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Novel half-sandwich η5-Cp*–rhodium(III) and η5-Cp*–ruthenium(II) complexes bearing bis(phosphino)amine ligands and their use in the transfer hydrogenation of aromatic ketones

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Two new half-sandwich η5-Cp*–rhodium(III) and η5-Cp*–ruthenium(II) complexes have been prepared from corresponding bis(phosphino)amine ligands, thiophene-2-(*N,N*-bis(diphenylphosphino)methylamine) or furfuryl-2-(*N,N*-bis(diphenylphosphino) amine). Structures of the new complexes have been elucidated by multinuclear one- and two-dimensional NMR spectroscopy, elemental analysis and IR spectroscopy. These Cp*–rhodium(III) and Cp*-ruthenium(II) complexes bearing bis(phosphino) amine ligands were successfully applied to transfer hydrogenation of various ketones by 2-propanol.

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Keywords: bis(phosphino)amine; Cp*; rhodium; ruthenium; transfer hydrogenation

Introduction

Bis(phosphino)amines which bear P—N—P fragments have attracted considerable interest in recent years because of their sophisticated coordination chemistry[1,2] and their potential use in catalytic applications. To date, a number of bis(phosphino) amine compounds have been synthesized and their transition metal chemistry – especially nickel,[3] rhodium,[4] ruthenium,[5] palladium, platinum and copper[6] – has been explored. The applications of P—N—P ligands are extensive both in organometallic chemistry and in homogeneous catalysis, as these ligands can be used for fine adjustment of the activity and selectivity of the catalyst,[5a] especially industrially important reactions such as polymerization,[7] allylic alkylation,[8] the Mizoroki–Heck reaction,[9] Suzuki–Miyaura coupling,[10] hydroformylation[11] and hydrogenation of olefins.[12] In the recent years, Cp* (pentamethylcyclopentadienyl) ligands have also emerged as a promising class of arene ligands for metal-catalyzed transfer hydrogenation.[4,13]

The hydrogenation of unsaturated ketones is a conceptually simple method for the preparation of saturated secondary alcohols, but the transfer hydrogenation version of this process is a more attractive route than H_2 hydrogenation.[14] Ruthenium(II) or rhodium (III) half-sandwich complexes bearing phosphorus-based ligands or Cp* ligands have been successfully employed in transfer hydrogenation of ketones.[15] Formic acid/triethylamine (TEAF), isopropyl alcohol (IPA) and amine-borane adducts are the most used hydrogen sources in transfer hydrogenation.[16] The advantages of transfer hydrogenation using 2-propanol as a hydrogen source are well documented in the literature.[17]

Bis(phosphino)amine ligands with P—N—P fragments have proved to be an effective arrangement for the construction of chelate phosphorus complexes. P—N—P skeletons have also proved to be versatile ligands and varying the substituents on both the P and N centers gives rise to the changes in the P—N—P angles.[18] These bis(phosphino)amine ligands have the advantages of being highly modular, relatively stable toward air or moisture, facile synthesis, easily optimized and ability to chelate transition metals such as ruthenium, rhodium, nickel, palladium, platinum or copper. Considerable attention has been focused on the preparation and properties of ruthenium and rhodium complexes due to their catalytic activities in transfer hydrogenation. There is also continuing interest in the chemistry of half-sandwich η5- Cp*–Rh(III) and η5-Cp*–Ru(II) metal complexes because of their possible use in various catalytic reactions.[15,19] The reactivity of η5-Cp*–Ru(II) with substituted P—N—P-based ligands have been reported by Balakrishna and co-workers[5]; however, to the best of our knowledge no reports of half-sandwich Cp*–Rh(III) complexes containing P—N—P type ligands have been reported so far. Recently, we also reported the synthesis of η5-Cp*–Ru(II) complexes with P—N—P ligands derived from 2- or 4-$CH(CH_3)_2$-substituted aniline and their application in ruthenium-catalyzed transfer hydrogenation.[15b] Following our interest in the coordination chemistry of P—N—P ligands and their use in transfer hydrogenation, we report herein the synthesis and characterization of half-sandwich η5-Cp*–Rh(III) and η5-Cp*–Ru(II) complexes derived from thiophene-2-(*N,N*-bis(diphenylphosphino)methylamine), or furfuryl-2-(*N,N*-bis (diphenylphosphino)amine). The catalytic behavior of these

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complexes in transfer hydrogenation of acetophenone derivatives is also discussed.

Results and Discussion

Synthesis of η^5-Cp*–Rh(III) and η^5-Cp*–Ru(II) Complexes Bearing Bis(phosphino)amine Ligands

In our synthetic work, as the first aim, we synthesized the bis (phosphino)amine ligands, 'thiophene-2-(*N*,*N*-bis(diphenylphosphino) methylamine), $(Ph_2P)_2NCH_2–C_4H_3S$ **1**', or 'furfuryl-2-(*N*,*N*-bis (diphenylphosphino)amine), $(Ph_2P)_2NCH_2–C_4H_3O$ **2**' according to the literature procedure.[10c,20]

Treatment of $[Rh(Cp^*)Cl_2]_2$ in THF solution with two equivalents of bis(phosphino)amine ligand **1** or **2** yielded the half-sandwich cationic Rh(III) complexes $[Rh((Ph_2P)_2NCH_2–C_4H_3S)(Cp^*)Cl]Cl$ **3** or $[Rh((Ph_2P)_2NCH_2–C_4H_3O)(Cp^*)Cl]Cl$ **4**, in 88% or 93% yield, respectively, as seen in Scheme 1. Complexation reactions were straightforward, with coordination to rhodium being carried out at room temperature, and compounds **3** and **4** were formed as air-stable orange microcrystalline powders. The ^{31}P-$\{^1H\}$ NMR spectra of free ligands **1** and **2** show singlets at $\delta = 59.11$ ppm and $\delta = 63.24$ ppm, respectively, due to the equivalent phosphorus nuclei of bis (phosphinoamine) ligands.[2,10] In contrast to free ligands, the phosphorus atoms of complexes **3** and **4** appeared as doublets at $\delta = 71.45$ ($^1J_{RhP} = 119.9$ Hz) and $\delta = 70.51$ ($^1J_{RhP} = 119.9$ Hz), respectively, and these spectra clearly indicate that both phosphorus atoms are bonded to the rhodium (supporting information, Fig. S1). The chemical shifts and expected doublets with appropriate Rh—P coupling constants in the ^{31}P NMR spectra of both rhodium complexes are in accordance with the corresponding values of chelate rhodium complexes with bis(phosphino)amines.[4] Furthermore, structures of complexes **3** and **4** have been elucidated by multinuclear one- and two-dimensional NMR, elemental analysis and IR spectroscopy, and all spectra are in agreement with the structures proposed in the Experimental section. To the best of our knowledge, the half-sandwich Cp*–Rh(III) complexes of P—N—P type ligands **3** or **4** were synthesized for the first time in this study.

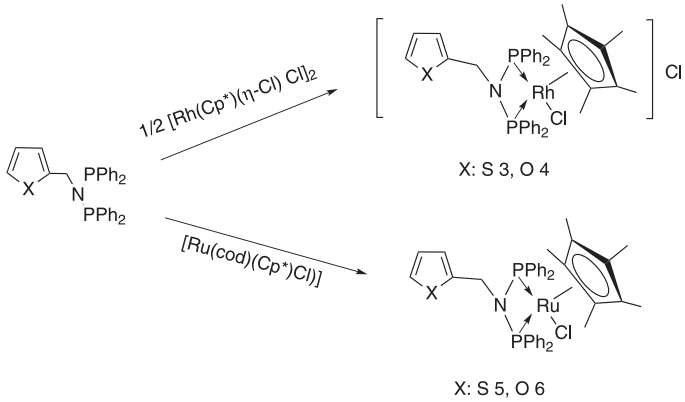
Reaction of [Ru(cod)(Cp*)Cl)] (cod = 1,5-cyclooctadiene) with bis(phosphino)amine ligand **1** or **2** in THF solution in a ratio of 1:1 at room temperature for 1 h gives a deep-red solution. After this time, the solution of complex **5** or **6** was filtered and the solvent was evaporated under vacuum; following recrystallization from diethyl ether/CH_2Cl_2, air-stable brown crystals were obtained in 92% or 89 % yield, respectively, as seen in Scheme 1. The ^{31}P-NMR spectra of neutral complexes $[Ru((Ph_2P)_2NCH_2–C_4H_3S)(Cp^*)Cl]$ **5** or $[Ru((Ph_2P)_2NCH_2–C_4H_3O)(Cp^*)Cl]$ **6** show a singlet at $\delta = 92.56$ ppm or $\delta = 92.04$ ppm, respectively, in line with the values previously observed for similar compounds[15b] (supporting information, Fig. S2). These spectra indicate that cod has been replaced by the chelating bis(phosphino)amine. Structures of **5** and **6** have also been elucidated by multinuclear one- and two-dimensional NMR, elemental analysis and IR spectroscopy. Spectra of **5** and **6** display all signals of coordinated ligands are in agreement with the structures proposed in the Experimental section.

Catalytic Transfer Hydrogenation of Aromatic Ketones

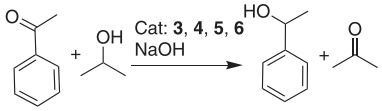
Catalytic transfer hydrogenation is one of the most basic but important reactions in organic chemistry. The activity of half-sandwich rhodium or ruthenium complexes is well known in this catalytic reaction.[13d] In particular, in our previous studies we reported that Rh(I) or Ru(II) complexes based on a P—N—P backbone are active catalysts in the transfer hydrogenation of aromatic ketones.[4,15b] But half-sandwich Cp*–Rh(III) complexes based on the P—N—P backbone have not been reported in transfer hydrogenation reactions so far. For these reasons, we decided to investigate the catalytic behavior of these novel Cp*–Rh (III) or Cp*–Ru(II) complexes bearing a P—N—P backbone in transfer hydrogenation of aromatic ketones.

The catalytic activities of half-sandwich Rh(III) complexes $[Rh((Ph_2P)_2NCH_2–C_4H_3S)(Cp^*)Cl]Cl$ **3** or $[Rh((Ph_2P)_2NCH_2–C_4H_3O)(Cp^*)Cl]Cl$ **4**, and half-sandwich Ru(II) complexes $[Ru((Ph_2P)_2NCH_2–C_4H_3S)(Cp^*)Cl]$ **5** or $[Ru((Ph_2P)_2NCH_2–C_4H_3O)(Cp^*)Cl]$ **6**, were tested on the transfer hydrogenation of acetophenone derivatives under variable conditions by 2-propanol (IPA), wherein IPA is the hydrogen source, as seen in Scheme 2. It was found that the factors acetophenone/complex/NaOH molar ratio and reaction temperature appeared to be essential to achieve high conversions. These Rh(III) and Ru(II) complexes catalyzed the reduction of acetophenone to 1-phenylethanol via hydrogen transfer from IPA with IPA/NaOH as the reducing system, and the results are summarized in Table 1.

Initially, to an iso-PrOH solution of half-sandwich Rh(III) complexes $[Rh((Ph_2P)_2NCH_2–C_4H_3S)(Cp^*)Cl]Cl$ **3** or $[Rh((Ph_2P)_2NCH_2–C_4H_3O)(Cp^*)Cl]Cl$ **4**, and half-sandwich Ru(II) complexes $[Ru((Ph_2P)_2NCH_2–C_4H_3S)(Cp^*)Cl]$ **5** or $[Ru((Ph_2P)_2NCH_2–C_4H_3O)(Cp^*)Cl]$ **6**, an appropriate amount of acetophenone and NaOH/iso-PrOH



Scheme 1. Synthesis of half-sandwich $[Rh((Ph_2P)_2NCH_2-C_4H_3S)(Cp^*)Cl]Cl$ **3** and $[Rh((Ph_2P)_2NCH_2-C_4H_3O)(Cp^*)Cl]Cl$ **4**, or $Ru((Ph_2P)_2NCH_2-C_4H_3S)(Cp^*)Cl]$ **5** and $[Ru((Ph_2P)_2NCH_2-C_4H_3O)(Cp^*)Cl]$ **6** complexes.



Scheme 2. Hydrogen transfer from 2-propanol to acetophenone by half-sandwich rhodium(III) complexes [Rh((Ph$_2$P)$_2$NCH$_2$-C$_4$H$_3$S)(Cp*)Cl]Cl **3** or [Rh((Ph$_2$P)$_2$NCH$_2$-C$_4$H$_3$O)(Cp*)Cl]Cl **4**, and ruthenium(II) complexes [Ru((Ph$_2$P)$_2$NCH$_2$-C$_4$H$_3$S)(Cp*)Cl] **5** or [Ru((Ph$_2$P)$_2$NCH$_2$-C$_4$H$_3$O)(Cp*)Cl] **6**, catalyst.

solutions were added, respectively, at room temperature (acetophenone/cat./NaOH; 100:1:5 molar ratios). The solution was stirred for 24 h and then examined by capillary GC analysis. At room temperature no appreciable formation of 1-phenylethanol was observed in any of the reactions (Table 1, entries 1–4). Employed acetophenone/cat./NaOH molar ratios and reaction temperatures were varied in order to find the optimal transfer hydrogenation conditions. The presence of base is absolutely necessary to observe appreciable conversions because base presumably facilitates catalysis by promoting formation of possibly [Ru]—H from the [Ru]—X (X: Cl, Br) pre-catalyst – transition metal hydride species which are an active species in this reaction, generated from alkoxide complexes.[16,21] A number of acceptable mechanisms are summarized elsewhere with the metal-catalyzed transfer hydrogenation reaction by metal hydride intermediates.[22,23] Kirchner and co-workers have also shown a reasonable mechanism for the transfer hydrogenation of ketones with CpRu–aminophosphine complexes.[22] According to this mechanism, after Br^- dissociation the alkoxide anion attacks the metal center, giving alkoxide-bearing CpRu–aminophosphine complex, and β-elimination from this complex yields the hydride-bearing CpRu–aminophosphine complex and acetone.[22] It may also be mentioned that the choice of base (KOH or NaOH) had little influence on the conversion. As seen in Table 1, optimization studies

Table 1. Transfer hydrogenation of acetophenone with iso-PrOH catalyzed by [Rh((Ph$_2$P)$_2$NCH$_2$–C$_4$H$_3$S)(Cp*)Cl]Cl **3**, [Rh((Ph$_2$P)$_2$NCH$_2$–C$_4$H$_3$O)(Cp*)Cl]Cl **4**, [Ru((Ph$_2$P)$_2$NCH$_2$–C$_4$H$_3$S)(Cp*)Cl] **5** and [Ru((Ph$_2$P)$_2$NCH$_2$-C$_4$H$_3$O)(Cp*)Cl] **6**

Entry	Catalyst	S/C/NaOH	Time	Conversion (%)[d]	TOF (h^{-1})[e]
1	3[a]	100:1:5	1 h	Trace	
2	4[a]	100:1:5	1 h	Trace	
3	5[a]	100:1:5	1 h	Trace	
4	6[a]	100:1:5	1 h	Trace	
5	3[b]	100:1	2 h	<5	
6	4[b]	100:1	2 h	<5	
7	5[b]	100:1	2 h	<5	
8	6[b]	100:1	2 h	<5	
9	3[c]	100:1:5	3 h	98	33
10	4[c]	100:1:5	3 h	99	33
11	5[c]	100:1:5	6 h	98	16
12	6[c]	100:1:5	6 h	99	17

Reaction conditions:
[a]At room temperature; acetophenone/cat./NaOH, 100:1:5.
[b]Refluxing in iso-PrOH; acetophenone/cat. 100:1, in the absence of base.
[c]Refluxing in iso-PrOH; acetophenone/cat./NaOH, 100:1:5.
[d]Determined by GC (three independent catalytic experiments).
[e]Referred at the reaction time indicated in column; TOF = (mol product/mol cat.) × h^{-1}.

of the catalytic reduction of acetophenone in 2-propanol showed that high conversion was obtained with a base/catalyst ratio of >5:1, and increasing the substrate-to-catalyst ratio does not lower the conversion of the product in most cases. The catalytic activity of half-sandwich Rh(III) complexes **3** or **4**, and half-sandwich Ru(II) complexes **5** or **6**, was significantly improved by an increase of reaction temperature from room temperature to 82°C, giving almost quantitative conversions of acetophenone. It should be noted that the catalytic activities in the studied transfer hydrogenation reaction were generally much higher for the half-sandwich Rh(III) complexes [Rh((Ph$_2$P)$_2$NCH$_2$–C$_4$H$_3$S)(Cp*)Cl]Cl **3** or [Rh((Ph$_2$P)$_2$NCH$_2$–C$_4$H$_3$O)(Cp*)Cl]Cl **4** than Ru(II) complexes [Ru((Ph$_2$P)$_2$NCH$_2$–C$_4$H$_3$S)(Cp*)Cl] **5** or [Ru((Ph$_2$P)$_2$NCH$_2$–C$_4$H$_3$O)(Cp*)Cl] **6** (Table 1, entries 9–12).

Because of the encouraging catalytic results complexes **3** and **4** were extensively investigated with a variety of substrates. The catalytic activities of complexes **3** and **4** significantly improved the reduction rate by an increase of reaction temperature from room temperature to 82°C, giving almost quantitative conversions of acetophenone derivatives (*p*-fluoroacetophenone, *p*-chloroacetophenone, *p*-bromoacetophenone, *p*-methoxyacetophenone, *o*-methoxyacetophenone) in the range 98–99% in 2–20 h, respectively (Table 2). It is well known that the electronic properties of substituents on the phenyl ring of acetophenone also cause changes in the reduction rate. The introduction of an electron-withdrawing group such as F, Cl or Br to the *p*-position of the aryl ring of the ketone improved the reduction rate, giving rise to easier hydrogenation (Table 2, entries 1–3 and 8–10).[24] An *o*- or *p*-substituted acetophenone with 2-methoxy or 4-methoxy (known as electron-donor substituent) is reduced more slowly than acetophenone, as seen in Table 2 (entries 6, 7, 13 and 14).

Finally, we extended our investigation to include the effect of bulkiness of the alkyl groups on catalytic activity. A variety of simple aryl alkyl ketones were reduced to the corresponding secondary alcohols. It was found that the catalytic activity highly depended on the steric hindrance of the alkyl group, and transformation to secondary alcohol gradually decreased by increasing the bulkiness of the alkyl groups,[25] as seen in Table 3.

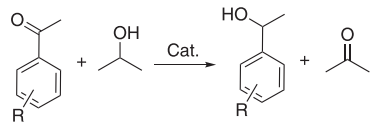
It is mentioned that, compared with our previous bis (phosphino)amine cod-Rh(I) Rh(I)[4] or Cp*–Ru(II)[15b] complexes, for the first time synthesized half-sandwich Cp*–Rh(III) complexes **3** or **4**, and half-sandwich Cp*–Ru(II) complexes **5** or **6**, provide higher turnover frequency (TOF) values in Ru(II)-catalyzed transfer hydrogenation of acetophenone derivatives but lower TOF values in Rh(I)-catalyzed transfer hydrogenation of acetophenone derivatives.

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. Chloro(pentamethylcyclopentadienyl)(cyclooctadiene)Ru(II), pentamethylcyclopentadienyl-Rh(III) chloride dimer, furfurylamine, thiophene-2-methylamine and Ph$_2$PCl are purchased from Fluka and were used as received. ^{1}H (at 400.1 MHz), ^{13}C (at 100.6 MHz) and ^{31}P-{^{1}H} NMR (at 162.0 MHz) spectra were recorded

Table 2. Transfer hydrogenation results for substituted acetophenones with complexes [Rh((Ph$_2$P)$_2$NCH$_2$–C$_4$H$_3$S)(Cp*)Cl]Cl **3** or [Rh((Ph$_2$P)$_2$NCH$_2$–C$_4$H$_3$O)(Cp*)Cl]Cl **4**[a]



Entry	R	Time	Conversion (%)[b]	TOF (h^{-1})[c]
Catalyst: [Rh((Ph$_2$P)$_2$NCH$_2$–C$_4$H$_3$S)(Cp*)Cl]Cl **3**				
1	4-F	2 h	99	50
2	4-Cl	3 h	98	33
3	4-Br	3 h	99	33
4	2-F	4 h	96	24
5	2-Br	3 h	98	33
6	2-MeO	10 h	97	10
7	4-MeO	20 h	99	5
Catalyst: [Rh((Ph$_2$P)$_2$NCH$_2$-C$_4$H$_3$O)(Cp*)Cl]Cl **4**				
8	4-F	2 h	98	49
9	4-Cl	3 h	98	33
10	4-Br	3 h	98	33
11	2-F	6 h	94	16
12	2-Br	4 h	96	24
13	2-MeO	10 h	99	10
14	4-MeO	20 h	98	5

[a]Catalyst (0.005 mmol), substrate (0.5 mmol), iso-PrOH (5 ml), NaOH (0.025 mmol), 82°C, respectively; concentration of acetophenone derivatives is 0.1 M.

[b]Purity of compounds is checked by NMR and GC (three independent catalytic experiments); yields are based on methyl aryl ketone.

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

on a Bruker Avance 400 spectrometer, with tetramethylsilane (TMS) as an internal reference for ^{1}H NMR and ^{13}C NMR or 85% H_3PO_4 as external reference for ^{31}P-{^{1}H} NMR. IR spectra were recorded on a Mattson 1000 ATI UNICAM FT-IR spectrometer as KBr pellets. Elemental analysis was carried out on a Fisons EA 1108 CHNS-O instrument. Melting points were recorded by a Gallenkamp model apparatus with open capillaries. Analyses by gas chromatography (GC) were performed on a Shimadzu 2010 Plus gas chromatograph equipped with a capillary column (5% biphenyl, 95% dimethylsiloxane) (30 m × 0.32 mm × 0.25 μm).

General Procedure for the Transfer Hydrogenation of Ketones

The typical procedure for the catalytic hydrogen transfer reaction was as follows. A solution of complexes [Rh((Ph$_2$P)$_2$NCH$_2$–C$_4$H$_3$S)(Cp*)Cl]Cl **3**, [Rh((Ph$_2$P)$_2$NCH$_2$–C$_4$H$_3$O)(Cp*)Cl]Cl **4**, [Ru((Ph$_2$P)$_2$NCH$_2$–C$_4$H$_3$S)(Cp*)Cl] **5**, [Ru((Ph$_2$P)$_2$NCH$_2$-C$_4$H$_3$O)(Cp*)Cl] **6**, NaOH (0.025 mmol) and the corresponding ketone (0.5 mmol) in degassed iso-PrOH (5 ml) were refluxed until the reactions were completed. After this period a sample of the reaction mixture was removed, diluted with acetone and analyzed immediately by GC. Conversions obtained were related to the residual unreacted ketone.

Syntheses and Characterization of Half-Sandwich [Rh((Ph$_2$P)$_2$NCH$_2$–C$_4$H$_3$S)(Cp*)Cl]Cl 3, [Rh((Ph$_2$P)$_2$NCH$_2$-C$_4$H$_3$O)(Cp*)Cl]Cl 4, [Ru((Ph$_2$P)$_2$NCH$_2$-C$_4$H$_3$S)(Cp*)Cl] 5 and [Ru((Ph$_2$P)$_2$NCH$_2$-C$_4$H$_3$O)(Cp*)Cl] 6 Complexes

Thiophene-2-(*N*,*N*-bis(diphenylphosphino)methylamine) (Ph$_2$P)$_2$NCH$_2$–C$_4$H$_3$S **1** and furfuryl-2-(*N*,*N*-bis(diphenylphosphino)amine) (Ph$_2$P)$_2$NCH$_2$–C$_4$H$_3$O **2** were synthesized according to the literature procedure.[10c,20]

Synthesis of [Rh((Ph$_2$P)$_2$NCH$_2$–C$_4$H$_3$S)(Cp)Cl]Cl **3***

A mixture of [Rh(Cp*)Cl$_2$]$_2$ (0.13 g, 0.20 mmol) and (Ph$_2$P)$_2$NCH$_2$–C$_4$H$_3$S **1** (0.19 g, 0.40 mmol) in 20 ml THF was stirred at room temperature for 0.5 h. The volume of solvent was then reduced to 0.5 ml before addition of diethyl ether (10 ml). The precipitated product was filtered and dried *in vacuo*, yielding [Rh((Ph$_2$P)$_2$NCH$_2$–C$_4$H$_3$S)(Cp*)Cl]Cl **3** as an orange microcrystalline powder (yield 0.28 g, 88%); m.p. 190–191°C. ^{1}H NMR (δ in ppm rel. to TMS, *J* Hz, in CDCl$_3$): 7.53–7.49 (m, 8H, *o*-protons of phenyls), 7.26–7.22 (m, 12H, *m*- and *p*-protons of phenyls), 7.09 (d, 1H, H-5, ^3J = 4.6 Hz), 6.50 (dd, 1H, H-4, ^3J = 3.2 and 4.6 Hz), 6.32 (d, 1H, H-3, ^3J = 3.2 Hz), 4.15 (dd, 2H, , CH$_2$, ^3J = 5.2 and 5.4 Hz), 1.38 (s, 15H, protons of Cp*); ^{13}C NMR (δ in ppm rel. to TMS, *J* Hz, in CDCl$_3$): 138.74 (C-2), 132.54 (d, *o*-carbons of phenyls, ^2J = 4.3 Hz), 131.65 (*p*-carbons of phenyls), 131.33 (d, *i*-carbons of phenyls, ^1J = 10.1 Hz), 129.01 (d, *m*-carbons of phenyls,^3J = 3.0 Hz), 128.33 (C-3), 127.56 (C-5), 126.77 (C-4), 90.56 (carbons Cp*), 47.08 (CH$_2$), 9.82 (carbons CH$_3$—Cp*), assignment was based on ^{1}H-^{13}C HETCOR and ^{1}H-^{1}H COSY spectra; ^{31}P-{^{1}H} NMR (δ in ppm rel. to H_3PO_4, in CDCl$_3$): 71.45 (d, NPP, $^1J_{RhP}$ = 119.9 Hz); selected IR (KBr pellet, in cm^{-1}): υ (P—N—P): 996, (P—Ph): 1436; Anal. Calcd for $C_{39}H_{40}NSCl_2P_2Rh$: calcd C 59.25, H 5.10, N 1.77; found C 59.12, H 5.06, N 1.72%.

Synthesis of [Rh((Ph$_2$P)$_2$NCH$_2$–C$_4$H$_3$O)(Cp)Cl]Cl **4***

To a solution of [Rh(Cp*)Cl$_2$]$_2$ (0.13 g, 0.21 mmol) in THF, a solution (THF, 30 ml) of (Ph$_2$P)$_2$NCH$_2$–C$_4$H$_3$O, **2** (0.19 g, 0.42 mmol) was added. The resulting reaction mixture was stirred at room temperature for 0.5 h. After this time, 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$_2$Cl$_2$, a yellow crystalline powder [Rh((Ph$_2$P)$_2$NCH$_2$–C$_4$H$_3$O)(Cp*)Cl]Cl **4** was obtained (yield 0.30 g, 93%); m.p. 181–182°C. ^{1}H NMR (δ in ppm rel. to TMS, *J* Hz, in CDCl$_3$): 7.54–7.48 (m, 8H, *o*-protons of phenyls), 7.28–7.24 (m, 12H, *m*- *and p*-protons of phenyls), 6.77 (br, 2H, H-5), 5.15 (br, 2H, H-4), 5.47 (br, 2H, H-3), 3.89 (br, 4H, CH$_2$), 1.41 (s, 15H, protons of Cp*); ^{13}C NMR (δ in ppm rel. to TMS, *J* Hz, in CDCl$_3$): 152.00 (br, C-2), 142.04 (C-5), 133.45 (*i*-carbons of phenyls), 132.47 (*o*-carbons of phenyls), 131.51 (*p*-carbons of phenyls), 128.95 (*m*-carbons of phenyls), 110.56 (C-4), 109.81 (C-3), 90.12 (carbons Cp*), 43.23 (—CH$_2$), 9.76 (carbons CH$_3$—Cp*); assignment was based on the ^{1}H-^{13}C HETCOR and ^{1}H-^{1}H COSY spectra; ^{31}P-{^{1}H} NMR (δ in ppm rel. to H_3PO_4, in CDCl$_3$): 70.51 (d, NPP, J_{RhP} = 119.9 Hz); Selected IR (KBr pellet, in cm^{-1}): υ (P—N—P): 924, (P—Ph): 1435; Anal. Calcd. for $C_{39}H_{40}NOCl_2P_2Rh$: calcd C 60.48, H 5.21, N 1.81; found C 60.42, H 5.16, N 1.78%.

Synthesis of [Ru((PPh$_2$)$_2$NCH$_2$–C$_4$H$_3$S)(Cp)Cl] **5***

To a solution of [Ru(cod)(Cp*)Cl)] (0.15 g, 0.38 mmol) in 10 ml THF, a solution (THF, 15 ml) of (PPh$_2$)$_2$NCH$_2$–C$_4$H$_3$S **1** (0.18 g, 0.38 mmol) was added. The resulting reaction mixture was

Table 3. Transfer hydrogenation results for substituted alkylphenylketones with the complex [Rh((Ph$_2$P)$_2$NCH$_2$–C$_4$H$_3$S)(Cp*)Cl]Cl **3** or [Rh((Ph$_2$P)$_2$NCH$_2$–C$_4$H$_3$O)(Cp*)Cl]Cl **4**[a]

Entry	Catalyst	Time	Substrate	Product	Conversion (%)[b]	TOF (h^{-1})[c]
1	**3**	4 h	Ph–CO–Et	Ph–CHOH-Et	98	25
2	**4**	4 h	Ph–CO–Et	Ph–CHOH-Et	97	24
3	**3**	6 h	Ph–CO–Pr	Ph–CHOH-Pr	99	17
4	**4**	6 h	Ph–CO–Pr	Ph–CHOH-Pr	98	16
5	**3**	10 h	Ph–CO–*i*-Pr	Ph–CHOH–*i*-Pr	99	10
6	**4**	10 h	Ph–CO–*i*-Pr	Ph–CHOH–*i*-Pr	98	10
7	**3**	24 h	Ph–CO–*t*-but	Ph–CHOH–*ter*-but	99	<5
8	**4**	24 h	Ph–CO–*t*-but	Ph–CHOH–*ter*-but	99	<5
9	**3**	8 h	$CH_3C(O)(CH_2)_3CH_3$	$CH_3C(OH)(CH_2)_3CH_3$	92	12
10	**4**	7 h	$CH_3C(O)(CH_2)_3CH_3$	$CH_3C(OH)(CH_2)_3CH_3$	95	14
11	**3**	6 h	$CH_3C(O)CH(CH_3)_2$	$CH_3C(OH)CH(CH_3)_2$	91	15
12	**4**	6 h	$CH_3C(O)CH(CH_3)_2$	$CH_3C(OH)CH(CH_3)_2$	97	16
13	**3**	8 h	$CH_3C(O)(CH_2)_2Ph$	$CH_3C(OH)(CH_2)_2Ph$	99	12
14	**4**	8 h	$CH_3C(O)(CH_2)_2Ph$	$CH_3C(OH)(CH_2)_2Ph$	98	12

[a]Catalyst (0.005 mmol), substrate (0.5 mmol), iso-PrOH (5 ml), NaOH (0.025 mmol), 82°C, respectively; concentration of alkylphenylketones is 0.1 M.
[b]Purity of compounds is checked by NMR and GC (three independent catalytic experiments); yields are based on methyl aryl ketone.
[c]TOF = (mol product/mol cat.) × h^{-1}.

allowed to proceed under stirring at room temperature for 1 h. After this time, the solution was filtered and the solvent evaporated under vacuum. The solid residue thus obtained was washed with diethyl ether (3 × 15 ml) and then dried under vacuum. Following recrystallization from diethyl ether/CH_2Cl_2, a brown crystalline powder [Ru((PPh$_2$)$_2$NCH$_2$–C$_4$H$_3$S)(Cp*)Cl] **5** was obtained (yield 0.27 g, 92%); m.p. 168–169°C. ^{1}H NMR (δ in ppm rel. to TMS, *J* Hz, in $CDCl_3$): 7.72 (dd, 8H, *o*-protons of phenyls, ^3J = 7.2 and 13.6 Hz), 7.54 (dd, 4H, *p*-protons of phenyls, ^3J = 6.6 and 12.4 Hz), 7.32 (m, 8H, *m*-protons of phenyls), 7.00 (d, 1H, H-5, ^3J = 5.2 Hz), 6.66 (dd, 1H, H-4, ^3J = 3.8 and 5.2 Hz), 6.39 (d, 1H, H-3, ^3J = 3.8 Hz), 4.45 (t, 2H, CH_2, ^3J = 11.6 Hz), 1.38 (s, 15H, protons of Cp*); ^{13}C NMR (d in ppm rel. to TMS, *J* Hz, in $CDCl_3$): 140.54 (C-2), 134.31 (t, *o*-carbons of phenyls, ^2J = 5.5 Hz), 132.83 (t, *p*-carbons of phenyls, ^4J = 6.0 Hz), 129.84 (d, *i*-carbons of phenyls, ^1J = 57.3 Hz), 127.86 (C-3), 127.41 (t, *m*-carbons of phenyls, ^3J = 4.0 Hz), 126.55 (C-4), 125.32 (C-5), 91.13 (carbons Cp*), 47.68 (CH_2), 9.88 (carbons CH_3—Cp*); assignment was based on ^{1}H-^{13}C HETCOR and ^{1}H-^{1}H COSY spectra; ^{31}P-{^{1}H} NMR (δ in ppm rel. to H_3PO_4, in $CDCl_3$): 92.56 (s, NPP); selected IR (KBr pellet, in cm^{-1}): υ (P—N—P): 986, (P—Ph): 1442; Anal. Calcd for $C_{39}H_{40}NSP_2RuCl$: C 62.18, H 5.35, N 1.86; found: C 62.08, H 5.29, N 1.82%.

Synthesis of [Ru((PPh$_2$)$_2$NCH$_2$–C$_4$H$_3$O)(Cp)Cl]* **6**

To a solution of [Ru(cod)(Cp*)Cl)] (0.13 g, 0.33 mmol) in 10 ml THF, a solution (THF, 30 ml) of (PPh$_2$)$_2$NCH$_2$–C$_4$H$_3$O, **2** (0.15 g, 0.33 mmol) was added. The resulting reaction mixture was stirred at room temperature for 1 h. After this time, the solution was filtered and the solvent evaporated under vacuum. The solid residue thus obtained was washed with diethyl ether (3 × 15 ml) and then dried under vacuum. Following recrystallization from diethyl ether/CH_2Cl_2, a dark-brown crystalline powder [Ru((PPh$_2$)$_2$NCH$_2$–C$_4$H$_3$O)(Cp*)Cl] **6** was obtained (yield 0.21 g, 89%); m.p. 169–171°C. ^{1}H NMR (δ in ppm rel. to TMS, *J* in Hz, $CDCl_3$) 7.45–7.47 (br, 8H, *o*-protons of phenyls), 7.28–7.32 (t, *m*-protons of phenyls, 8H, ^4J = 7.40 Hz), 7.06–7.14 (dd, 4H, *p*-protons of phenyls, ^5J = 7.3 and 8.6 Hz), 7.00 (br, H-5, 1H), 6.05 (br, 1H, H-4), 5.74 (d, 1H, H-3, ^3J = 2.8 Hz), 4.44 (br, 2H, CH_2), 1.37 (s, 15H, protons of Cp*); ^{13}C NMR (δ in ppm rel. to TMS, *J* in Hz, $CDCl_3$): 151.29 (C-2), 141.30 (C-5), 134.78 (*o*-carbons of phenyls), 133.91 (*i*-carbons of phenyls), 129.49 (*p*-carbons of phenyls), 126.73 (*m*-carbons of phenyls), 110.38 (C-4), 109.29 (C-3), 90.03 (carbons Cp*), 45.93 (CH_2), 9.89 (carbons CH_3—Cp*); assignment was based on ^{1}H-^{13}C HETCOR and ^{1}H-^{1}H COSY spectra; ^{31}P-{^{1}H} NMR (δ in ppm rel. to H_3PO_4, $CDCl_3$): 92.04 (s, NPP); selected IR (KBr pellet, in cm^{-1}): υ (P—N—P): 924, (P—Ph): 1434; Anal. Calcd for $C_{39}H_{40}NOP_2RuCl$: C 63.54, H 5.47, N 1.90; found: C 63.42, H 5.41, N 1.85%.

Conclusions

We have synthesized new half-sandwich η^5-Cp*–Rh(III) and η^5-Cp*–Ru(II) complexes bearing bis(phosphino)amine ligands. Cp*–Rh(III) complexes **3** and **4**, based on a P—N—P backbone, were easily synthesized for the first time from the $[Rh(Cp^*)Cl_2]_2$ and bis(phosphino)amine ligands **1** or **2**, at room temperature, respectively. η^5-Cp*–Rh(III) and η^5-Cp*–Ru(II) complexes were used for transfer hydrogenation of aromatic and aliphatic substituted ketones. We have found that these Cp*–Rh(III) and Cp*–Ru(II) complexes are efficient homogeneous catalytic systems that can catalyze the reduction of various ketones via hydrogen transfer from 2-propanol and readily lead to secondary alcohols from high yields. The procedure is simple and efficient towards various aryl ketones. Furthermore, the modular construction of these catalysts and their flexibility toward transfer hydrogenation make these systems to pursue.

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References

[1] A. Schmidpeter, R. Böhm, H. Groeger, *Angew. Chem. Int. Ed. Engl.* **1964**, *3*, 704.
[2] a) A. M. Z. Slawin, M. B. Smith, J. D. Woollins, *J. Chem. Soc. Dalton Trans.* **1998**, 1537; b) F. Agbossou, J. F. Carpentier, F. Hapiot, *Coord.*

Chem. Rev. **1998**, *178–180*, 1615; c) P. J. Dyson, Z. Fei, *Coord. Chem. Rev.* **2005**, *249*, 2056; d) N. Biricik, F. Durap, C. Kayan, B. Gümgüm, *Heteroatom Chem.* **2007**, *18*, 613; e) N. Biricik, F. Durap, B. Gümgüm, Z. Fei, R. Scopelliti, *Transition Met. Chem.* **2007**, *32*, 877; f) B. Gümgüm, O. Akba, F. Durap, L. T. Yıldırım, D. Ülkü, S. Özkar, *Polyhedron* **2006**, *25*, 3133.

[3] O. Akba, F. Durap, M. Aydemir, A. Baysal, B. Gümgüm, S. Özkar, *J. Organomet. Chem.* **2009**, *694*, 731.

[4] M. Aydemir, N. Meriç, C. Kayan, F. Ok, A. Baysal, *Inorg. Chim. Acta* **2013**, *398*, 1.

[5] a) M. S. Balakrishna, K. Ramaswamy, R. M. Abhyankar, *J. Organomet. Chem.* **1998**, *560*, 131; b) M. S. Balakrishna, R. Panda, D. C. Smith Jr, A. Klaman, S. P. Nolan, *J. Organomet. Chem.* **2000**, *599*, 159.

[6] a) F. Majoumo-Mbe, P. Lonnecke, E. V. Novikova, G. P. Belov, E. Hey-Hawkins, *J. Chem. Soc. Dalton Trans.* **2005**, 3326; b) F. Durap, N. Biricik, B. Gümgüm, S. Özkar, W. H. Ang, R. Scopelliti, P. J. Dyson, *Polyhedron* **2008**, *27*, 196.

[7] a) C. Qi, S. Zhang, J. Sun, *Appl. Organometal. Chem.* **2006**, *20*, 138; b) Z. Sun, F. Zhu, Q. Wu, S. Lin, *Appl. Organometal. Chem.* **2006**, *20*, 175.

[8] a) Y. Wang, H. Guo, K. L. Ding, *Tetrahedron: Asymm.* **2000**, *11*, 4153; b) Y. Wang, X. Li, K. L. Ding, *Tetrahedron Lett.* **2002**, *43*, 159.

[9] a) M. T. Reetz, G. Lohmer, R. Schwickardi, *Angew. Chem. Int. Ed.* **1997**, *36*, 1526; b) D. L. Zotto, E. Zangrando, W. Baratta, A. Felluga, P. Martinuzzi, P. Rigo, *Eur. J. Inorg. Chem.* **2005**, 4707; c) B. Gümgüm, N. Biricik, F. Durap, İ. Özdemir, N. Gürbüz, W. H. Ang, P. J. Dyson, *Appl. Organometal. Chem.* **2007**, *21*, 711.

[10] a) M. L. Clarke, D. J. Cole-Hamilton, J. D. Woollins, *J. Chem. Soc. Dalton Trans.* **2001**, 2721; b) N. Biricik, F. Durap, C. Kayan, B. Gümgüm, N. Gürbüz, İ. Özdemir, W. H. Ang, Z. Fei, R. Scopelliti, *J. Organomet. Chem.* **2008**, *693*, 2693;c) M. Aydemir, A. Baysal, F. Durap, B. Gümgüm, S. Özkar, L. T. Yıldırım, *Appl. Organometal. Chem.* **2009**, *23*, 467.

[11] a) C. Abu-Gnim, I. Amer, *J. Organomet. Chem.* **1996**, *516*, 235; b) M. R. Zubiri, L. C. Matthew, D. F. Foster, D. J. Cole-Hamilton, A. M. Z. Slawin, J. D. Woollins, *J. Chem. Soc. Dalton Trans.* **2001**, 969.

[12] a) R. W. Guo, A. J. Lough, R. H. Morris, D. T. Song, *Organometallics* **2004**, *23*, 5524; b) B. Pugin, H. U. Blaser, *Adv. Synth. Catal.* **2006**, *348*, 1743.

[13] a) K. T. Prasad, B. Therrien, K. M. Rao, *J. Organomet. Chem.* **2008**, *693*, 3049; b) A. J. Blacker, S. B. Duckett, J. Grace, R. N. Perutz, A. C. Whitwood, *Organometallics* **2009**, *28*, 1435; c) K. Takahashi, M. Yamashita, Y. Tanaka, K. Nozaki, *Angew. Chem. Int. Ed.* **2012**, *51*, 4383; d) C. G. Arena, A. Cuzzola, D. Drommi, *Polyhedron* **2012**, *48*, 221.

[14] R. A. W. Jhonstone, A. H. Wilby, I. D. Entwistle, *Chem. Rev.* **1985**, *85*, 129.

[15] a) A. C. Marr, M. Nieuwenhuyzen, C. L. Pollock, G. C. Saunders, *Organometallics* **2007**, *26*, 2659; b) M. Aydemir, A. Baysal, *J. Organomet. Chem.* **2010**, *695*, 2506; c) W. N. O. Wylie, A. J. Lough, R. H. Morris, *Organometallics* **2012**, *31*, 2137.

[16] S. Gladiali, E. Alberico, *Chem. Soc. Rev.* **2006**, *35*, 226.

[17] a) S. H. Deshpande, A. S. Kelkar, R. G. Gonnade, S. K. Shingote, R. V. Chaudhari, *Catal. Lett.* **2010**, *138*, 231; b) R. Noyori, S. Hashiguchi, *Acc. Chem. Res.* **1997**, *30*, 97; c) K. Everaere, A. Mortreux, J. Carpentier, *Adv. Synth. Catal.* **2003**, *345*, 67.

[18] H.-J. Chen, J. M. Barendt, R. C. Haltiwanger, T. G. Hill, A. D. Norman, *Phosphorus, Sulfur* **1986**, *26*, 155.

[19] a) M. Achard, N. Derrien, H.-J. Zhang, B. Demerseman, C. Bruneau, *Org. Lett.* **2009**, *11*, 185; b) A. Reyna-Madrigal, A. Moreno-Gurrola, O. Perez-Camacho, M. E. Navarro-Clemente, P. Juarez-Saavedra, M. A. Leyva-Ramirez, A. M. Arif, R. D. Ernst, M. A. Paz-Sandoval, *Organometallics* **2012**, *31*, 7125.

[20] M. Aydemir, A. Baysal, E. Şahin, B. Gümgüm, S. Özkar, *Inorg. Chim. Acta* **2011**, *378*, 10.

[21] a) I. Nieto, M. S. Livings, J. B. Sacci III, L. E. Reuther, M. Zeller, E. T. Papish, *Organometallics* **2011**, *30*, 6339; b) T. Ikariya, A. J. Blacker, *Acc. Chem. Res.* **2007**, *40*, 1300.

[22] C. Standfest-Hauser, C. Slugovc, K. Mereiter, R. Schmid, K. Kirchner, L. Xiao, W. Weissensteiner, *J. Chem. Soc. Dalton Trans.* **2001**, 2989.

[23] a) C. P. Casey, S. W. Singer, D. R. Powell, R. K. Hayashi, M. Kavana, *J. Am. Chem. Soc.* **2001**, *123*, 1090; b) J. Hannedouche, G. J. Clarkson, M. Wills, *J. Am. Chem. Soc.* **2004**, *126*, 986; c) J. S. Chen, Y. Li, Z. Dong, B. Li, J. Gao, *Tetrahedron Lett.* **2004**, *45*, 8415.

[24] a) J. W. Faller, A. R. Lavoie, *Organometallics* **2001**, *20*, 5245; b) İ. Özdemir, S. Yaşar, *Transition Met. Chem.* **2005**, *30*, 831.

[25] a) J.-X. Gao, X.-D. Yi, P.-P. Xu, C.-L. Tang, H.-L. Wan, T. Ikariya, *J. Organomet. Chem.* **1999**, *592*, 290; b) J.-X. Gao, H. Zhang, X.-D. Yi, P.-P. Xu, C.-L. Tang, H.-L. Wan, K.-R. Tsai, T. Ikariya, *Chirality* **2000**, *12*, 383; c) Z.-R. Dong, Y.-Y. Li, J.-S. Chen, B.-Z. Li, Y. Xing, J.-X. Gao, *Org. Lett.* **2005**, *6*, 7.

Supporting Information

Additional supporting information may be found in the online version of this article at the publisher's web site.

Figure S1. The ^{31}P-{^{1}H} NMR spectra of half-sandwich [Rh((Ph_2P)$_2$ NCH_2-C_4H_3S)(Cp*)Cl]Cl **3** or [Rh((Ph_2P)$_2NCH_2$-C_4H_3O)(Cp*)Cl]Cl **4**, complexes.

Figure S2. The ^{31}P-{^{1}H} NMR spectra of half-sandwich [Ru((Ph_2P)$_2$ NCH_2-C_4H_3S)(Cp*)Cl] **5** or [Ru((Ph_2P)$_2NCH_2$-C_4H_3O)(Cp*)Cl] **6** complexes.