Aminophosphine ligands $R_2P(CH_2)_nNH_2$ and ruthenium hydrogenation catalysts $RuCl_2(R_2P(CH_2)_nNH_2)_2$†

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The aminophosphine ligands $R_2P(CH_2)_2NH_2$ and $R_2P(CH_2)_3NH_2$ (R = Ph, ^{i}Pr, ^{t}Bu) were isolated in good to excellent yields from the reaction of $LiPR_2$ with $Cl(CH_2)_2N(TMS)_2$ and $Cl(CH_2)_3N(TMS)_2$, respectively, followed by hydrolysis. This approach allows fine tuning of the ligands' stereoelectronic properties through the variation of the substituents on the phosphine. The aminophosphine ligands were used to prepare the ruthenium complexes $RuCl_2(R_2P(CH_2)_2NH_2)_2$ and $RuCl_2(R_2P(CH_2)_3NH_2)_2$ by reacting a 2:1 mixture of the respective ligand and $[RuCl_2(cod)]_n$ in an appropriate solvent. The resulting complexes were found to be excellent catalysts for the hydrogenation of ketones and imines.

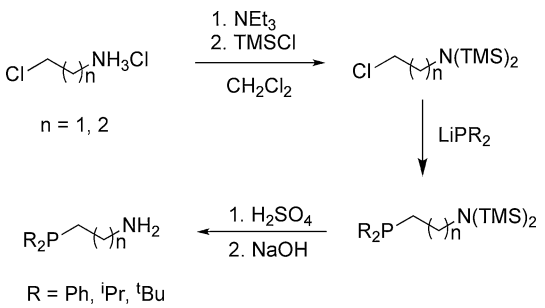
Introduction

The hydrogenation of ketones and imines represents one of the fundamental processes in synthetic organic chemistry and, as a result, significant effort has been devoted towards the development of practical protocols for this transformation.[1–4] This has led to a variety of notable chiral and achiral catalysts. The most well-known are the Noyori type $RuCl_2$(diphosphine)-(diamine) and $RuCl_2(PR_3)_2$(diamine) complexes.[1,3] We have demonstrated that ruthenium aminophosphine catalysts of the type $RuCl_2$(aminophosphine)$_2$ and $RuCl_2$(diphosphine)-(aminophosphine) are also very effective for the hydrogenation of carbonyl (ketones and aldehydes) and imine substrates.[5a–5c] Both the Noyori type and aminophosphine catalysts share a common mechanistic pathway during ketone hydrogenation: the presence of a mutually *cis* Ru-H $\cdots$ H-N moiety in the active ruthenium dihydride catalysts which is generated from the dichloride compounds in the presence of a base and hydrogen gas.[5,6]

Recently, metal complexes containing protic aminophosphine ligands have been shown to be very versatile in a variety of other catalytic reductions such as the hydrogenation of esters,[7] epoxides,[8] imides,[8b–8d] N-acylcarbamates[8a,d,e] and N-acylsulfonamides.[8e] Other applications include transfer hydrogenation[9] and carbon-carbon[10] bond formation, including a variety of asymmetric processes.[5,11,12] One of the drawbacks to the use of aminophosphines for large scale applications is the lack of readily available ligands in commercial and industrial quantities. As part of our research endeavour to develop practical and facile large scale processes for the synthesis of aminophosphine ligands we discovered that the achiral aminophosphine ligands $R_2P(CH_2)_2NH_2$ and $R_2P(CH_2)_3NH_2$ can be prepared and isolated in high yields from the reaction of a metal phosphide (MPR_2, M = Li, Na, K; R = alkyl, aryl) with $Cl(CH_2)_2N(TMS)_2$ and $Cl(CH_2)_3N(TMS)_2$.[13] The latter compounds are derived from commercially available chloroalkylammonium salts. The preparation of $RuCl_2(Ph_2P(CH_2)_2NH_2)_2$ was reported previously.[5a,5d] Here we report the synthesis of the related compounds $RuCl_2(R_2P(CH_2)_2NH_2)_2$ (R = ^{i}Pr, ^{t}Bu) and $RuCl_2(R_2P(CH_2)_3NH_2)_2$ (R = Ph, ^{i}Pr, ^{t}Bu) and their use for the hydrogenation of a variety of carbonyl and imine substrates.

Results and discussion

A variety of procedures are reported in the literature for the preparation of aminophosphine ligands.[11] The procedure outlined in Scheme 1 represents a general and efficient procedure for the synthesis of aminophosphine ligands of the type $R_2P(CH_2)_2NH_2$ and $R_2P(CH_2)_3NH_2$ (R = alkyl, aryl).



Scheme 1 Preparation of $R_2P(CH_2)_2NH_2$ and $R_2P(CH_2)_3NH_2$.

The precursor compounds N,N′-bis(trimethylsilyl)-2-chloroethanamine and N,N′-bis(trimethylsilyl)-3-chloropropanamine were prepared from chloroethylammonium chloride and chloropropylammonium chloride, respectively.[14] A solution of the precursor in THF was added dropwise to an ice-cold solution of lithium phosphide in THF. The mixture was brought to reflux and after cooling to room temperature, hydrolysis with dilute sulfuric acid solution and neutralization with sodium hydroxide

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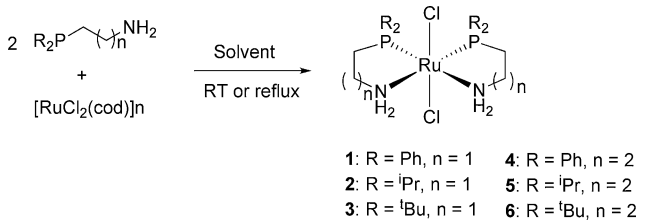
† Electronic supplementary information (ESI) available: NMR spectra (^{1}H, ^{13}C and ^{31}P{^{1}H}) of the 6 aminophosphine ligands. CCDC reference number 733474. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b911459a

solution, the crude aminophosphine was obtained by partitioning in hexanes and removal of the solvent under vacuum. The pure ligands were obtained by vacuum distillation and isolated as colourless to pale yellow viscous oils.

The ruthenium complexes $RuCl_2(R_2P(CH_2)_2NH_2)_2$ and $RuCl_2(R_2P(CH_2)_3NH_2)_2$ were prepared by reacting a mixture of the respective ligand and $[RuCl_2(cod)]_n$ in an appropriate solvent and were isolated as yellow to yellow-brown solids (Scheme 2).



Scheme 2 Preparation of $RuCl_2(R_2P(CH_2)_2NH_2)_2$ and $RuCl_2(R_2P(CH_2)_3NH_2)_2$.

A range of isomers are obtained depending on the ligand, the solvent used and the reaction conditions employed. The procedures described in this study focussed on selectively obtaining the *trans*-dichloride compounds. Complex **1** was obtained by stirring a 2:1 mixture of $Ph_2P(CH_2)_2NH_2$ and $[RuCl_2(cod)]_n$ in methylene chloride at room temperature. Refluxing in THF or toluene results in a mixture of the *trans*-dichloride and *cis*-dichloride isomers that are difficult to quantify and characterize because of their insolubility in most common organic solvents. Refluxing a 2:1 mixture of $^iPr_2P(CH_2)_2NH_2$ and $[RuCl_2(cod)]_n$ or $^tBu_2P(CH_2)_2NH_2$ and $[RuCl_2(cod)]_n$ in toluene results exclusively in the *trans*-dichloride complexes **2** and **3**, whereas if the reactions are conducted in THF a mixture of *cis*- and *trans*-dichloride isomers resulted. Complexes **4** and **5** were obtained by refluxing a 2:1 mixture of the ligands $Ph_2P(CH_2)_3NH_2$ and $^iPr_2P(CH_2)_3NH_2$, respectively, and $[RuCl_2(cod)]_n$ in toluene. The synthesis of complex **6** required refluxing a 2:1 mixture of $^tBu_2P(CH_2)_3NH_2$ and $[RuCl_2(cod)]_n$ in methylene chloride.

Complex **1** is very sparingly soluble in dichloromethane and DMSO. It is insoluble in most other solvents including THF, toluene, ethanol, 2-propanol, ether and hexanes. Complexes **2** and **3** are sparingly soluble in THF and toluene; slightly soluble in methylene chloride, ethanol and 2-propanol; and insoluble in diethyl ether and hexanes. Complexes **4–6** are more soluble than their $RuCl_2(R_2P(CH_2)_2NH_2)_2$ analogues and dissolve in toluene, methylene chloride, ethanol and 2-propanol. They are insoluble in diethyl ether and hexanes. All of the complexes are air stable as dry solids and can be stored in air for several months. On the other hand, their solutions are susceptible to slow oxidation in air and are best stored and handled under inert atmosphere.

The single crystal X-ray structure of **2** is shown in Fig. 1. The complex crystallizes as a distorted octahedron with *trans* chlorides and mutually *cis* phosphines and NH_2 moieties. The chloride ligands are bent towards the nitrogen atoms (Cl1-Ru-Cl2 = 166.31(4)°), possibly due to hydrogen bonding to the NH_2 moieties.

Ruthenium aminophosphine complexes of the type $RuCl_2(aminophosphine)_2$ can be used as catalysts for the hydrogenation of ketones, imines and aldehydes. Table 1 shows

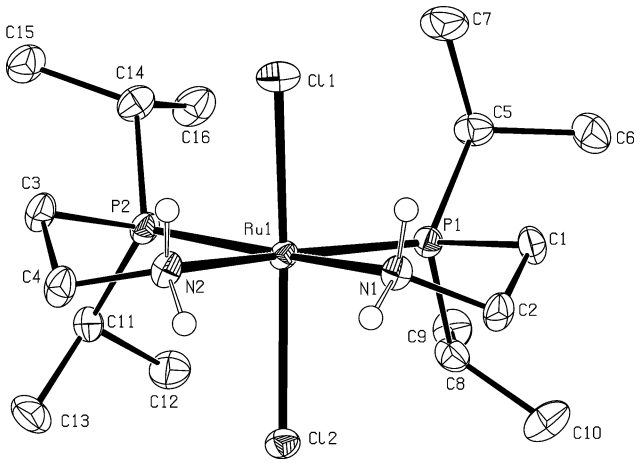


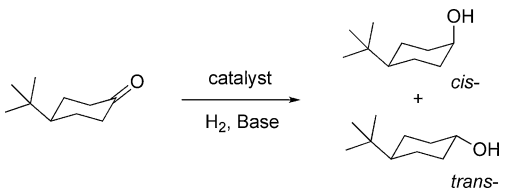
Fig. 1 X-Ray structure of *trans*-$RuCl_2(^iPr_2P(CH_2)_2NH_2)_2$, (**2**). Displacement ellipsoids are shown at 30% probability and the hydrogen atoms (except for NH_2) are omitted for clarity. Selected bond distances (Å) and angles (°): Ru1-Cl1 = 2.407(1); Ru1-Cl2 = 2.437(1); Ru1-P1 = 2.297(1); Ru1-P2 = 2.277(1); Ru1-N1 = 2.174(3); Ru1-N2 = 2.179(3); P1-Ru1-N1 = 83.46(9); P2-Ru2-N2 = 83.91(8); P2-Ru1-P1 = 106.39(4); N2-Ru1-N1 = 86.19(12); Cl1-Ru1-P1 = 86.84(4); Cl2-Ru1-P1 = 92.63(4); Cl2-Ru1-N1 = 86.55(9); Cl2-Ru1-N2 = 87.22(9); Cl2-Ru1-P2 = 96.61(4); Cl1-Ru1-Cl2 = 166.31(4).

the results of the hydrogenation of a variety of ketones including α,β-unsaturated ketones, and imines catalyzed by complexes **1** to **6**.

Complexes **1**, **2**, **4** and **5** are far more active than **3** and **6** (Table 1), hence a more limited range of substrates were investigated for the latter two. The lower activities of these tert-butyl complexes indicate that steric inhibitions are more significant than nucleophilicity of the ligands for this class of catalysts.

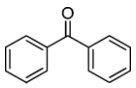
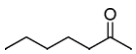
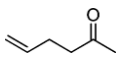
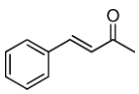
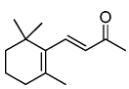
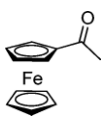
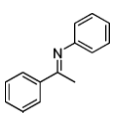
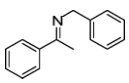
Chemoselective hydrogenation of ketones is important for a variety of industrial applications, and is valuable for the production of pharmaceuticals, flavours and fragrances. The catalysts are excellent for the chemoselective hydrogenation of alkenones yielding the unsaturated alcohols (entries 22–36, Table 1) as the only detectable products. The chemoselective hydrogenation of benzalacetone (entries 29–32, Table 1) and β-ionone (entries 33–36, Table 1) are important in the flavour and fragrance industry.

The hydrogenation of 4-tert-butylcyclohexanone is also a valuable process in the fragrance industry since the alcohol product 4-tert-butyl-cyclohexanol is the precursor for the fragrance 4-tert-butylcyclohexyl acetate (Woody acetate), which is produced on a 15 000 ton per year scale (Scheme 3, Table 2). Stoichiometric reduction of 4-tert-butylcyclohexanone with borohydride reagents produces an alcohol that contains mainly the *trans*-alcohol (70%) relative to the *cis*-alcohol (30%).[15] The acetate fragrance derived from this alcohol is an inferior product relative to those derived



Scheme 3 Hydrogenation of 4-tert-butylcyclohexanone.

Table 1 Hydrogenation of ketones and imines in the presence of KO^{t}Bu in 2-propanol (10 atm H_2)[a]

Entry	Substrate	Cat.	S:C	T/°C	Time/h	Conv. (%)[b]
1		**1**	5000	25	2	100
2		**2**	1800	25	2	100
3		**3**	1000	25	24	40
4		**3**	1000	50	2	78
5		**4**	5000	25	2	100
6		**5**	2000	25	2	100
7		**6**	1000	25	24	90
8		**1**	1500	25	2	100
9		**2**	1500	25	2	100
10		**3**	1000	25	24	12
11		**3**	1000	50	2	96
12		**4**	1500	25	2	100
13		**5**	2000	25	2	100
14		**6**	1000	25	24	33
15		**1**	2000	25	4	100
16		**2**	2000	25	4	100
17		**3**	1000	25	24	46
18		**3**	1000	50	2	95
19		**4**	2000	25	4	100
20		**5**	2000	25	5	100
21		**6**	1000	25	24	81
22[c]		**1**	1000	25	2	100
23[c]		**2**	1000	25	4	100
24[c]		**3**	1000	25	24	17
25[c]		**3**	1000	50	2	58
26[c]		**4**	1000	25	2	100
27[c]		**5**	1000	25	2	100
28[c]		**6**	1000	25	24	34
29[c]		**1**	1000	25	2	100
30[c]		**2**	1000	25	2	100
31[c]		**4**	1000	25	2	100
32[c]		**5**	1000	25	2	100
33[c]		**1**	1000	25	2	100
34[c]		**2**	500	25	2	100
35[c]		**4**	500	25	2	100
36[c]		**5**	500	25	2	100
37		**1**	1000	25	5	100
38		**2**	500	25	4	100
39		**3**	1000	25	24	0
40		**3**	1000	50	2	6
41		**4**	1000	25	5	100
42		**5**	500	25	4	100
43		**6**	1000	25	24	53
44		**1**	500	25	12	100
45		**2**	500	25	12	100
46		**4**	500	25	12	100
47		**5**	500	25	12	100
48		**1**	500	25	12	100
49		**2**	250	25	24	73
50		**4**	500	25	12	100

[a] A weighed amount of the catalyst was added to a solution of the substrate in 2-propanol and the mixture was stirred for the allotted time under hydrogen gas. [b] Determined by GC or HPLC analysis. [c] Only C=O bond reduced.

from alcohols with a high *cis*-content. Hence, there is a desire for catalysts that are effective for the stereoselective formation of a product high in the *cis*-component. The ruthenium catalysts enable the hydrogenation of 4-tert-butylcyclohexanone and complexes **2** and **4** produce alcohol in an excellent *cis*/*trans* ratio (entries 2 and 5, Table 2).

Table 2 Hydrogenation of 4-tert-butylcyclohexanone in the presence of KO^{t}Bu in 2-propanol (10 atm H_2)[a]

Entry	Cat.	S:C	T/°C	Time/h	Conv. (%)[b]	*cis*/*trans*
1	**1**	650	25	2	100	86:14
2	**2**	1000	25	3	100	96:4
3	**3**	1000	25	24	58	23:77
4	**3**	1000	50	2	100	22:78
5	**4**	1000	25	3	100	98:2
6	**5**	1000	25	3	20	83:17
7	**6**	1000	25	24	90	60:40

[a] A weighed amount of the catalyst was added to a solution of the substrate in 2-propanol and the mixture was stirred for the allotted time under hydrogen gas. [b] Determined by NMR.

Table 3 Hydrogenation of norcamphor in the presence of KO^{t}Bu in 2-propanol (10 atm H_2)[a]

Entry	Cat.	S:C	T/°C	Time/h	Conv. (%)[b]	*endo*/*exo*
1	**1**	700	25	2	100	99:1
2	**2**	650	25	17	100	87:13
3	**3**	1000	25	24	17	62:38
4	**3**	1000	50	2	74	56:44
5	**4**	1000	25	2	100	99:1
6	**5**	1000	25	2	10	87:13
7	**6**	1000	25	24	90	46:54

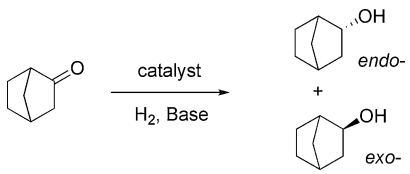
[a] A weighed amount of the catalyst was added to a solution of the substrate in 2-propanol and the mixture was stirred for the allotted time under hydrogen gas. [b] Determined by NMR.

Table 4 Hydrogenation of acetophenone using **2**/KO^{t}Bu as catalyst in 2-propanol (10 atm H_2)[a]

Entry	S:C	T/°C	Time/h	Conv. (%)[b]
1	10 000	20	4	100
2	100 000	50	2	100
3	500 000	50	12	100
4	1 000 000	50	24	98

[a] A weighed amount of the catalyst was added to a solution of the substrate in 2-propanol and the mixture was stirred for the allotted time under hydrogen gas. [b] Determined by GC analysis.

Stereoselective hydrogenation of norcamphor is important in the pharmaceutical industry since *endo*-norborneol is used to prepare a variety of anti-asthmatic and anti-inflammatory drugs (Scheme 4, Table 3).[16] Unfortunately, stoichiometric reduction of norcamphor with various borohydride reagents only gives good to moderate yields (60–80%) of the desired *endo*-norborneol.[15]



Scheme 4 Hydrogenation of norcamphor.

Table 5 Hydrogenation of 4-tert-butylcyclohexanone using **2**/KO^{t}Bu as catalyst in 2-propanol (10 atm H_2)[a]

Entry	S:C	T/°C	Time/h	Conv. (%)[b]	cis:trans
1	10 000	20	4	100	96:4
2	100 000	50	2	100	95:5
3	500 000	50	12	100	95:5
4	1 000 000	50	24	80	95:5

[a] A weighed amount of the catalyst was added to a solution of the substrate in 2-propanol and the mixture was stirred for the allotted time under hydrogen gas. [b] Determined by NMR.

Hydrogenation of norcamphor using catalysts **1-6** produces *endo*- and *exo*-norborneol in an excellent ratio for complexes **1** and **4** (entries 1 and 5, Table 3). Interestingly, complex **4** is very effective for producing both *cis*-tert-butylcyclohexanol (*cis*:*trans* = 98:2) and *endo*-norborneol (*endo*:*exo* = 99:1).

In general, the hydrogenation reactions are very responsive to temperature and pressure, which allows these reactions to be easily scaled. The effect of temperature is illustrated in Table 2 and 3 for complex **3**, which demonstrates higher reactivity at elevated temperatures.

Highly active and efficient hydrogenation catalysts have the advantage of scalability relative to other reduction protocols. Tables 4 and 5 illustrate the optimization of the hydrogenation of acetophenone and 4-tert-butylcyclohexanone, respectively using **2** as the catalyst. These results show that high substrate to catalyst ratios of up to 1 000 000 to 1 can be achieved under relatively mild conditions, with retention of product selectivity even at elevated temperatures.

Conclusions

This work outlines a general and scalable process for the synthesis of a variety of aminophosphine ligands of the type $R_2P(CH_2)_nNH_2$. These ligands are easily converted to their respective ruthenium compounds $RuCl_2(Ph_2P(CH_2)_nNH_2)_2$ by reacting a mixture of the ligands and $[RuCl_2(cod)]_n$. The ruthenium compounds are excellent catalysts for the hydrogenation of a variety of ketone and imine substrates. Chemoselective and stereoselective hydrogenation of a variety of substrates were demonstrated. The reactions have been optimized and enabled the achievement of substrate to catalyst ratios of up to 1 000 000 to 1. The demonstrated activity, chemoselectivity and diastereoselectivity of these catalysts merit exploration of chiral aminophosphine ligands and their catalysts as limited studies have been reported to date. Our studies on the synthesis of a variety of chiral aminophosphine ligands and their catalysts will be reported in due course.

Experimental

General comments

Unless otherwise stated, all preparations and manipulations were carried out under purified argon atmosphere with the use of standard Schlenk, vacuum line, and glovebox techniques in dry, oxygen-free solvents. Tetrahydrofuran (THF), diethyl ether, toluene, dichloromethane and hexanes were dried and purified using an Innovative Technologies solvent purification system. Deuterated solvents were obtained from Cambridge Isotope Laboratories, and were degassed with argon and dried over molecular sieves (3 Å, beads, 8–12 mesh, Sigma Aldrich). Varian Gemini 400 MHz and 300 MHz spectrometers were employed for recording ^{1}H (400 MHz and 300 MHz), ^{13}C{^{1}H} (100 MHz and 75 MHz), and ^{31}P{^{1}H} (161 MHz and 121 MHz) NMR spectra at ambient temperature. All ^{31}P spectra were recorded with proton decoupling, and ^{31}P chemical shifts were measured relative to 85% H_3PO_4 as an external reference. All ^{1}H chemical shifts were measured relative to partially deuterated solvent peaks but are reported relative to tetramethylsilane. Reaction progress and products were also analyzed using either an Agilent Technologies 7890A GC system or an Agilent Technologies 1200 Series HPLC.

Unless otherwise stated all chemicals were purchased from Sigma Aldrich. The ruthenium precursor $[RuCl_2(cod)]_n$ was prepared by a literature procedure.[17] Ruthenium trichloride was purchased from Pressure Chemicals. Imines were prepared from the corresponding ketones and amines using established literature methods.[18] The precursor compounds 2-[N,N-bis-(trimethylsilyl)amino]-1-chloroethane and 3-[N,N-bis-(trimethylsilyl)amino]-1-chloropropane were prepared according to reported procedures.[14] The ligands 2-(diphenylphosphino)-ethanamine,[19] 2-(diisopropylphosphino)ethanamine,[19a] 2-(di-tert-butylphosphino)ethanamine,[19a] 3-(diphenylphosphino)-propanamine,[19c] were previously reported. Argon gas (ultra high purity grade) and hydrogen gas (grade 4.8) were obtained from BOC Gases Canada and used without further purification.

Small scale hydrogenation screening reactions were conducted in a Parr Series 5000 Multireactor apparatus. Larger scale hydrogenation reactions were conducted in a Parr 100 ml pressure reactor.

Preparation of aminophosphine ligands

2-(Diphenylphosphino)ethanamine

Butyllithium (155 ml of a 1.6 M solution in hexane) was added dropwise to a cold (0 °C) solution of diphenylphosphine (45 g, 0.24 mol) in THF (200 ml). The mixture was stirred for 2 hours at room temperature and a solution of N,N′-bis(trimethylsilyl)-2-chloroethanamine (54 g, 0.24 mol) added slowly at 0 °C. The mixture was refluxed for 4 hours then cooled to room temperature. Water (50 ml) was added, followed by 2.0 M H_2SO_4 solution (200 ml). After stirring for 1 hour at room temperature a solution of 4.0 M NaOH solution (220 ml) was then added, and the mixture stirred for 1 hour. Hexane (200 ml) was added and the aqueous phase was separated and removed. The organic layer was dried (Na_2SO_4), filtered through a pad of silica gel, and evaporated to yield the aminophosphine, which was purified by vacuum distillation. Yield: 52.3 g, 94%. δ_H (400 MHz; $CDCl_3$) 1.17 (2 H, s, NH_2), 2.23 (2 H, t, *J* 3.8, CH_2), 2.81–2.87 (2 H, m, CH_2), 7.30–7.31 and 7.41–7.43 (10 H, m, Ph); δ_C (100 MHz; $CDCl_3$) 33.3, 39.6, 128.7, 132.9 and 138.7; δ_P (121 MHz, $CDCl_3$) –20.7 (s).

2-(Diisopropylphosphino)ethanamine

A THF (100 ml) solution of chlorodiisopropylphosphine (30 g, 0.20 mol) was added dropwise at 0 °C to a suspension of lithium granules (5.0 g, 0.72 mol) in THF (100 ml), and the mixture stirred

for 72 hours at room temperature. The mixture was filtered and the filtrate cooled to 0 °C and a solution of N,N′-bis(trimethylsilyl)-2-chloroethanamine (44.2 g, 0.20 mol) added slowly. The mixture was refluxed for 4 hours then cooled to room temperature. Water (50 ml) was added, followed by 2.0 M H_2SO_4 solution (160 ml). After stirring for 1 hour at room temperature a solution of 4.0 M NaOH solution (180 ml) was then added, and the mixture stirred for 1 hour. Hexane (200 ml) was added and the aqueous phase was separated and removed. The organic layer was dried (Na_2SO_4), filtered through a pad of silica gel, and evaporated to yield the aminophosphine, which was purified by vacuum distillation. Yield: 28.2 g, 89%. δ_H (300 MHz; $CDCl_3$) 0.85–0.94 (12 H, m, CH_3), 1.07 (2 H, s, NH_2), 1.35 (2 H, td, J 8.1 and 3.3, CH_2), 1.57 (2 H, septet of doublet, J 7.1 and 2.4, CH), 2.68 (2H, quartet, J 7.8 Hz, CH_2); δ_C (75 MHz; $CDCl_3$) 18.7, 20.1, 23.2, 26.6 and 41.4; δ_P (121 MHz, $CDCl_3$) −2.0 (s).

2-(Di-tert-butylphosphino)ethanamine

A THF (100 ml) solution of chlorodi-tert-butylphosphine (42 g, 0.23 mol) was added dropwise at 0 °C to a suspension of lithium granules (5.0 g, 0.72 mol) in THF (100 ml), and the mixture stirred for 72 hours at room temperature. The mixture was filtered and the filtrate cooled to 0 °C and a solution of N,N′-bis(trimethylsilyl)-2-chloroethanamine (51.7 g, 0.23 mol) added slowly. The mixture was refluxed for 4 hours then cooled to room temperature. Water (50 ml) was added, followed by 2.0 M H_2SO_4 solution (200 ml). After stirring for 1 hour at room temperature a solution of 4.0 M NaOH solution (220 ml) was then added, and the mixture stirred for 1 hour. Hexane (200 ml) was added and the aqueous phase was separated and removed. The organic layer was dried (Na_2SO_4), filtered through a pad of silica gel, and evaporated to yield the aminophosphine, which was purified by vacuum distillation. Yield: 40.3 g, 91%. δ_H (300 MHz; $CDCl_3$) 0.94 (18 H, d, J 11.1, CH_3), 1.08 (2 H, s, NH_2), 1.36 (2 H, td, J 7.5 and 4.5, CH_2), 2.67 (2H, quartet, J 7.5 Hz, CH_2); δ_C (75 MHz; $CDCl_3$) 26.3, 29.6, 31.0 and 42.9; δ_P (121 MHz, $CDCl_3$) 21.2 (s).

3-(Diphenylphosphino)propanamine. This was prepared as outlined above for 2-(diphenylphosphino)ethanamine, by using N,N′-bis(trimethylsilyl)-3-chloropropanamine. Yield: 91%. δ_H (400 MHz; $CDCl_3$) 1.0 (2 H, s, NH_2), 1.53–1.61 (2 H, m, CH_2), 2.04–2.08 (2 H, m, CH_2), 2.75 (2H, t, J 7.0 Hz, CH_2), 7.29–7.41 (10H, m, Ph); δ_C (75 MHz; $CDCl_3$) 25.5, 30.4, 43.6, 128.6, 132.9 and 139.0; δ_P (121 MHz, $CDCl_3$) −15.1 (s).

3-(Diisopropylphosphino)propanamine. This was prepared as outlined above for 2-(diisopropylphosphino)ethanamine, by using N,N′-bis(trimethylsilyl)-3-chloro-propanamine. Yield: 85%. δ_H (300 MHz; C_6D_6) 0.59 (2 H, s, NH_2), 0.89–0.99 (12 H, m, CH_3), 1.16–1.22 (2 H, m, CH_2), 1.22–1.55 (4H, m, CH and CH_2), 2.51 (2H, t, J 6.8, CH_2); δ_C (75 MHz; $CDCl_3$) 18.1, 20.1, 23.5, 32.6 and 43.7; δ_P (121 MHz, C_6D_6) 3.6 (s).

3-(Di-tert-butylphosphino)propanamine. This was prepared as outlined above for 2-(di-tert-butylphosphino)ethanamine, by using N,N′-bis(trimethylsilyl)-3-chloro-propanamine. Yield: 78%. δ_H (300 MHz; C_6D_6) 0.54 (2 H, s, NH_2), 1.03 (18 H, d, J 10.5 CH_3), 1.23–1.30 and 1.47–1.60 (4 H, m, CH_2), 2.57 (2H, t, J 6.8, CH_2); δ_C (75 MHz; C_6D_6) 18.3, 29.6, 31.0, 34.8 and 43.5; δ_P (121 MHz, C_6D_6) 28.3 (s).

Preparation of ruthenium aminophosphine catalysts

***Trans*-$RuCl_2(Ph_2P(CH_2)_2NH_2)_2$, 1.** A mixture of $[RuCl_2(cod)]_n$ (0.60 g, 2.1 mmol) and $Ph_2P(CH_2)_2NH_2)_2$ (1.0 g, 4.4 mmol) was stirred in methylene chloride (5 ml) under argon for 3 hours. The mixture was concentrated under vacuum and hexane (50 ml) was added and the resulting suspension stirred for an additional 30 minutes. The product was filtered, washed with hexane (3 × 10 ml) and dried under vacuum. Yield: 0.50 g, 37%. (Found: C, 53.61; H, 5.39; N, 4.37%. $C_{28}H_{32}Cl_2N_2P_2Ru$ requires C, 53.34; H, 5.12; N, 4.44%). The NMR spectra of **1** correspond to those previously reported.[5a]

***Trans*-$RuCl_2(^iPr_2P(CH_2)_2NH_2)_2$, 2.** A mixture of $[RuCl_2(cod)]_n$ (15.8 g, 56.6 mmol) and $^iPr_2P(CH_2)_2NH_2)_2$ (18.1 g, 112 mmol) was refluxed in toluene (200 ml) under argon for 6 hours. The mixture was cooled to room temperature and ether (300 ml) was added and the suspension stirred for 1 hour. The product was filtered, washed with ether (3 × 50 ml) and dried under vacuum. Yield = 20.2 g, 81%. (Found: C, 39.15; H, 8.40; N, 5.63%. $C_{16}H_{40}Cl_2N_2P_2Ru$ requires C, 38.87; H, 8.15; N, 5.67%). δ_H (CD_2Cl_2) 1.17–1.38 (24 H, m, CH_3), 2.00 (4 H, m, CH_2), 2.52 (4 H, d of septet, J_{HP} 9.3 and J_{HH} 10.5, CH), 3.06–3.19 (4 H, m, CH_2), 3.65 (4 H, br, NH_2); δ_P (CD_2Cl_2) 64.2 (s).

***Trans*-$RuCl_2(^tBu_2P(CH_2)_2NH_2)_2$, 3.** A mixture of $[RuCl_2(cod)]_n$ (11.5 grams, 41.2 mmol) and $^tBu_2P(CH_2)_2NH_2)_2$ (15.6 grams, 82.5 mmol) was refluxed in toluene (120 ml) under argon for 8 hours. The mixture was cooled to room temperature and ether (250 ml) was added and the suspension stirred for 1 hour. The product was filtered, washed with ether (3 × 50 ml) and dried under vacuum. Yield: 20.1 g, 88%. (Found: C, 43.66; H, 9.06; N, 5.08%. $C_{20}H_{48}Cl_2N_2P_2Ru$ requires C, 43.63; H, 8.79; N, 5.09%). δ_H (CD_2Cl_2), 1.35 (36 H, d, J_{HP} 16.2, CH_3), 2.11–2.20 (4 H, m, CH_2), 3.12–3.23 (4 H, m, CH_2), 3.95 (4 H, br, NH_2); δ_P (CD_2Cl_2) 66.8 (s).

***Trans*-$RuCl_2(Ph_2P(CH_2)_3NH_2)_2$, 4.** A mixture of $[RuCl_2(cod)]_n$ (1.41 g, 5.04 mmol) and $Ph_2P(CH_2)_3NH_2$ (2.5 g, 10.3 mmol) was refluxed in toluene (15 ml) for 4 hours. The mixture was cooled to room temperature and ether (60 ml) was added. After stirring for another 30 minutes the yellow-brown solid was filtered, washed with ether and dried under vacuum. Yield = 2.9 g (86%). (Found: C, 54.92; H, 5.87; N, 4.27%. $C_{30}H_{36}Cl_2N_2P_2Ru$ requires C, 54.71; H, 5.51; N, 4.25%). δ_H (CD_2Cl_2), 1.83–1.87 (2 H, m, CH_2), 1.99–2.04 (2 H, m, CH_2), 2.22–2.29 (2 H, m, CH_2), 2.64–2.70 (4 H, m, CH_2), 2.97 (4 H, br, NH_2), 3.27–3.34 (2 H, m, CH_2), 7.06–7.82 (20 H, m, Ph); δ_P (CD_2Cl_2) 33.8 (s).

***Trans*-$RuCl_2(^iPr_2P(CH_2)_3NH_2)_2$, 5.** A mixture of $[RuCl_2(cod)]_n$ (1.88 g, 6.72 mmol) and $^iPr_2P(CH_2)_3NH_2$ (2.4 g, 13.7 mmol) was refluxed in toluene (15 ml) for 4 hours. The mixture was cooled to room temperature and ether (80 ml) was added. After stirring for another 30 minutes the yellow solid was filtered, washed with ether and dried under vacuum. Yield = 3.0 g (86%). (Found: C, 41.60; H, 8.72; N, 5.38%. $C_{18}H_{44}Cl_2N_2P_2Ru$ requires C, 41.38; H, 8.49; N, 5.36%). δ_H (CD_2Cl_2), 1.22–1.28 (24 H, m, CH_3), 2.47–2.60 (4 H, m, CH_2), 2.59–2.65 (4 H, m, CH_2), 2.72–2.90 (4 H, m, CH_2), 3.16 (4 H, br, NH_2), 3.36–3.45 (2 H, m, CH), 3.87–3.92 (2 H, m, CH); δ_P (CD_2Cl_2) 43.2 (s).

***Trans*-$RuCl_2(^tBu_2P(CH_2)_3NH_2)_2$, 6.** A mixture of $[RuCl_2(cod)]_n$ (1.47 g, 5.25 mmol) and $^tBu_2P(CH_2)_3NH_2$ (2.20 g, 10.8 mmol) in methylene chloride (5 ml) was stirred for 2 hours at room temperature then refluxed for 3 hours. The mixture was cooled to room temperature and hexanes (50 ml) was added. After stirring for an additional hour, the yellow-brown solid was filtered, washed with hexanes and dried under vacuum. Yield = 1.0 g (33%). (Found: C, 45.84; H, 9.36; N, 5.10%. $C_{22}H_{52}Cl_2N_2P_2Ru$ requires C, 45.67; H, 9.06; N, 4.84%). δ_H (CD_2Cl_2), 1.15 (36 H, d, J_{HP} 10.0, CH_3), 1.48–1.53 (4H, m, CH_2), 1.94 (4 H, d of quintet, J_{HP} 7.8 and J_{HH} 7.9, CH_2), 3.10 (4 H, d of t, J 15.0 and J 7.5, CH_2), 3.61 (2 H, br, NH_2), 4.20 (2 H, br, NH_2); δ_P (DMSO) 28.1 (s).

General procedure for the hydrogenation of ketones and imines

In a typical hydrogenation procedure weighed amounts of the respective catalyst and KO^{t}Bu were added to a solution of the substrate in the desired solvent under hydrogen gas. The pressure and temperature were adjusted to the desired values and the reaction progress was monitored by the change in pressure or by withdrawing a sample of the reaction mixture and assaying the conversion by NMR, GC or HPLC. After completion of the reaction, the solvent was removed from the crude product by evaporation under reduced pressure. The products were purified by filtering a hexane solution of the crude product through a pad of silica gel, then removing the hexane under reduced pressure. The conversion and purity of the products were assessed using NMR.

Example: hydrogenation of acetophenone. A weighed amount of 2 (5.0 mg, 0.01 mmol) and KO^{t}Bu (10 mg) were added to a solution of acetophenone (2.0 g, 16.6 mmol) in 2-propanol in a 100 ml Parr pressure reactor under a flow of argon. The mixture was degassed with argon and then with hydrogen. It was finally pressurized to 10 atm of hydrogen and stirred at room temperature. After completion of the reaction, the solvent was removed from the crude product by evaporation under reduced pressure. Hexanes (5 ml) was added and the solution was filtered through a pad of silica gel. The solvent was then removed under reduced pressure to yield the pure product. The NMR and GC spectra of the product showed 100 percent conversion of the ketone to phenylethanol. Yield = 1.98 g, 97%.

S:C ratio = 10 000:1. A weighed amount of **2** (3.2 mg, 0.0065 mmol) and KO^{t}Bu (100 mg) were added to a solution of the substrate (7.80 g, 65 mmol) in 2-propanol in a 100 ml Parr pressure reactor under a flow of argon. The mixture was de-gassed with argon and then with hydrogen. It was finally pressurized to 10 atm of hydrogen and stirred at room temperature for 4 hours. The NMR and GC spectra showed complete conversion of the ketone to the alcohol.

S:C ratio = 100 000:1. A weighed amount of 2 (5 mg) was dissolved in 10.0 ml of 2-propanol. An aliquot of 1.0 ml of the diluted catalyst solution (0.5 mg of catalyst, 0.001 mmol) and KO^{t}Bu (150 mg) were added to a solution of the substrate (12.15 g, 101 mmol) in 2-propanol in a 100 ml Parr pressure reactor under a flow of argon. The mixture was degassed with argon and then with hydrogen. It was finally pressurized to 10 atm of hydrogen and stirred at 50 °C for 2 hours. The NMR and GC spectra showed complete conversion of the ketone to the alcohol.

S:C ratio = 500 000:1. A weighed amount of **2** (5 mg) was dissolved in 10.0 ml of 2-propanol. An aliquot of 1.0 ml of this catalyst solution was further diluted to 10.0 ml with 2-propanol. An aliquot of 2.0 ml of the dilute catalyst solution (0.1 mg, 0.0002 mmol) and KO^{t}Bu (150 mg) were added to a solution of the substrate (12.15 g, 101 mmol) in 2-propanol in a 100 ml Parr pressure reactor under a flow of argon. The mixture was degassed with argon and then with hydrogen. It was finally pressurized to 10 atm of hydrogen and stirred at 50 °C for 12 hours. The NMR and GC spectra showed complete conversion of the ketone to the alcohol.

S:C ratio = 1 000 000:1. A weighed amount of **2** (5 mg) was dissolved in 10.0 ml of 2-propanol. An aliquot of 1.0 ml of this catalyst solution was further diluted to 10.0 ml with 2-propanol. An aliquot of 1.0 ml of the dilute catalyst solution (0.05 mg, 0.0001 mmol) and KO^{t}Bu (150 mg) were added to a solution of the substrate (12.15 g, 101 mmol) in 2-propanol in a 100 ml Parr pressure reactor under a flow of argon. The mixture was degassed with argon and then with hydrogen. It was finally pressurized to 10 atm of hydrogen and stirred at 50 °C for 24 hours. The NMR and GC spectra showed 98% conversion of the ketone to the alcohol.

X-Ray structure determination of complex 2

Crystals suitable for single crystal X-ray diffraction studies were obtained by slowly cooling a hot solution of the compound in toluene to room temperature. The X-ray diffraction data were collected using a Nonius Kappa-CCD diffractometer with MoKα radiation (λ = 0.71073 Å). The CCD data were integrated and scaled using the Denzo-SMN package. The structures were solved and refined using SHELXTL V5.1. Refinement was by full-matrix

Table 6 Summary of crystal data, details of intensity collection and least-squares refinement parameters for **2**

Empirical formula	$C_{16}H_{40}Cl_2N_2P_2Ru$
Formula weight	494.41
Crystal size/mm	0.12 × 0.17 × 0.37
Crystal class	Monoclinic
Space group	$P\,2_1/c$
T/K	150.0
a/Å	11.4627(3)
b/Å	13.1649(6)
c/Å	15.2297(5)
α/°	90
β/°	104.992(2)
γ/°	90
V/Å^3	2220.0(1)
ρ_{calc}/Mg m^{-3}	1.479
μ (Mo Kα)/mm^{-1}	1.093
F(000)	1032
Range θ collected/°	2.77 to 27.51
No. of reflections	13589
Independent reflections	5063
R_1 ($I > 2\,\sigma(I)$)[a]	0.0466
wR_2 (all data)[a]	0.1022
Goodness of fit	1.079
Parameters refined	216
Maximum peak in final ΔF map/e Å^{-3}	1.617

[a] Definition of R indices: $R_1 = \sum(F_o - F_c)/\sum(F_o)$; $wR_2 = [\sum[w(F_o^2 - F_c^2)2]/\sum[w(F_o^2)^2]]^{1/2}$.

least-squares on F^2 using all data (negative intensities included).[20] Crystallographic data for compound **2** is given in Table 6.

CCDC reference number 733474.†

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