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A modular design of metal catalysts for the transfer hydrogenation of aromatic ketones

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The ability of transition metal catalysts to add or remove hydrogen from organic substrates by transfer hydrogenation is a valuable synthetic tool. Towards a series of novel metal complexes with a P-NH ligand, $[Ph_2PNHCH_2\text{-}C_4H_3O]$ derived from furfurylamine were synthesized. Reaction of $[Ph_2PNHCH_2\text{-}C_4H_3O]$ 1 with $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$, $[Ru(\eta^6\text{-benzene})(\mu\text{-Cl})Cl]_2$, $[Rh(\mu\text{-Cl})(cod)]_2$ and $[Ir(\eta^5\text{-}C_5Me_5)(\mu\text{-Cl})Cl]_2$ gave a range of new monodentate complexes $[Ru(Ph_2PNHCH_2\text{-}C_4H_3O)(\eta^6\text{-}p\text{-cymene})Cl_2]$ 2, $[Ru(Ph_2PNHCH_2\text{-}C_4H_3O)(\eta^6\text{-benzene})Cl_2]$ 3, $[Rh(Ph_2PNHCH_2\text{-}C_4H_3O)(cod)Cl]$ 4, and $[Ir(Ph_2PNHCH_2\text{-}C_4H_30)(\eta^5\text{-}C_5Me_5)Cl_2]$ 5, respectively. All new complexes were fully characterized by analytical and spectroscopic methods. $^{31}P\text{-}\{^1H\}$ NMR, distortionless enhancement by polarization transfer (DEPT) or $^1H\text{-}^{13}C$ heteronuclear correlation (HETCOR) experiments were used to confirm the spectral assignments. Following activation by KOH, compounds 2–5 catalyzed the transfer hydrogenation of acetophenone derivatives to 1-phenylethanol derivatives in the presence of iso-PrOH as the hydrogen source. Notably $[Ru(Ph_2PNHCH_2\text{-}C_4H_3O)(\eta^6\text{-benzene})Cl_2]$ 3 acts as an excellent catalyst, giving the corresponding alcohols in 98–99% yield in 20 min at 82°C (time of flight ≤ 297 h^{-1}) for the transfer hydrogenation reaction in comparison to analogous rhodium or iridium complexes.

Supporting information may be found in the online version of this article.

Keywords: aminophosphine; transfer hydrogenation; rhodium; iridium; ruthenium

Introduction

Since its discovery, transfer hydrogenation using ruthenium complexes as catalysts has been an increasingly useful tool in organic synthesis,[1–3] allowing transformations otherwise very difficult or almost impossible to carry out. Catalytic transfer hydrogenation with the aid of a stable hydrogen donor is a useful alternative method for catalytic hydrogenation by molecular hydrogen.[4] In transfer hydrogenation, organic molecules such as primary and secondary alcohols[5] or formic acid and its salts[6] have been employed as the hydrogen source. The use of the hydrogen donor has some advantages over the use of molecular hydrogen since it avoids risks and the constraints associated with hydrogen gas, as well as the necessity for pressure vessels and other equipment. Iso-PrOH is a popular reactive solvent for transfer hydrogenation reactions since it is easy to handle and is relatively non-toxic, environmentally benign and inexpensive. The volatile acetone by-product can also be easily removed to shift unfavourable equilibria.

There are several metal sources available that have to mediate the hydride transfer from the donor to the substrate. Even if main-group metals like aluminium have historically been used in the transfer hydrogenation reactions,[7,8] today's catalysts of choice are transition metal complexes predominantly of ruthenium, rhodium or iridium.[9,10] In general, asymmetric hydrogenation is mediated by a complex bearing one of these transition metals, among which our focus has been Ru. One reason is that the Ru catalysts have excellent performance.[11,12] Another reason is that Ru enjoys a cost advantage relative to other asymmetric hydrogenation metals such as Rh.[13]

Synthesis of new aminophosphines to stabilize transition metals in low valent states is considered to be the most challenging task in view of their potential utility in a variety of metal-mediated organic transformations.[14,15] To date, a number of such systems with a variety of backbone frameworks have been synthesized and their transition metal chemistry has been explored.[16] Tertiary phosphines have long been used in the synthesis of transition metal complexes with catalytic properties.[17,18]

Extending our programme in the design and study of useful catalysts, herein we describe the coordination chemistry of the P-NH ligand, $[Ph_2PNHCH_2\text{-}C_4H_3O]$ with selected transition metals (Ru(II), Rh(I), Ir(III)). The syntheses and full characterization of four aminophosphine complexes – $[Ru(Ph_2PNHCH_2\text{-}C_4H_3O)(\eta^6\text{-}p\text{-cymene})Cl_2]$ **2**, $[Ru(Ph_2PNHCH_2\text{-}C_4H_3O)(\eta^6\text{-benzene})Cl_2]$ **3**, $[Rh(Ph_2PNHCH_2\text{-}C_4H_3O)(cod)Cl]$ **4**, and $[Ir(Ph_2PNHCH_2\text{-}C_4H_3O)(\eta^5\text{-}C_5Me_5)Cl_2]$ **5** – were elucidated by a combination of multinuclear NMR spectroscopy, IR spectroscopy and elemental analysis. We also report the catalytic activity in transfer hydrogenation reactions of acetophenone derivatives with iso-PrOH.

Experimental

Analytical

NMR analyses

All ^1H and ^{13}C NMR measurements were performed in $CDCl_3$ and recorded on a Bruker Avance 400 spectrometer. ^1H NMR spectra were collected at 400 MHz using an 8000 Hz spectral width, a relaxation delay of 3.95 s, a pulse width of 30°, 30k data points and $CDCl_3$ (7.27 ppm) as an internal reference. ^{13}C NMR spectra were collected at 100 MHz using a 24 000 Hz spectra width, a relaxation

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delay of 1.4 s, 75k data points, a pulse width of 30° and $CDCl_3$ (77.23 ppm) as the internal reference. ^{31}P NMR spectra were collected at 162 MHz using a 65 000 Hz spectra width, a relaxation delay of 0.5 s, 150k data points, a pulse width of 30° and $CDCl_3$ as the external reference.

Melting points

Melting point determinations were performed on samples using a Gallenkamp model (Sanyo Biomedical Equipment) apparatus with a ramp rate of 5°C min^{-1}.

FT-IR

FT-IR spectra were recorded on a Mattson 1000 ATI Unicam FT-IR spectrometer (ATI-UNICAM Inc.). Optical-grade, random cuttings of KBr (International Crystal Laboratories, Garfield, NJ, USA) were ground with 1.0 wt% of the sample for FT-IR analysis.

Materials

Unless otherwise stated, all reactions were carried out under argon using Schlenk glassware. Solvents were dried using established procedures and distilled under argon immediately prior to use. The starting materials $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$,[19] $[Ru(\eta^6\text{-benzene})(\mu\text{-Cl})Cl]_2$,[20] $Rh(\mu\text{-Cl})(cod)]_2$[21] and $[Ir(\eta^5\text{-}C_5Me_5)(\mu\text{-Cl})Cl]_2$[22] were prepared according to literature procedures. Analytical-grade and deuterated solvents were purchased from Merck. PPh_2Cl and furfurylamine are purchased from Fluka and used as received.

GC Analyses and General Procedure for the Transfer Hydrogenation of Ketones

GC analyses were performed on an HP 6890N gas chromatograph equipped with 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 110°C; initial time 1 min; solvent delay 4.48 min; temperature ramp 80°C min^{-1}; final temperature 200°C; final time 21.13 min; injector port temperature 200°C; detector temperature 200°C, injection volume 2.0 μl. Typical procedure for the catalytic hydrogen transfer reaction: a solution of complexes $[Ru(Ph_2PNHCH_2\text{-}C_4H_3O)(\eta^6\text{-}p\text{-cymene})Cl_2]$ **2**, $[Ru(Ph_2PNHCH_2\text{-}C_4H_3O)(\eta^6\text{-benzene})Cl_2]$ **3**, $[Rh(Ph_2PNHCH_2\text{-}C_4H_3O)(cod)Cl]$ **4** or $[Ir(Ph_2PNHCH_2\text{-}C_4H_3O)(\eta^5\text{-}C_5Me_5)Cl_2]$ **5** (0.005 mmol), KOH (0.025 mmol) and the corresponding ketone (0.5 mmol) in degassed iso-PrOH (5 ml) were refluxed for 45 min for **2**, 20 min for **3**, 2 h for **4** and 4 h for **5**. After this period a sample of the reaction mixture was taken off, diluted with acetone and analysed immediately by GC. Conversions obtained are related to the residual unreacted ketone.

Synthesis of the Ligand and its Transition Metal Complexes

*Furfuryl-(N-*diphenylphosphino)amine, $[Ph_2PNHCH_2\text{-}C_4H_3O]$ **1**

Chlorodiphenylphosphine (0.237 g, 1.02 mmol) was added dropwise over a period of 15 min to a stirred solution of furfurylamine (0.099 g, 1.02 mmol) and triethylamine (0.104 g, 1.02 mmol) in THF (40 ml) at 0°C. The mixture was then stirred at room temperature for 1 h and the white precipitate (triethylammonium chloride) was filtered under argon and the solvent was removed under reduced pressure. The residue was then washed with dried cold diethyl ether (2 × 10 ml) and dried *in vacuo* to produce a clear, white viscous oily compound **1**. Yield 0.261 g, 91.1%. ^1H NMR (δ in ppm rel. to TMS, *J* Hz, in $CDCl_3$): δ = 7.45–7.48 (m, *o*-protons of phenyls, 4H), 7.36–7.41 (m, *m*- and *p*-protons of phenyls, 6H), 7.35 (d, H-5, 1H, ^3J 2.0 Hz), 6.30 (dd, H-4, 1H, ^3J 2.0 and 3.2), 6.11 (d, H-3, 1H, ^3J 3.2 Hz), 4.01 (dd, -CH_2-, 2H, ^3J 6.8 and 8.8 Hz), 2.38 (dt, -NH-, 1H, *J* 6.8 and 13.2 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 43.09 (-CH_2-), 106.27 (C-3), 110.26 (C-4), 141.71 (d, C-5), 128.30 (d, *m*-carbons of phenyls, $^3J(^{31}P\text{-}^{13}C)$ 6.3 Hz), 128.58 (s, *p*-carbons of phenyls), 131.44 (d, *o*-carbons of phenyls, $^2J(^{31}P\text{-}^{13}C)$ 19.0 Hz), 140.95 ppm (d, *i*-carbons of phenyls, $^1J(^{31}P\text{-}^{13}C)$ 12.1 Hz), 154.95 (d, C-2, $^3J(^{31}P\text{-}^{13}C)$ 6.0 Hz), assignment was based on the $^1H\text{-}^{13}C$ heteronuclear correlation (HETCOR), distortionless enhancement by polarization transfer (DEPT) and $^1H\text{-}^1H$ correlation spectroscopy (COSY) spectra; ^{31}P NMR (δ in ppm rel. to H_3PO_4, in $CDCl_3$): 42.71 (s); IR, (KBr): u = 804 (P-N), 1434 (P-Ph), 3383 (N-H) cm^{-1}; $C_{17}H_{16}ONP$ (281.3 g mol^{-1}): calc. C 72.59, H 5.73, N 4.98; found C 72.49, H 5.64, N 4.95.

[Ru(Ph$_2$PNHCH$_2$-C$_4$H$_3$O)(η^6-p-cymene)Cl$_2$] **2**

To a solution of $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$ (0.312 g, 0.51 mmol) in tetrahydrofuran, a solution (THF, 30 ml) of $[Ph_2PNHCH_2\text{-}C_4H_3O]$ **1** (0.287 g, 1.02 mmol) was added. The resulting reaction mixture was allowed to proceed with 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 × 10 ml) and then dried under vacuum. Following recrystallization from diethylether/CH_2Cl_2, a red crystalline powder was obtained. Yield 0.560 g, 93.5%, m.p. = 192–193°C. ^1H NMR (δ in ppm rel. to TMS, *J* Hz, in $CDCl_3$): 7.93–7.97 (m, 4H, *o*-protons of phenyls), 7.42–7.59 (m, 6H, *m- and p*-protons of phenyls), 7.20 (br, 1H, H-5), 6.16 (br, 1H, H-4),), 6.01 (br, 1H, H-3), 5.27 (d, 2H, ^3J = 5.3 Hz, aromatic protons of *p*-cymene), 5.10 (d, 2H, ^3J = 5.7 Hz, aromatic protons of *p*-cymene), 3.61 (dt, 1H, ^3J = 6.4 and 13.0 Hz, NH), 3.51 (dd, 2H, ^3J = 6.6 and 7.3 Hz, -CH_2-), 2.64 (m, 1H, -CH- of *p*-cymene), 1.97 (s, 3H, CH_3-Ph of *p*-cymene), 0.86 (d, 6H, ^3J = 6.8 Hz, $(CH_3)_2$CHPh of *p*-cymene); ^{13}C NMR (δ in ppm rel. to TMS, *J* Hz, in $CDCl_3$): 17.44 (CH_3Ph of *p*-cymene), 21.32 ($(CH_3)_2$CHPh of *p*-cymene), 30.06 (-CH- of *p*-cymene), 40.08 (d, ^2J = 10.1 Hz, -CH_2-), 86.19, 91.08 (aromatic carbons of *p*-cymene), 94.08, 108.21 (quaternary carbons of *p*-cymene), 106.71 (C-3), 110.14 (C-4), 141.43 (C-5), 128.14 (d, ^3J = 10.1 Hz, *m*-carbons of phenyls), 130.77 (d, ^4J = 2.0 Hz, *p*-carbons of phenyls), 132.86 (d, ^2J = 11.1 Hz, *o*-carbons of phenyls), 133.95 (d, ^1J = 51.3 Hz, *i*-carbons of phenyls), 152.96 (d, ^3J = 6.0 Hz, C-2); assignment was based on the $^1H\text{-}^{13}C$ HETCOR, DEPT and $^1H\text{-}^1H$ COSY spectra; ^{31}P NMR (δ in ppm rel. to H_3PO_4, in $CDCl_3$): 60.98 (s); IR, (KBr): u = 845 (P-N), 1433 (P-Ph), 3375 (N-H) cm^{-1}; $C_{27}H_{30}NPORuCl_2$ (587.5 g mol^{-1}): calc. C 55.20, H 5.15, N 2.38; found C 55.01, H 5.11, N 2.35.

Synthesis of [Ru(Ph$_2$PNHCH$_2$-C$_4$H$_3$O)(η^6-benzene)Cl$_2$] **3**

A mixture of $[Ru(\eta^6\text{-benzene})(\mu\text{-Cl})Cl]_2$ (0.255 g, 0.51 mmol) and $[Ph_2PNHCH_2\text{-}C_4H_3O]$ (0.287 g, 1.02 mmol) in 15 ml THF was stirred at room temperature for 2 h. The volume of the 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 **3** as a red microcrystalline powder. Yield 0.510 g, 94.1%, m.p. = 180°C (dec.). ^1H NMR (400.1 MHz, $CDCl_3$) δ = 7.91–7.97 (m, 4H, *o*-protons of phenyls), 7.51–7.52 (m, 6H, *m- and p*-protons of phenyls), 7.22 (d, 1H, ^3J = 1.8 Hz, H-5), 6.17 (dd, 1H, ^3J = 1.8 and 3.2 Hz, H-4), 6.02 (d, 1H, ^3J = 3.1 Hz, H-3), 5.41 (s, 6H, aromatic protons of benzene), 3.68 (dd, 2H, ^3J = 7.6 and 7.8 Hz, -CH_2-), 3.55 (m, 1H, NH); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 40.20 (d, ^2J = 9.1 Hz, -CH_2-), 88.78 (d, ^2J = 4.0 Hz, aromatic carbon of benzene), 106.92

(C-3), 110.18 (C-4), 141.61 (C-5), 128.38 (d, ^3J = 11.1 Hz, *m*-carbons of phenyls), 131.02 (d, ^4J = 3.0 Hz, *p*-carbons of phenyls), 132.67 (d, ^2J = 11.1 Hz, *o*-carbons of phenyls), 133.92 (d, ^1J = 54.3 Hz, *i*-carbons of phenyls), 152.70 (d, ^3J = 7.0 Hz, C-2); assignment was based on the ^{1}H-^{13}C HETCOR, DEPT and ^{1}H-^{1}H COSY spectra; ^{31}P-{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 61.63 (s); IR, (KBr): *u* = 916 (P-N), 1433 (P-Ph), 3334 (N-H) cm^{-1}; $C_{23}H_{22}NPORuCl_2$ (531.4 g mol^{-1}): calc. C 51.98, H 4.17, N 2.64; found C 51.85, H 4.14, N 2.61.

Synthesis of [Rh(Ph_2PNHCH_2-C_4H_3O)(cod)Cl] ***4***

A mixture of [Rh(μ-Cl)(cod)]$_2$ (0.252 g, 0.51 mmol) and [Ph_2PNHCH_2-C_4H_3O] (0.287 g, 1.02 mmol) in 15 ml THF was stirred at room temperature for 3 h. The volume of the 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 **4** as a yellow microcrystalline solid. Yield 0.420 g, 88.8%, m.p. = 118–120°C. ^{1}H NMR (400.1 MHz, $CDCl_3$) δ = 7.83–7.87 (m, 4H, *o*-protons of phenyls), 7.44–7.51 (m, 6H, *m- and p*-protons of phenyls), 7.30 (d, 1H, ^3J = 1.9 Hz, H-5), 6.24 (dd, 1H, ^3J = 1.9 and 2.1 Hz, H-4), 6.10 (d, 1H, ^3J = 2.8 Hz, H-3), 5.56 (br, 2H, CH of cod), 4.22 (m, 1H, NH), 3.77 (br, 2H, -CH_2-), 2.94 (br, 2H, CH of cod), 2.30 (m, 4H, CH_2 of cod), 1.95 (br, 4H, CH_2 of cod); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 28.57 (CH_2 of cod (a)), 32.85 (d, ^2J = 5.0 Hz, CH_2 of cod (b)), 40.28 (d, ^2J = 10.1 Hz, -CH_2-), 70.94 (d, ^1J = 4.0 Hz, CH of cod (a)), 105.21 (d, ^1J = 6.0 Hz, CH of cod (b)), 106.76 (C-3), 110.20 (C-4), 141.78 (C-5), 128.33 (d, ^3J = 10.1 Hz, *m*-carbons of phenyls), 130.62 (d, ^4J = 2.0 Hz, *p*-carbons of phenyls), 133.36 (d, ^2J = 12.1 Hz, *o*-carbons of phenyls), 132.26 (d, ^1J = 45.3 Hz, *i*-carbons of phenyls), 153.01 (d, ^3J = 8.1 Hz, C-2); assignment was based on the ^{1}H-^{13}C HETCOR, DEPT and ^{1}H-^{1}H COSY spectra; ^{31}P-{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 61.57 (d, ^1J (^{103}Rh-^{31}P) = 157.14 Hz); IR, (KBr): *u* = 3454 (N-H), 1011 (P-N), 1436 (P-Ph) cm^{-1}. $C_{25}H_{28}NOPRhCl$ (527.8 g mol^{-1}): calc. C 56.89, H 5.34, N 2.65; found C 56.82, H 5.31, N 2.61.

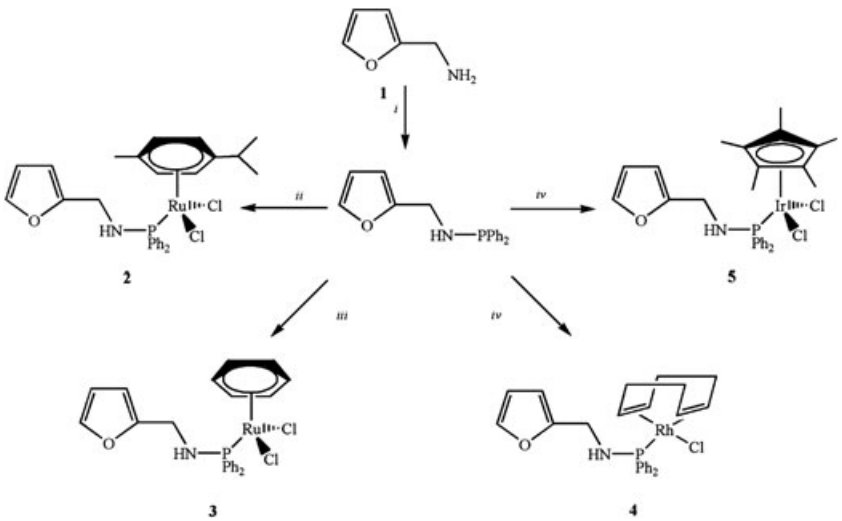
Synthesis of [Ir(Ph_2PNHCH_2-C_4H_3O)(η^5-C_5Me_5)Cl_2] ***5***

A mixture of [Ir(η^5-C_5Me_5)(μ-Cl)Cl]$_2$ (0.414 g, 0.51 mmol) and [Ph_2PNHCH_2-C_4H_3O] (0.287 g, 1.02 mmol) in 15 ml tetrahydrofuran was stirred at room temperature for 3 h. The volume of the 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 **5** as an orange microcrystalline solid. Yield 0.630 g, 91.0%, m.p. = 196.5–198.5°C. ^{1}H NMR (400.1 MHz, $CDCl_3$) δ = 7.87–7.93 (m, 4H, *o*-protons of phenyls), 7.46–7.47 (m, 6H, *m- and p*-protons of phenyls), 7.21 (d, 1H, ^3J = 1.7 Hz, H-5), 6.18 (dd, 1H, ^3J = 1.7 and ^3J = 2.8 Hz, H-4), 6.12 (d, 1H, ^3J = 2.8 Hz, H-3), 3.85 (m, 1H, NH), 3.74 (dd, 2H, ^3J = 7.0 and 7.2 Hz, -CH_2-), 1.41 (d, 15H, ^4J = 2.1 Hz, CH_3 of Cp* (C_5Me_5); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 8.24 (C_5Me_5), 40.79 (d, ^2J = 8.1 Hz, -CH_2-), 92.36 (d, ^2J = 12.0 Hz, C_5Me_5), 106.59 (C-3), 110.19 (C-4), 141.36 (C-5), 127.91 (d, ^3J = 11.1 Hz, *m*-carbons of phenyls), 130.84 (d, ^4J = 3.0 Hz, *p*-carbons of phenyls), 131.33 (d, ^1J = 61.4 Hz, *i*-carbons of phenyls), 133.41 (d, ^2J = 11.1 Hz, *o*-carbons of phenyls), 153.31 (d, ^3J = 7.0 Hz, C-2); assignment was based on the ^{1}H-^{13}C HETCOR, DEPT and ^{1}H-^{1}H COSY spectra; ^{31}P-{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 34.33 (s); IR, (KBr): *u* =3338 (N-H), 885 (P-N), 1436 (P-Ph) cm^{-1}. $C_{27}H_{31}NOPIrCl_2$ (679.6 g mol^{-1}): calc. C 47.72, H 4.60, N 2.06; found C 47.68, H 4.55, N 2.04.

Results and Discussion

Synthesis and Characterization of the Complexes

As shown in Scheme 1, furfuryl-2-(*N*-diphenylphosphino)amine, [Ph_2PNHCH_2-C_4H_3O] **1** was prepared from the commercially available starting material furfurylamine and one equivalent of PPh_2Cl in the presence of triethylamine by aminolysis.[23,24] The ^{31}P NMR spectrum of **1** showed a single resonance at δ(P) 42.71 ppm, similar to those found for closely related compounds (see supplementary info. Figure 1).[25,26] [Ph_2PNHCH_2-C_4H_3O] **1** is not stable and decomposes rapidly on exposure to air or moisture. Solutions of **1** in $CDCl_3$, prepared under anaerobic conditions, are also unstable and decompose gradually to give the corresponding oxide and bis(diphenylphosphino)monoxide [$P(O)Ph_2PPh_2$] derivatives. **1** was fully characterized by multinuclear NMR, infrared spectroscopy and microanalysis. In the ^{1}H NMR spectrum, the NH resonance of **1** was observed as slightly broad pseudo-triplet or doublet of triplets at 2.38 ppm due to the multiple coupling $^3J_{(CHNH)}$ and $^2J_{(NHP)}$ and this



Scheme 1. Synthesis of [Ph_2PNHCH_2-C_4H_3O] and its [Ru(Ph_2PNHCH_2-C_4H_3O)(η^6-*p*-cymene)Cl_2] **2**, [Ru(Ph_2PNHCH_2-C_4H_3O)(η^6-benzene)Cl_2] **3**, [Rh(Ph_2PNHCH_2-C_4H_3O)(cod)Cl] **4** and [Ir(Ph_2PNHCH_2-C_4H_3O)(η^5-C_5Me_5)Cl_2] **5** complexes. (i) 1 equiv. Ph_2PCl, 1 equiv. Et_3N, THF; (ii) 1/2 equiv. [Ru(Ph_2PNHCH_2-C_4H_3O)(η^6-*p*-cymene)Cl_2], THF; (iii) 1/2 equiv. [Ru(η^6-benzene)(μ-Cl)Cl]$_2$, THF; (iv) 1/2 equiv. [Rh(μ-Cl)(cod)]$_2$, Thf; (v) 1/2 equiv. [Ir(η^5-C_5Me_5)(μ-Cl)Cl]$_2$, THF.

was confirmed by H/D exchange experiment. The signal of NH simply disappeared from the spectrum. Furthermore, characteristic $J_{(31P\text{-}13C)}$ coupling constants of the carbons of the phenyl rings were observed in the ^{13}C NMR spectrum (including *i*-, *o*-, *m*-, *p*-carbons of phenyl rings; for details see experimental section), which are consistent with the literature values.[27]

The reaction of stoichiometric amounts of $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$ and $[Ph_2PNHCH_2\text{-}C_4H_3O]$ **1** affords complex $[Ru(Ph_2PNHCH_2\text{-}C_4H_3O)(\eta^6\text{-}p\text{-cymene})Cl_2]$ **2** in high yield as an air-stable, red microcrystalline powder (Scheme 1). **1** was expected to cleave the $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$ dimer to give the corresponding complex **2** via monohapto coordination of the aminophosphine group. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of **2** shows a single resonance at 60.98 ppm, in line with the values previously observed for similar compounds[28] (see Table 1 and supplementary info Figure 1). Analysis by ^1H NMR reveals this compound to be diamagnetic, exhibiting signals corresponding to the aromatic rings at 7.93–7.42 ppm. Another set of signals consisting of two doublets centred at 5.27 and 5.10 ppm is due to the presence of the aromatic protons in the *p*-cymene group (the presence of one (broad) or two signals corresponding to CH *p*-cymene protons in the ^1H NMR spectrum, consistent with a *Cs* symmetry of complex and with free rotation of the arene ligand).[29,30] Furthermore, in the ^{13}C NMR spectrum of **2**, $J_{(31P\text{-}13C)}$ coupling constants of the carbons of the phenyl rings were observed, which are consistent with the literature values.[31] The structure of **2** was further confirmed by IR spectroscopy and microanalysis, and found to be in good agreement with the theoretical values.

We also examined some simple coordination chemistry of **1** with $[Ru(\eta^6\text{-benzene})(\mu\text{-Cl})Cl]_2$ precursor. This ligand was also expected to cleave the $[Ru(\eta^6\text{-benzene})(\mu\text{-Cl})Cl]_2$ dimer to yield the corresponding complex **3** via monohapto coordination of the aminophosphine group. This complex is highly soluble in CH_2Cl_2 but slightly soluble in hexane, so it can be crystallized from CH_2Cl_2/hexane solution. The chemical purity of the complex **3** was confirmed by a single $^{31}P\text{-}\{^1H\}$ NMR signal at 61.63 ppm (see Table 1 and supplementary info Figure 1). The ^1H NMR spectrum of complex **3** is in agreement with the proposed structure (Table 2). Furthermore, in the $^{13}C\text{-}\{^1H\}$ NMR spectrum of **3**, $J(^{31}P\text{-}^{13}C)$ coupling constants of the carbons of the phenyl rings were observed, which are consistent with the literature values[32–34] (for details, see Experimental section). The structural composition of complex **3** was further confirmed by IR spectroscopy and microanalysis, and found to be in good agreement with the theoretical values.

We also examined some simple coordination chemistry of $[Ph_2PNHCH_2\text{-}C_4H_3O]$ with $[Rh(\mu\text{-Cl})(cod)]_2$ and $[Ir(\eta^5\text{-}C_5Me_5)(\mu\text{-Cl})Cl]_2$ precursors. Reactions of $[Ph_2PNHCH_2\text{-}C_4H_3O]$ with $Rh(\mu\text{-Cl})(cod)]_2$ and $[Ir(\eta^5\text{-}C_5Me_5)(\mu\text{-Cl})Cl]_2$ in THF in a ratio of 1:1/2 at room temperature for 3 h gave a microcrystalline precipitate of neutral complexes **4** and **5**, respectively. Bridge cleavage of the dimer $[Rh(\mu\text{-Cl})(cod)]_2$ with $[Ph_2PNHCH_2\text{-}C_4H_3O]$ gave the mononuclear compound $[Rh(Ph_2PNHCH_2\text{-}C_4H_3O)(cod)Cl]$ **4** in good yield. The coordination of the ligand through the P donor was confirmed by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy. The spectrum recorded in deuterated chloroform at room temperature shows a doublet centred at δ(P) 61.57 ppm with a $J_{(P\text{-}Rh)} = 157.1$ Hz[35,36] (see Table 1 and supplementary info Figure 2). IR spectroscopy and elemental analysis of product **4** are consistent with the suggested molecular formula. ^1H and ^{13}C NMR spectra of compound **4** display all the signals of coordinated ligands (Table 1 and 2; for details see Experimental section). As for the characterization of complex **5**, in $^{31}P\text{-}\{^1H\}$ NMR, a singlet at 34.33 ppm was assigned to $[Ir(Ph_2PNHCH_2\text{-}C_4H_3O)(\eta^5\text{-}C_5Me_5)Cl_2]$ **5** (see supplementary info, Figure 2), in line with the values previously observed for similar compounds[37] (see Table 1). Analysis by ^1H NMR reveals this compound to be diamagnetic, exhibiting signals corresponding to the proposed structure (Table 2). Furthermore, in the $^{13}C\text{-}\{^1H\}$ NMR spectrum of **5**, $J(^{31}P\text{-}^{13}C)$ coupling constants of the carbons of the phenyl rings were observed (for details see Experimental section). The structure of **5** was further confirmed by IR spectroscopy and microanalysis, and found to be in good agreement with the theoretical values. (Table 2)

Table 1. Selected ^1H, ^{31}P NMR data for ligand **1** and its complexes **2–5**

Compound	$\delta(^1H)$			$\delta(^{31}P)$
	CH_2	NH	Aromatics (Ph)	
1	4.01 (dd, *J* 6.8; 8.8 Hz)	2.38 (dt, *J* 6.8; 13.2 Hz)	7.36–7.48	42.71
2	3.51 (dd, *J* 6.6; 7.3 Hz)	3.61 (dt, *J* 6.4; 13.0 Hz)	7.42–7.97	60.98
3	3.68 (dd, *J* 7.6; 7.8 Hz)	3.55 (m)	7.51–7.97	61.63
4	3.77 (br)	4.22 (m)	7.44–7.87	61.57[a]
5	3.74 (dd, *J* 7.0; 7.2 Hz)	3.85 (m)	7.46–7.93	34.33

[a] $^1J(^{103}Rh\text{-}^{31}P) = 157.1$ Hz.

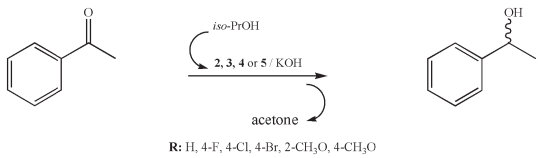
Table 2. Selected ^1H NMR data for ligand **1** and its complexes **2–5**

Compound	$\delta(^1H)$		
	H(3)	H(4)	H(5)
1	6.11 (d, *J* 3.2 Hz)	6.30 (dd, *J* 2.0; 3.2 Hz)	7.35 (d, *J* 2.0 Hz)
2	6.01 (br)	6.16 (br)	7.20 (br)
3	6.02 (d, *J* 3.1 Hz)	6.17 (dd, *J* 1.8; 3.1 Hz)	7.22 (d, *J* 1.8 Hz)
4	6.10 (d, *J* 2.8 Hz)	6.24 (dd, *J* 1.9; 2.1 Hz)	7.30 (d, *J* 1.9 Hz)
5	7.21 (d, *J* 2.8 Hz)	6.18 (dd, *J* 1.7; 2.9 Hz)	7.21 (d, *J* 1.7 Hz)

Catalytic transfer hydrogenation of acetophenone derivatives

Iso-PrOH is the conventional hydrogen source having favourable properties; it is stable, easy to handle (b.p. 82°C), non-toxic, environmentally friendly, inexpensive and the acetone product is readily removable.[38] The activity of Ru(II) arene complexes is well known in this catalytic process.[39,40] Recently, we reported that the novel half-sandwich complexes, based on ligands with a P-N and P-O backbone, are active catalysts in the reduction of aromatic ketones.[41–44] The observed activity of these complexes has encouraged us to investigate other analogous ligands and other transition metal complexes of these ligands. A complex with sp^3-hybridized nitrogens containing N-H bonds displays higher reaction rate. On the other hand, the presence of an N-H group in the ligands makes it possible to stabilize a six-membered cyclic transition state by forming a hydrogen bond with the oxygen atom of ketones.[45–47]

In a preliminary study, the obtained complexes **2–5** were examined in the reduction of acetophenone to the corresponding alcohol in iso-PrOH solution (Scheme 2) and the results are listed in Table 3. At room temperature no appreciable formation of 1-phenylethanol was observed (Table 3, entries 1–4). As can be inferred from Table 3 (entries 5–8), the catalysts as well as the presence of KOH are necessary to observe appreciable conversions. The base facilitates the formation of an alkoxide by abstracting a proton of the alcohol and subsequently this alkoxide undergoes β-elimination to give ruthenium hydride, which is the mechanism proposed by several groups who have studied the ruthenium-catalyzed transfer hydrogenation reaction by metal hydride intermediates.[48,49] In addition, we have expanded the substrate-to-catalyst ratio to observe the effect on catalytic efficiency. As shown in Table 3, increasing the substrate-to-catalyst ratio does not damage the conversion of the product in most cases except that the reaction time lengthened. Remarkably, the transfer hydrogenation of acetophenone could be achieved to 99% yield even when the substrate-to-catalyst ratio reached 500:1.



Scheme 2. General reaction scheme for the metal-catalyzed hydrogen transfer from iso-PrOH to acetophenone.

When the reaction temperature was increased to 82°C smooth reduction of acetophenone into 1-phenylethanol occurred, with conversions of 98–99% after 45 min, 20 min, 2 h and 4 h for **2**, **3**, **4** and **5**, respectively. From the results observed, it is noteworthy that complexes **2**, **3**, **4** and **5** display the differences in reactivities, with a complex/KOH ratio of 1/5. From these preliminary experimental results, it can be concluded that the η6-benzene–ruthenium complex **3** is more effective than the other complexes. In addition, the catalytic efficiency was seen to be dependent on the arene ligand. That is to say, the catalytic activity was affected by type of arene moieties. Furthermore, it should be pointed out that complex **3** is far more active than the corresponding precursor, $[Ru(\eta^6\text{-benzene})(\mu\text{-Cl})Cl]_2$ (37% maximum yield in 24 h).[50]

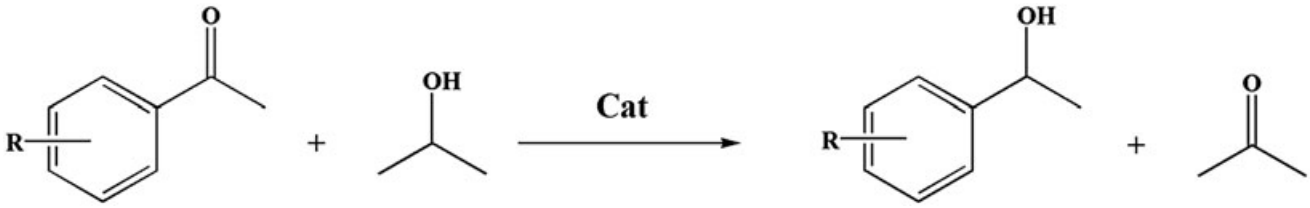
Encouraged by the activities obtained in these preliminary studies, we next extended our investigations to include hydrogenation of substituted acetophenone derivatives. The catalytic reduction of acetophenone derivatives was tested using the conditions optimized for acetophenone. The results are summarized in Table 4. The fourth column in Table 4 illustrates conversions of

Table 3. Transfer hydrogenation of acetophenone with iso-PrOH catalysed by $[Ru(Ph_2PNHCH_2\text{-}C_4H_3O)(\eta^6\text{-}p\text{-cymene})Cl_2]$ **2**, $[Ru(Ph_2PNHCH_2\text{-}C_4H_3O)(\eta^6\text{-benzene})Cl_2]$ **3**, $[Rh(Ph_2PNHCH_2\text{-}C_4H_3O)(cod)Cl]$ **4** and $[Ir(Ph_2PNHCH_2\text{-}C_4H_3O)(\eta^5\text{-}C_5Me_5)Cl_2]$ **5**

Entry	Catalyst	S/C/KOH	Time	Conversion (%)[e]	TOF (h^{-1})[f]
1	**2**[a]	100:1:5	1 h	<3	—
2	**3**[a]	100:1:5	1 h	<3	—
3	**4**[a]	100:1:5	1 h	<3	—
4	**5**[a]	100:1:5	1 h	<3	—
5	**2**[b]	100:1	1 h	<5	—
6	**3**[b]	100:1	1 h	<5	—
7	**4**[b]	100:1	1 h	<5	—
8	**5**[b]	100:1	1 h	<5	—
9	**2**[c]	500:1:5	3 h	99 ± 03	33
10	**3**[c]	500:1:5	1 h	99 ± 05	99
11	**4**[c]	500:1:5	8 h	97 ± 02	12
12	**5**[c]	500:1:5	12 h	98 ± 04	<10
13	**2**[d]	100:1:5	45 min	98 ± 04	132
14	**3**[d]	100:1:5	20 min	99 ± 03	297
15	**4**[d]	100:1:5	2 h	98 ± 05	49
16	**5**[d]	100:1:5	4 h	97 ± 03	24

Reaction conditions:
[a]At room temperature; acetophenone/Ru/KOH, 100:1:5.
[b]Refluxing in iso-PrOH; acetophenone/Ru, 100:1, in the absence of base.
[c]Refluxing in iso-PrOH; acetophenone/Ru/KOH, 500:1:5.
[d]Refluxing in iso-PrOH; acetophenone/Ru/KOH, 100:1:5.
[e]Determined by GC (three independent catalytic experiments).
[f]Referred at the reaction time indicated in column; TOF = (mol product/mol Ru(II) cat.) h^{-1}.

Table 4. Transfer hydrogenation results for substituted acetophenones with the catalyst systems prepared from $[Ph_2PNHCH_2\text{-}C_4H_3O]$ and $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$, $[Ru(\eta^6\text{-benzene})(\mu\text{-Cl})Cl]_2$, $[Rh(\mu\text{-Cl})(cod)]_2$ and $[Ir(\eta^5\text{-}C_5Me_5)(\mu\text{-Cl})Cl]_2$[a]



Entry	R	Time	Conversion (%)[b]	TOF (h^{-1})[c]
Cat: Ru(II)-*p*-cymene complex **2**				
1	4-F	45 min	99 ± 05	132
2	4-Cl	45 min	98 ± 03	130
3	4-Br	45 min	95 ± 05	127
4	2-MeO	45 min	92 ± 03	123
5	4MeO	45 min	90 ± 05	120
Cat: Ru(II)-benzene complex **3**				
6	4-F	20 min	99 ± 03	297
7	4-Cl	20 min	97 ± 03	291
8	4-Br	20 min	96 ± 05	288
9	2-MeO	20 min	94 ± 06	282
10	4MeO	20 min	93 ± 02	279
Cat: Rh(I)-cod complex **4**				
11	4-F	2 h	99 ± 04	50
12	4-Cl	2 h	98 ± 04	49
13	4-Br	2 h	97 ± 05	49
14	2-MeO	2 h	89 ± 06	45
15	4MeO	2 h	85 ± 03	43
Cat: Ir(III)-Cp* complex **5**				
16	4-F	4 h	98 ± 04	25
17	4-Cl	4 h	97 ± 06	24
18	4-Br	4 h	96 ± 02	24
19	2-MeO	4 h	91 ± 05	23
20	4MeO	4 h	90 ± 04	23

[a]Catalyst (0.005 mmol), substrate (0.5 mmol), iso-PrOH (5 ml), KOH (0.025 mmol%), 82°C, 45 min for **2**, 20 min for **3**, 2 h for **4** and 4 h for **5**, respectively; the 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}.

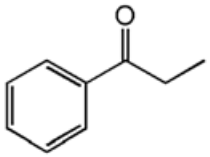
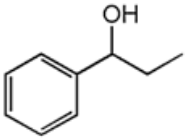
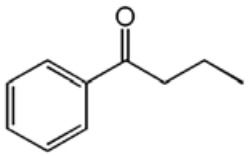
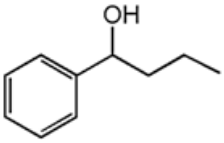
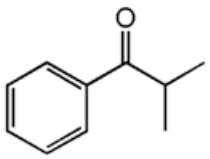
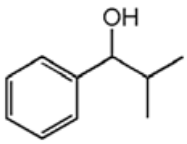
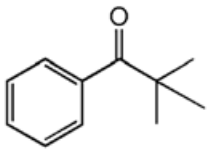
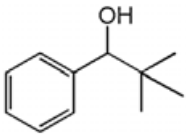
the reduction performed in a 0.1 M of iso-PrOH solution containing **2**, **3**, **4** or **5** and KOH (ketone:Ru:KOH = 100:1:5). It is expected that electronic properties (the nature and position) of the substituents on the phenyl ring of the ketone cause the changes in the reduction rate. An *ortho*- or *para*-substituted acetophenone with an electron donor substituent, i.e. 2-methoxy or 4-methoxy, is reduced more slowly than acetophenone (Table 4, entries 4, 5, 9, 10, 14, 15, 19 and 20).[51] 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 decreased the electron density of the C O bond so that the activity was improved, giving rise to easier hydrogenation.[52,53]

Additionally, we further extended our study from acetophenone to other aryl alkyl ketones and the results are summarized in Table 5. A variety of simple aryl alkyl ketones were transformed to the corresponding secondary alcohols. It was found that the activity is highly dependent on the steric bulkiness of the alkyl group.[54] The reactivity gradually decreased by increasing the bulkiness of the alkyl groups.[55] That is to say, when the size of the alkyl group was increased, the activity was remarkably decreased.[56,57]

Conclusions

We have synthesized a novel aminophosphine ligand and its selected transition metal (Ru(II), Rh(I), Ir(III)) complexes based on furfuryl-(*N*-diphenylphosphino)amine monodentate ligand. We have found that these complexes are efficient homogeneous catalytic systems that can be readily implemented and lead to secondary alcohols from good to excellent yields. In particular, Ru(II)–benzene aminophosphine complex showed strong catalytic activity in the transfer hydrogenation reaction compared to the analogous Ru(II)-*p*-cymene, Rh(I)-cod and Ir(III)-Cp* complexes. The procedure is simple and efficient towards various aryl ketones.

Table 5. Transfer hydrogenation results for substituted alkyl phenyl ketones with the catalyst systems prepared from $[Ph_2PNHCH_2\text{-}C_4H_3O]$ and $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$, $[Ru(\eta^6\text{-benzene})(\mu\text{-Cl})Cl]_2$, $[Rh(\mu\text{-Cl})(cod)]_2$ and $[Ir(\eta^5\text{-}C_5Me_5)(\mu\text{-Cl})Cl]_2$[a]

Entry	Catalyst	Time (h)	Substrate	Product	Conversion (%)[b]	TOF (h^{-1})[c]
1	**2**	2			98 ± 06	49
2	**3**	1			98 ± 03	98
3	**4**	6			99 ± 05	17
4	**5**	12			97 ± 04	8
5	**2**	3			98 ± 03	33
6	**3**	1			98 ± 04	98
7	**4**	7			99 ± 06	14
8	**5**	14			98 ± 05	7
9	**2**	5			99 ± 04	20
10	**3**	2			98 ± 05	49
11	**4**	12			98 ± 07	8
12	**5**	24			99 ± 07	<5
13	**2**	8			99 ± 04	12
14	**3**	3			99 ± 03	33
15	**4**	14			97 ± 05	<10
16	**5**	30			98 ± 03	<5

[a]Catalyst (0.005 mmol), substrate (0.5 mmol), iso-PrOH (5 ml), KOH (0.025 mmol%), 82°C, respectively; the concentration of alkyl phenyl ketones 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}.

SUPPORTING INFORMATION

Supporting information may be found in the online version of this article.

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