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Ketone H_2-hydrogenation catalysts: Ruthenium complexes with the headphone-like ligand bis(phosphaadamantyl)propane

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Dedicated to Professor Brian James on the occasion of his 70th birthday.

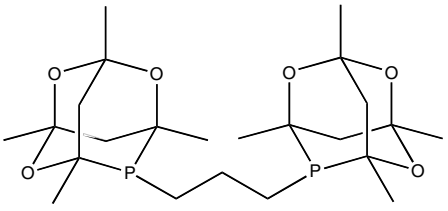
Abstract

Treatment of 1,3-diphosphinopropane with acetylacetone in the presence of HCl gives the new chiral bis(phosphaadamantyl)propane ligand (bpap) (**1**) as a mixture of diastereoisomers. Recrystallization from ethanol gives a mixture enriched in *rac* diastereoisomer (90% *rac*/10% *meso*). The enriched mixture reacts with $[RuHCl(PPh_3)_3]$ in refluxing THF to give $[RuHCl(bpap)(PPh_3)]$ (**2**) in 73% yield. Compound **2** reacts readily with chiral diamines giving octahedral *trans*-[RuHCl(bpap)(diamine)] complexes **3** (diamine = (1*R*,2*R*)-1,2-diaminocyclohexane) and **4** (diamine = (1*R*,2*R*)-1,2-diphenylethylenediamine). Compounds **3** and **4** are very active catalysts for H_2-hydrogenation of neat acetophenone in the presence of KO^{t}Bu as a strong base under mild conditions (room temperature, 3 atm of H_2). The low ee values for 1-phenethanol can be attributed to the similar shapes of two terminal adamantoid cages and the flexible backbone of the bpap ligand. The structures of complexes **2** and **3** have been determined by single-crystal X-ray diffraction.

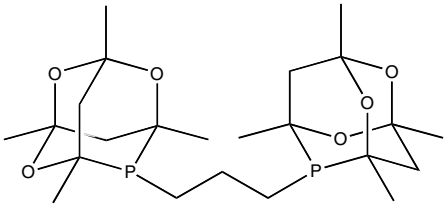
Keywords: Chiral diphosphine; Ruthenium hydride; Ketone hydrogenation

1. Introduction

The development of new diphosphine ligands has been the subject of much research in the past decades, stimulated mostly by the potential use of these ligands in transition metal complexes for homogeneous catalysis. Of particular significance for asymmetric catalysis has been the advent of chiral diphosphines such as DIOP [1], BINAP [2], DIPAMP [3] and DUPHOS [4]. In this paper, we report the synthesis of the chiral diphosphine bis(phosphaadamantyl)propane (bpap) (**1**) and the synthesis, properties and preliminary catalytic studies of the its chlorohydridoruthenium(II) complexes.



meso-**1**



rac-**1**

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Diphosphine **1** can be prepared as a mixture of *meso* and *rac* isomers in a one-pot procedure. Ligand **1** has previously been shown to have an unusually large cone angle of 173° which cannot be reduced by intermeshing [5] and an evaluation of its electronic properties from the ν(CO) of [Ni(CO)$_2$(**1**)] showed that **1** has a σ-basicity/π acidity more akin to diphosphines containing P(aryl)$_2$ than P(alkyl)$_2$ groups [6].

Some transition metal complexes having the *meso*/*rac*-bpap ligand have already been reported [5] and Pd-catalyzed tandem isomerisation-carbonylation of internal alkenes to linear esters has been described [6]. Here, we report the first use of **1** in an asymmetric catalytic transformation, the hydrogenation of prochiral ketones.

2. Experimental

2.1. General

All reactions were performed using either standard Schlenk or glove box techniques with either an argon or a dinitrogen atmosphere. Tetrahydrofuran, diethyl ether and hexanes were purified and dried by reflux under an argon atmosphere over sodium using benzophenone as an indicator. Solvents for NMR were purchased from Cambridge Isotope Laboratories: benzene-d_6 was kept over molecular sieves and THF-d$_8$ (in ampoules) was used as received. [RuHCl(PPh$_3$)$_3$] [7] and 1,3-diphosphinopropane [8] were prepared as previously reported. (1*R*,2*R*)-1,2,-diaminocyclohexane (*R*,*R*-dach) and (1*R*,2*R*)-1,2-diphenyl-ethylenediamine (*R*,*R*-dpen) were purchased from Sigma–Aldrich and used without further purification.

^{1}H and ^{31}P NMR spectra were recorded on a Varian Gemini 300 spectrometer at 300 MHz (^{1}H) and 121.5 MHz (^{31}P). ^{1}H NMR shifts are referred to tetramethylsilane and ^{31}P to 85% H_3PO_4 as an external reference. IR spectra were obtained on a PE Spectrum BX FT-IR spectrometer as Nujol mulls. Elemental analyses were done on a Perkin–Elmer 2400 C/H/N/S analyzer. X-ray data were collected on a Nonius Kappa-CCD diffractometer using Mo Kα radiation and refined using SHELXTL-6.1 software. Samples from catalytic tests were analyzed for conversion and ee using a Perkin–Elmer Autosystem XL gas chromatograph with a Chrompack capillary column ChiraSilDex CB (25 m × 0.25 mm). The carrier gas was H_2 at a column pressure of 5 psi, with an oven temperature of 130 °C, injector temperature of 250 °C, and FID temperature of 275 °C. The retention times were: acetophenone 5.0 min, (*R*)-1-phenylethanol 8.5 min and (*S*)-1-phenylethanol 9.1 min. The injected sample volume was 1 μL.

2.2. Synthesis of bpap ligand (*1*)

The phosphine $H_2P(CH_2)_3PH_2$ (2.0 ml, 18.5 mmol) was added dropwise over 5 min to a stirred solution of 2,4-pentanedione (11.40 g, 114 mmol) in aqueous HCl (40 ml, 5 M, 200 mmol). After 1 h a white precipitate began to form but the reaction mixture was stirred for a further 72 h. The white solid product was then filtered off in air, washed with water (2 × 20 ml) and then dried in vacuo to give 5.24 g (60%) of **1**. Recrystallisation of the approximately 1:1 mixture of *meso*/*rac* isomers of **1** from boiling ethanol (0.5 g of **1** with 10 ml of ethanol) gave a solid containing predominantly (9:1) *rac*-**1** with 76% recovery. EI mass spectrum: *m*/*z* 472 (M^+). *Anal.* Calc. for **1**: C, 58.5; H, 8.1. Found: C, 58.3; H, 8.4%. ^{1}H NMR ($CDCl_3$) δ 1.50–2.00 (m, 14H, cage CH_2, propane bridge), 1.25–1.48 (m, 24H, cage CH_3). ^{31}P NMR ($CDCl_3$) −30.2 (s, *meso* isomer), −31.0 (s, *rac* isomers).

2.3. Preparation of [RuHCl(bpap)(PPh$_3$)] (*2*)

Dry THF (8 ml) was added to 9:1 mixture of *rac*/*meso*-**1** (0.177 g, 0.375 mmol) and [RuHCl(PPh$_3$)$_3$] (0.320 g, 0.35 mmol) and the mixture refluxed for 2 h under an argon atmosphere giving a deep violet solution. The solvent was removed in vacuo. The solid residue was extracted with dry THF (2 ml) and filtered to remove insoluble impurities. The resulting solution was concentrated in vacuo to approximately 0.5 ml. Dry hexanes (15 ml) was added, precipitating a dark violet product. This mixture was left stirring overnight. The pale violet liquid above the precipitate was decanted and additional hexanes (approximately 5 ml) added and stirring continued for 3 h. Finally, the violet product was collected by filtration, washed with hexanes and vacuum dried. Yield: 220 mg (73%). The product is soluble in THF, ether and sparingly soluble in hexanes.

Crystals suitable for X-ray structural determination were obtained spontaneously from a C_6D_6 solution without evaporation. The structure coordinates have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 287142. ^{1}H NMR (THF-d$_8$) δ −17.62 (ddd, 1H, RuH, $^2J_{HP}$ = 20.2, 22.1 and 35.7 Hz,), 0.50–4.56 (m, 60H, cage CH, propane bridge), 6.73–7.09 (m, 15H, phenyl from PPh$_3$); ^{31}P NMR (THF-d$_8$) δ 27.44 (ddd, $^2J_{PP}$ = 246.7 and 32.0 Hz, $^2J_{PH}$ = 20.2), 40.99 ppm (ddd, $^2J_{PP}$ = 246.7 and 7.8 Hz, $^2J_{PH}$ = 22.1 Hz), 80.96 ppm (ddd, $^2J_{PP}$ = 32.0 and 7.8 Hz, $^2J_{PH}$ = 35.7), IR (Nujol, cm^{-1}): 1858, 1881 (RuH). *Anal.* Calc. for **2**: C, 56.14; H, 6.24. Found: C, 55.88; H, 6.73%.

2.4. Preparation of trans-[RuHCl(bpap)(R,R-dach)] (*3*)

R,*R*-dach (0.015 g, 0.13 mmol) was added to a solution of **2** (0.090 g, 0.10 mmol) in dry diethyl ether (1 ml). The formation of a sparingly soluble, pale yellow green product followed immediately. The resulting mixture was stirred for additional 30 min. Dry hexanes was added (5 ml) and stirring continued overnight. The liquid above the precipitate was decanted and additional hexanes (2 ml) was added. After 2 h the pale yellow-green product was collected by filtration, washed with hexanes and vacuum dried. Yield: 51 mg (70%). The product is very soluble in THF and benzene, poorly soluble in ether and insoluble in hexanes. ^{1}H

NMR (C_6D_6) δ −19.08 (dd, 1H, RuH *rac*-**1**, $^2J_{HP} = 24.7$, 29.4 Hz), −19.22 (dd, 1H, RuH *rac*-**1**, $^2J_{HP} = 23.7$, 31.2 Hz), −18.01 (t, 1H, RuH *meso*-**1**, $^2J_{HP} = 25.8$ Hz), 0.39–3.31 (m, CH in cage and propane bridge), 3.78 (s), 4.46 (s), 4.69 (s); ^{31}P NMR (C_6D_6): δ 46.74 (bd, $^2J_{PP} = 8.5$ Hz), 47.85 (bd, $^2J_{PP} = 8.5$), 48.1 (bd, $^2J_{PP} = 14$ Hz), 50.6 (bd, $^2J_{PP} = 9.5$ Hz), 51.6 (bd, $^2J_{PP} = 9.5$), 51.65 (bd, $^2J_{PP} = 14$ Hz). IR (Nujol, cm^{-1}): 720 (m), 1373 (s), 1458 (s), 1996 (w, RuH), 3163, 3307, 3329, 3366 (w, NH). *Anal*. Calc. for **3**: C, 48.05; H, 7.38; N, 3.88. Found: C, 47.89; H, 7.45; N, 4.28%.

2.5. Preparation of trans-[RuHCl(bpap)(R,R-dpen)] (4)

A similar procedure as for **3** was used to prepare **4**: 0.046 g (0.052 mmol) of **2** and 0.012 g (0.057 mmol) of *R*,*R*-dpen gave 29 mg (82%) of the product. The product is pale yellow, soluble in THF and benzene and insoluble in hexanes. ^{1}H NMR (C_6D_6) δ −18.65 (dd, RuH *rac*-**1**, $^2J_{HP} = 25.2$, 28.5 Hz), −18.79 (dd, RuH *rac*-**1**, $^2J_{HP} = 24.6$, 30.6 Hz), −17.75 (t, RuH *meso*-**1**, $^2J_{HP} = 22.2$ Hz) 1.03–5.53 (m), 6.70–7.16 (m, 2Ph); ^{31}P NMR (C_6D_6) δ 48.7 (br d, $^2J_{PP} = 8.1$ Hz), 51.5 (br d, $^2J_{PP} = 8.1$ Hz), 52.1 (br d, $^2J_{PP} = 10.1$ Hz), 53.0 (bd, $^2J_{PP} = 10.1$ Hz), 54.2 (br d, $^2J_{PP} = 9.3$), 54.3 (bd, $^2J_{PP} = 9.3$ Hz). IR (Nujol, cm^{-1}): 1987 (m, RuH), 3151, 3252, 3306 (w, NH). *Anal*. Calc. for **4**: C, 54.04; H, 6.74; N, 3.4. Found: C, 53.50; H, 6.55; N, 2.87%.

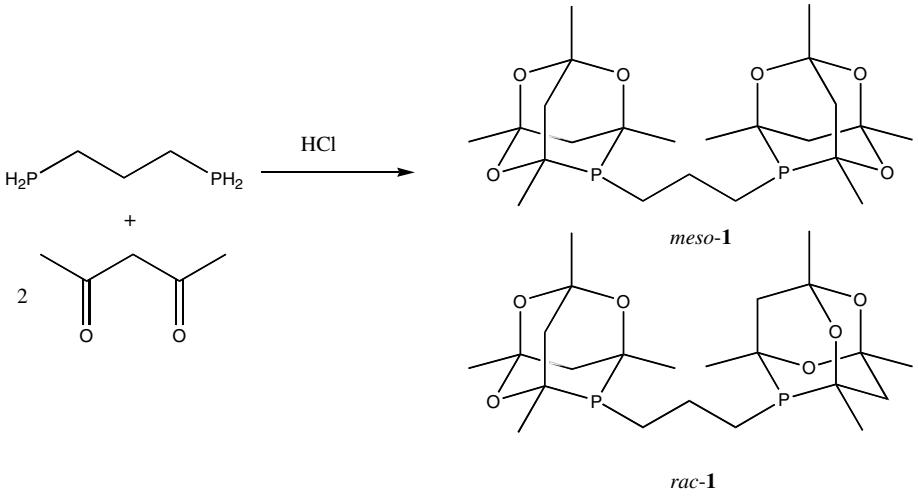
2.6. Hydrogenation of acetophenone catalyzed by 3 or 4

To previously dried and degassed acetophenone (0.5 g) in a Schlenk bomb, 5 mg of KO^{t}Bu and 5 mg of **3** or 5 mg of **4** were added under a dinitrogen atmosphere. The bombs were evacuated and refilled with dihydrogen gas at liquid nitrogen temperature, which gave approximately 3 atm of dihydrogen in the bombs when warmed to room temperature. The reactions were carried at 20 °C. The sampling was done under a flow of hydrogen when the H_2 pressure would fall to atmospheric. After each sample, the Schlenk bomb was cooled to the liquid nitrogen temperature to raise the pressure back. The samples were diluted with ethanol and analyzed by GC.

3. Results and discussion

3.1. The synthesis of bpap (1)

Treatment of 1,3-diphosphinopropane with acetylacetone in the presence of HCl gave the desired diphosphine **1** in 60% yield as a mixture of diastereoisomers (Eq. (1)). Samples rich in *rac* diastereoisomer (90%) are readily obtained by recrystallisation of the mixture from ethanol (see Section 2).



(1)

The appearance of ligand **1** in crystal structures of its compounds (see below for example) is reminiscent of a pair of headphones. The terminal adamantanoid cages are the source of the chirality but in the enantiomeric forms will have very similar (and quite symmetrical) shapes and therefore might not be expected to give high enantioselectivities.

3.2. Synthesis and properties of [RuHCl(bpap)(PPh3)]

Refluxing [$RuHCl(PPh_3)_3$] and a 9:1 mixture of *rac*/*meso*-**1** in dry THF under an argon atmosphere produces the deep violet complex [RuHCl(bpap)(PPh_3)] (**2**). Complex **2** is soluble in most common solvents (THF, diethyl ether, benzene, etc.) and crystallizes readily from concentrated solutions at room temperature or when cooled. Crystals of **2**, as a benzene solvate, suitable for X-ray crystallography were grown from a concentrated C_6D_6 solution. The structure is shown in Fig. 1 and is that of a distorted square pyramid with the hydride *trans* to chloride ligand and the P(2) atom from the bpap ligand in the apical

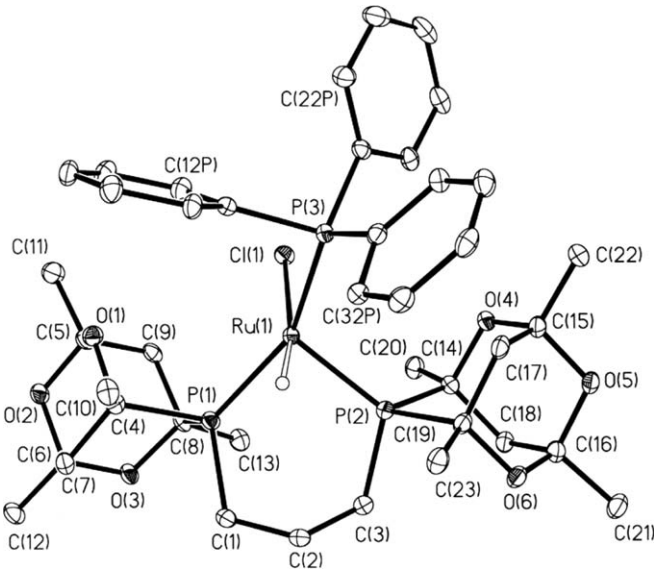


Fig. 1. ORTEP3 presentation and atom numbering scheme for **2**. H atoms are omitted for clarity (except the hydride), ellipsoid probability 50%.

position of the pyramid. The P(3), from the triphenylphosphine ligand, lies roughly *trans* to the P(1) of the diphosphine ligand with a P(1)–Ru–P(3) angle of 152.26(2)°. Other significant distances and angles, along with selected crystallographic data are given in Tables 1 and 2.

Out of several possible conformations that the six member chelating ring can adopt [9], the one in **2** lies close to a twist-boat (see Fig. 2). Ru(II) and C(2) located in the C3 bridge of bpap are in the flagpole positions of this conformation. The rigid cage around each phosphorus atom and the flexibility of the C3 backbone that lacks any substituents favor this conformation.

The ^{1}H and ^{31}P NMR spectra of **2** suggest that the geometry found in the crystal structure is retained in the solution. The hydride region of the ^{1}H NMR spectrum shows a doublet of doublets of doublets centered at

Table 1
Crystallographic data for complex $[RuHCl(bpap)(PPh_3)]\cdot 2C_6D_6$ (**2**)

Empirical formula	$C_{53}H_{65}ClO_6P_3Ru$
Formula weight	1028.49
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	14.4810(2)
b (Å)	12.8960(2)
c (Å)	26.4460(5)
β (°)	98.7670(7)
V (Å^3)	4881.01(14)
T (K)	150(1)
Z	4
Crystal size (mm)	$0.30\times0.25\times0.16$
D_{calc} (Mg/m^3)	1.400
R indices R_1	0.0672
R indices (all data) wR_2	0.0878
Reflections collected	33 671
Independent reflections	11 149

Table 2
Selected distances and angles for complex **2**

Distances (Å)			
Ru(1)–H(1Ru)	1.58(2)	P(1)–C(1)	1.843(2)
Ru(1)–P(1)	2.3088(6)	P(1)–C(8)	1.887(2)
Ru(1)–P(2)	2.2119(6)	P(2)–C(3)	1.838(2)
Ru(1)–P(3)	2.3544(6)	P(2)–C(14)	1.896(3)
Ru(1)–Cl(1)	2.4879(6)	P(2)–C(19)	1.900(3)
Angles (°)			
H(1Ru)–Ru(1)–Cl(1)	168.8(8)	H(1Ru)–Ru(1)–P(3)	86.5(8)
P(2)–Ru(1)–P(1)	93.54(2)	C(14)–P(2)–C(19)	92.36(11)
P(2)–Ru(1)–P(3)	109.17(2)	C(8)–P(1)–C(4)	92.42(11)
P(1)–Ru(1)–P(3)	152.26(2)	C(1)–C(2)–C(3)	113.9(2)
H(1Ru)–Ru(1)–P(1)	80.6(8)	C(1)–P(1)–Ru(1)	118.51(8)
H(1Ru)–Ru(1)–P(2)	80.6(8)	C(3)–P(2)–Ru(1)	116.23(8)

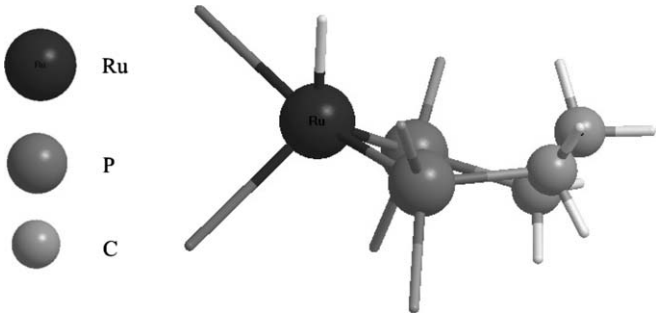


Fig. 2. The conformation of the six member Ru–bpap chelate is close to a twist-boat. In this diagram, the PPh_3 ligand is reduced to the P atom, the cage is reduced to the C atoms bonded to P(1) and P(2) and the hydrogens on C3 bridge are shown.

−17.43 ppm with $^{2}J_{HP}$ values of 20.2, 22.1 and 35.7 Hz suggesting that the hydride is *cis* to all three phosphorus atoms. The three phosphorus signals in the ^{31}P NMR spectrum are also doublet of doublets of doublets. The small $^{2}J_{P(1)P(2)}$ and $^{2}J_{P(2)P(3)}$ values of 7.8 and 32 Hz are consistent with P(1) being *cis* to P(2) and P(2) *cis* to P(3). The large $^{2}J_{P(1)P(3)}$ of 248 Hz is consistent with P(1) being *trans* to P(3). The IR spectrum (Nujol mull) of **2** shows two medium bands at 1881 and 1858 cm^{-1} assigned to ν(RuH).

When dry and crystalline, the violet [RuHCl(bpap)(PPh_3)] very slowly changes colour to brown when exposed to air for longer than 3 days. However, in wet and non-deaerated solvents it decomposes rapidly to give brown solutions.

3.3. Synthesis and properties of the trans-[RuHCl(bpap)(diamine)] complexes

[RuHCl(bpap)(PPh_3)] reacts with (1*R*,2*R*)-1,2-diaminocyclohexane (*R*,*R*-dach) and (1*R*,2*R*)-1,2-diphenylethylenediamine (*R*,*R*-dpen) in diethyl ether under a dinitrogen atmosphere and at room temperature to give pale yellow-green, ether-insoluble complexes *trans*-[RuHCl(bpap)(*R*,*R*-dach)] (**3**) and *trans*-[RuHCl(bpap)(*R*,*R*-dpen)] (**4**).

The crystals of **3** obtained from a benzene-d_6 solution layered with hexanes were of poor quality, which enabled only an approximate establishment of the geometry of the complex by X-ray diffraction. Fig. 3 shows two out of four molecules of *trans*-[RuHCl(bpap)(*R*,*R*-dach)] found in the unit cell. The molecules are diastereomers because of the two diphosphine enantiomers present. The molecule depicted on the left chelates in a δ-skew conformation for bpap and λ for the diamine. The other, on the right, chelates in a λ-skew for bpap and λ for the *R*,*R*-dach. The hydride could not be located in the difference map but is expected to be *trans* to the chloride ligand on the basis of the anticipated octahedral geometry. This is the first report on a diastereomeric complex containing the bpap ligand.

As the coordination number of Ru(II) changes from five in **2** to six in **3** and **4**, the conformation of the six member chelate ring also changes. In the complex **3** it lies between that of a skew and a half-chair conformations (see Fig. 4). The rigid structure of ligand **1** promotes this unusual conformation.

Both the ^{1}H and ^{31}P NMR spectra support the proposed octahedral geometry. The hydride region of the ^{1}H NMR spectrum has two doublet of doublets centered at −19.08 and −19.22 ppm consistent with the two diastereomers. There is also an additional (low intensity) triplet resonance at −18.01 ppm due to the complex containing *meso*-**1**. The $^{2}J_{PH}$ coupling constant values (24.3, 29.7; 24.1, 31.2 Hz and 25.7 Hz) are consistent with the hydride ligand located *cis* to the phosphorus atoms of the bpap ligand. The ^{31}P NMR spectrum consists of three broad overlapping pairs of doublets. The $^{2}J_{PP}$ coupling constants values were established from computer modeling since it was not feasible to obtain them from the signals. As in the case of **2** the values are small (8.5, 14, and 9.5 Hz).

Based on its ^{31}P and ^{1}H NMR spectra, we propose similar structures for the complexes **4** and **3**. The hydride region in the ^{1}H NMR spectrum of *trans*-[RuHCl(bpap)(*R*,*R*-dpen)] in C_6D_6 also has two doublets of doublets centered at −18.65 and −18.79 ppm and a triplet at −17.75 ppm with respective coupling constants of: 25.2 Hz, 28.5 Hz; 24.6, 30.6 Hz and 22.2 Hz.

Both IR spectra show the frequencies characteristic for this type of compounds. They have a medium intensity ν(RuH) at 1997 cm^{-1} and 1996 cm^{-1} for **3** and **4**, respectively, and three weak ν(NH) in the region 3367–3151 cm^{-1}.

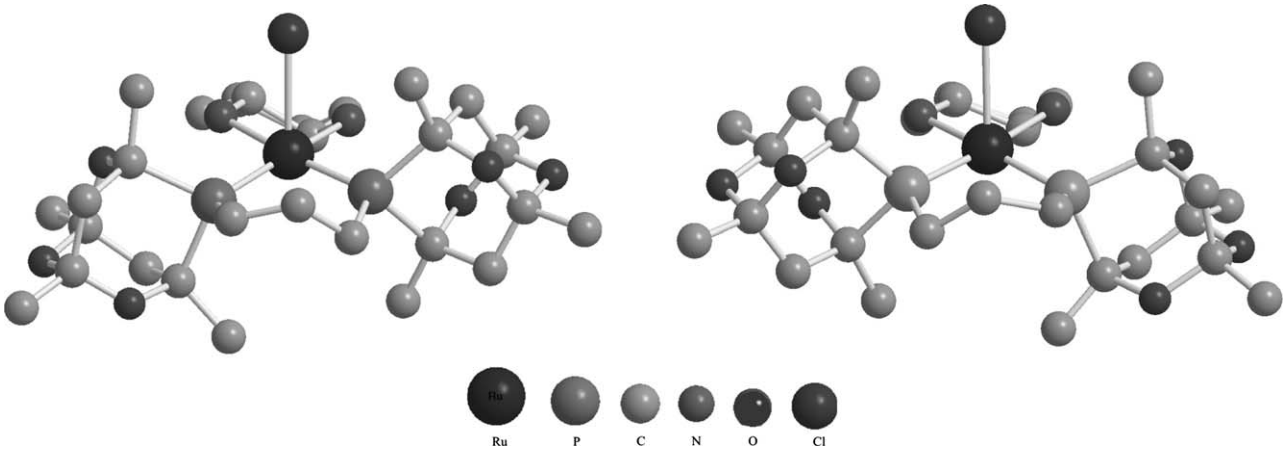


Fig. 3. Chem3D drawings of two diastereomers of **3**.

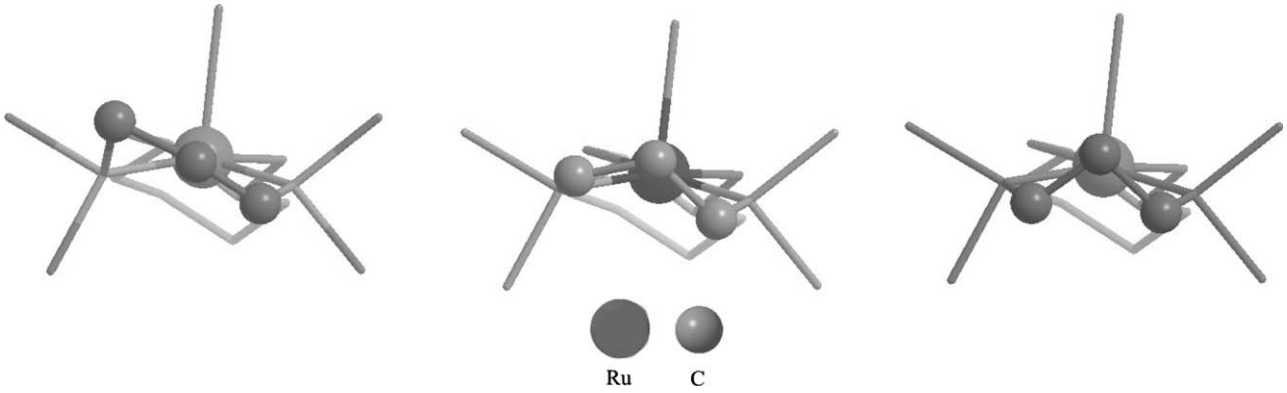


Fig. 4. The conformation of six member ring in **3** (middle) lies between the skew (left) and half chair (right).

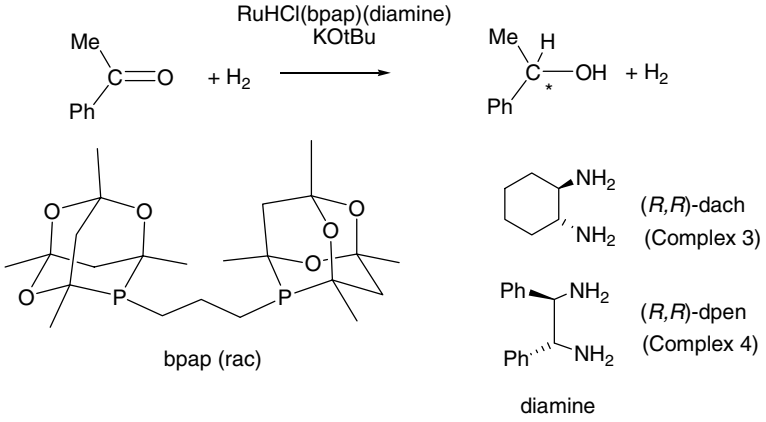


Fig. 5. Hydrogenation (3 atm H_2) of acetophenone catalyzed by complexes **3** and **4** in neat ketone at 20 °C.

3.4. The catalytic activity of trans-[RuHCl(bpap)(diamine)] complexes

Complexes **3** and **4** were tested for their catalytic activity for the hydrogenation at 3 atm of acetophenone and both showed high activity in the presence of small amounts of potassium *tert*-butoxide as base, in the neat ketone at 20 °C (Fig. 5). Using **3**, full conversion of ketone to 1-phenethanol was achieved in less than 2 h with substrate:catalyst:base = 600:1:6.5. Under the same conditions, **4** proved to be less active converting the ketone fully in 4.5 h. However, neither complexes gave significant ee in the 1-phenethanol produced: with 3, 3% (*S*) and with 4, 8% (*S*). This did not change over the course of the catalytic hydrogenation reactions, which were monitored over the reaction time.

The reactivity of these new Ru(II) chlorohydrido catalyst precursors is high and comparable with other similar *trans*-[RuHCl(diphosphine)(diamine)] precatalysts previously reported by some of us [10,11]. However, only essentially racemic alcohol is obtained. This might be a consequence of bpap having rather symmetrical cages as the P-substituents and a flexible backbone. The fact that bpap is present in the ruthenium diamine complex in both enantiomeric forms does not necessarily explain the low ee. For example, the complex with racemic tol-BINAP, *trans*-[$RuCl_2$(tol-BINAP)((*S*,*S*)-dpen)], is a precatalysts for the hydrogenation of acetophenone to (*S*)-1-phenylethanol in 91% ee [12].

4. Conclusion

Reaction of the rigid and chiral bidentate diphosphine **1** with [$RuHCl(PPh_3)_3$] in refluxing THF under an argon atmosphere leads to the formation of deep-violet complex [RuHCl(bpap)(PPh_3)]. This complex easily separates from concentrated solutions as a crystalline solid either at room temperature or on cooling. The distorted square pyramidal geometry around the Ru(II) center, common for the complexes of the type [RuHCl(diphosphine)(PPh_3)], has been confirmed by X-ray crystallography and ^1H and ^{31}P NMR spectra.

This complex reacts easily with the diamines in dry ether under a dinitrogen atmosphere giving pale yellow precipitates of *trans*-[RuHCl(bpap)(diamine)] (diamine = *R*,*R*-dach and *R*,*R*-dpen). These octahedral complexes are precatalysts to very active catalysts for the hydrogenation of acetophenone under mild conditions and high substrate/precatalysts ratios. The very low ee of the product 1-phenethanol is attributed to the symmetrical structure of the phospha-adamantyl cages in bpap.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2005.11.018.

References

[1] H.B. Kagan, T.-P. Dang, J. Am. Chem. Soc. 94 (1972) 6429.
[2] R. Noyori, H. Takaya, Acc. Chem. Res. 23 (1990) 345.
[3] M.D. Fryzuk, B. Bosnich, J. Am. Chem. Soc. 99 (1977) 6262.
[4] M.J. Burk, J. Am. Chem. Soc. 113 (1991) 8518.
[5] V. Gee, A.G. Orpen, H. Phetmung, P.G. Pringle, R.I. Pugh, Chem. Commun. (1999) 901.
[6] R.I. Pugh, P.G. Pringle, E. Drent, Chem. Commun. (2001) 1476.
[7] R. Abbel, K. Abdur-Rashid, M. Faatz, A. Hadzovic, A.J. Lough, R.H. Morris, J. Am. Chem. Soc. 127 (2005) 1870.
[8] L. Maier, Helv. Chim. Acta 49 (1966) 842.
[9] P.A. MacNeil, N.K. Roberts, B. Bosnich, J. Am. Chem. Soc. 103 (1981) 2273.
[10] K. Abdur-Rashid, A.J. Lough, R.H. Morris, Organometallics 19 (2000) 2655.
[11] K. Abdur-Rashid, A.J. Lough, R.H. Morris, Organometallics 20 (2001) 1047.
[12] T. Ohkuma, H. Doucet, T. Pham, K. Mikami, T. Korenaga, M. Terada, R. Noyori, J. Am. Chem. Soc. 120 (1998) 1086.