanol when **3** and **4** are used as the catalytic precursors, with a substrate-to-catalyst molar ratio of 100:1 in isopropanol at 82°C (Table 1, entries 5 and 6). It should also be pointed out that complexes **3** and **4** are more active catalysts than the corresponding precursor $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$ (41% maximum yield in 24 h) with a 1/14 complex/NaOH ratio.[68] Furthermore, with a complex/NaOH ratio of 1/5, the complexes are very active leading to a quantitative transformation of the acetophenone, with a good turnover frequency (TOF) of less than 594 h^{-1}.

As seen from Table 1, the catalytic activities in the studied hydrogen transfer reactions are generally much higher for **3** than for **4**. For example, under identical conditions, transfer hydrogenation of acetophenone derivatives with **3** leads to 99% conversions within 10 min, whereas with **4**, similar 98% conversions are achieved only after 25 min (Table 1, entries 5 and 6). Complexes **3** and **4** were widely investigated with different substrates. The catalytic reduction of acetophenone derivatives was tested with the conditions optimized for acetophenone and the results are summarized in Table 2, which illustrates conversions for the reduction performed in 0.1 M isopropanol solution containing **3** or **4** and NaOH (ketone/catalyst/NaOH = 100:1:5). Electronic properties of the substituents on the phenyl ring of the ketone cause the changes in the reduction rate. An *ortho*- or *para*-substituted acetophenone with an electron-donor substituent, i.e. 2-methoxy

Table 2. Transfer hydrogenation results for substituted acetophenones with catalyst systems **3** and **4**[a]



Entry	R	Time	Conversion (%)[b]	TOF (h^{-1})[c]
Catalyst: **3**				
1	4-F	5 min	99	1176
2	4-Cl	5 min	98	1176
3	4-Br	10 min	97	582
4	2-MeO	25 min	96	230
5	4-MeO	15 min	94	376
Catalyst: **4**				
6	4-F	20 min	99	297
7	4-Cl	20 min	97	291
8	4-Br	30 min	97	194
9	2-MeO	1.5 h	96	64
10	4-MeO	1 h	93	93

[a]Catalyst (0.005 mmol), substrate (0.5 mmol), isopropanol (5 ml), NaOH (0.025 mmol%), 82°C, concentration of acetophenone derivatives is 0.1 M.

[b]Purity of compounds checked by ^{1}H NMR and GC (three independent catalytic experiments), yields are based on methylaryl ketone.

[c]TOF = (mol product/mol catalyst) × h^{-1}.

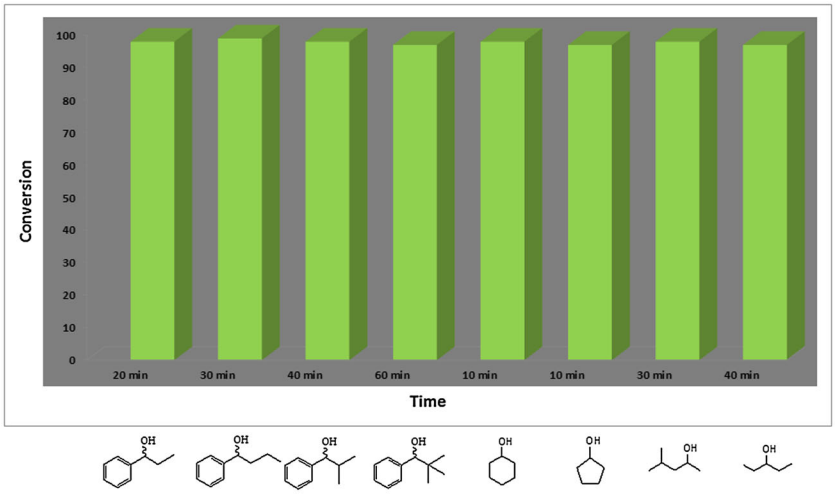


Figure 1. Transfer hydrogenation results for substituted alkylphenyl ketones with catalyst system **3**. Catalyst (0.005 mmol), substrate (0.5 mmol), isopropanol (5 ml), NaOH (0.025 mmol%), 82°C, concentration of alkylphenyl ketones is 0.1 M.

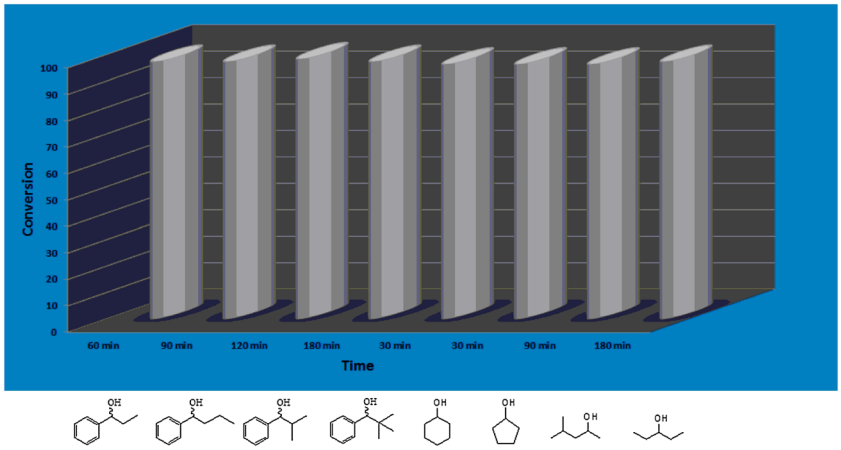


Figure 2. Transfer hydrogenation of various simple ketones with isopropanol catalysed by **4**. Refluxing in isopropanol; acetophenone/catalyst/NaOH = 100:1:5.

or 4-methoxy, is reduced more slowly than acetophenone (Table 2, entries 4, 5, 9 and 10).[69] In addition, the introduction of electron-withdrawing substituents, such as F, Cl and Br, to the *para*-position of the aryl ring of the ketone decreases the electron density of the C=O bond so that the activity is improved giving rise to easier hydrogenation.[70,71] Examination of the results indicates clearly that for each of the tested complexes the best yield is achieved in the reduction of acetophenone derivatives when **3** is used as the catalyst precursor.

We also carried out further experiments to investigate the effect of the bulkiness of the alkyl groups on the catalytic activity. The results are shown in Figs. 1 and 2. A variety of simple arylalkyl ketones were transformed to the corresponding secondary alcohols. It is observed that the activity is dependent on the steric hindrance of the alkyl group. The reactivity gradually reduces on increasing the bulkiness of the alkyl groups.[72–75] Encouraged by the high catalytic activities obtained in these studies, we next extended our investigations to include hydrogenation of various simple ketones. Investigation of catalytic activity of these complexes shows that they are efficient catalysts affording almost quantitative transformation of the ketones in short times, and complex **3** is more active than complex **4** (Figs. 1 and 2). For example, hydrogenation of cyclohexanone can be achieved in approximately 10 and 30 min using **3** and **4**, respectively. Consequently, one can easily conclude that the catalytic activity of Ru–AMPP is generally much higher in the studied hydrogen transfer reactions than that of Ru–phosphinite.

Conclusions

In summary, we have synthesized both new tridendate AMPP and phosphinite ligands and their Ru(II) complexes. We have found that these complexes are efficient homogeneous catalytic systems that can be readily implemented. In particular, the Ru(II)–AMPP complex showed higher catalytic activity in the transfer hydrogenation reaction than the analogous Ru(II)–phosphinite complex. The modular construction of these catalysts towards transfer hydrogenation means that these are systems to pursue.

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