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Novel catalytic hydrogenolysis of silyl enol ethers by the use of acidic ruthenium dihydrogen complexes

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Abstract

Treatment of 1-trimethylsilyloxy-1-cyclohexene (**1a**) in the presence of a catalytic amount of the acidic dihydrogen complex $[RuCl(\eta^2\text{-}H_2)(dppe)_2]OTf$ (**4a**) [dppe = 1,2-bis(diphenylphosphino)ethane, $OTf = OSO_2CF_3$] (10 mol.%) under 1 atm of H_2 in anhydrous $ClCD_2CD_2Cl$ at 50 °C for 8 h afforded cyclohexanone (**3a**) and Me_3SiH in quantitative NMR yields. Silyl enol ethers such as 1-triethylsilyloxy-1-cyclohexene (**1b**), 1-*t*-butyldimethylsilyloxy-1-cyclohexene (**1c**), and other trimethylsilylethers (**1d**, **1e**, and **1f**) reacted similarly with H_2 to afford the corresponding ketones and trialkylsilanes. The direct proton transfer from H_2 to the trimethylsilyl enol ethers (**1a** and **1d**–**1f**) was confirmed by the experiments employing D_2 gas, where α-monodeuterated ketones (**3a′** and **3d′**–**3f′**) were obtained in high yields. The enantioselective protonation of prochiral silyl enol ethers with 1 atm of H_2 by employing $[RuCl(\eta^2\text{-}H_2)((S)\text{-BINAP})_2]OTf$ (**4e**) [BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl] and $[RuCl(\eta^2\text{-}H_2)((R, R)\text{-CHIRAPHOS})_2]OTf$ (**4f**) [CHIRAPHOS = 2,3-bis(diphenylphosphino)butane] showed that no enantioselectivity was observed in either catalytic or stoichiometric protonation reactions under various reaction conditions. The reaction of $[RuHCl(dppe)_2]$ (**5a**) with one equivalent of Me_3SiOTf under 1 atm of H_2 produced rapidly **4a**, concurrent with the formation of Me_3SiH. Based on these studies, the mechanism for this novel hydrogenolysis of silyl enol ethers is proposed which involves heterolytic cleavage of the coordinated H_2 on the ruthenium atom caused by the nucleophilic attack of the oxygen atom of enol ethers to give ketones and Me_3SiOTf, and the subsequent reaction of the resultant complex **5a** with Me_3SiOTf under 1 atm of H_2 to regenerate the original dihydrogen complex **4a**. On the other hand, the stoichiometric reaction of a lithium enolate **6e** with one equivalent of **4e** at −78 °C in CH_2Cl_2 under 1 atm of H_2 afforded 2-methyl-1-tetralone (**3e**) with 75% ee (*S*) in >95% yield, together with the formation of $[RuHCl((S)\text{-BINAP})_2]$ (**5e**).

Keywords: Hydrogenolysis; Dihydrogen complexes; Silyl enol ethers; Asymmetric protonation

1. Introduction

Extensive studies on dihydrogen complexes have been performed to reveal their bonding and structures as well as their reactivities [1–4]. In the bonding between a metal (M) and dihydrogen (H_2), σ donation from the σ bonding orbital of H_2 to the d-orbital of metal depletes the electron density on the H_2, while back-bonding from the metal to the antibonding σ* orbital of H_2 increases the electron density on the H_2. The contribution of the former bonding is believed to be higher than the latter in most of dihydrogen complexes, so that the coordinated H_2 is expected to be more acidic than free H_2. Actually, treatment of some dihydrogen complexes with a variety of bases gives rise to the heterolytic cleavage of

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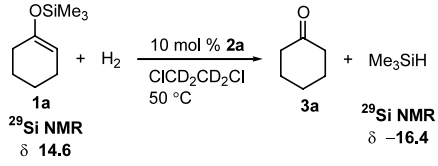
coordinated H_2 [2]. The systematic research of ligand effects on the reactivity of coordinated H_2 has led to the synthesis of a series of acidic dihydrogen complexes. However, development of catalytic hydrogenation reactions by using the unique properties of coordinated H_2 has been still limited [5–7].

During the long-standing studies on the reactivities of dinitrogen complexes of the type $M(N_2)_2(L)_4$ (M = Mo or W; L = phosphine) [8], we have recently succeeded in the transformation of coordinated N_2 on tungsten into NH_3 by treatment with H_2 mediated by [RuCl(diphosphine)$_2$]X complexes or sulfido-bridged dinuclear molybdenum complexes [9]. In these reactions, only one of the two hydrogen atoms of H_2 activated by the complexes is used for the N–H bond formation, while the other is not employed for the product formation. Thus, the reactions are stoichiometric and the activated H_2 only behaves as a proton. However, this finding has led us to find novel hydrogenolysis of silyl enol ethers to form ketones and silanes by employing acidic η^2-H_2 complexes [RuCl(η^2-H_2)(diphosphine)$_2$]X as catalysts [10]. It is to be noted that treatment of silyl enol ethers with H_2 in the presence of the Wilkinson catalyst [$RhCl(PPh_3)_3$] results in the hydrogenation of the C=C bond [11]. Preliminary results on the hydrogenolysis have already been reported in a communication form [12]. In the present contribution we describe the more detailed results of a conceptually new type of the hydrogenolysis reactions.

2. Results and discussion

2.1. Novel catalytic hydrogenolysis of trialkylsilyl enol ethers by using acidic Ru(η^2-H_2) complexes

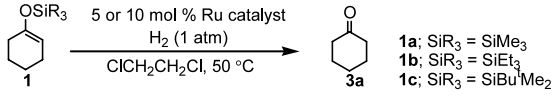
When 1-trimethylsilyloxy-1-cyclohexene (**1a**) was treated with 1 atm of H_2 in the presence of a catalytic amount of [RuCl(dppe)$_2$]OTf (**2a**) (10 mol.%) in anhydrous $ClCD_2CD_2Cl$ at 50 °C for 8 h in an NMR tube, ^1H and $^{29}Si\{^1H\}$-NMR analysis of the reaction mixture clearly showed the quantitative formation of cyclohexanone (**3a**) and Me_3SiH ($^{29}Si\{^1H\}$-NMR δ −16.4) (Scheme 1). However, the reaction was very slow at room temperature. Under 1 atm of H_2 at room temperature, complex **2a** is known to be quantitatively transformed into [RuCl(η^2-H_2)(dppe)$_2$]OTf (**4a**) with relatively high acidity (pK_a = 6.0) [9,13,14]. In contrast, the ^1H and $^{31}P\{^1H\}$-NMR analysis of the reaction mixture of complex **2a** with **1a** or **3a** in $ClCD_2CD_2Cl$ indicated that both **1a** and **3a** are not coordinated to the metal at ambient temperature or even 50 °C, probably due to the steric effect of the phosphine ligands around the metal.



Scheme 1.

Several acidic Ru(η^2-H_2) complexes were employed as catalyst for the hydrogenolysis of **1a**. Typical results are shown in Table 1. In all cases, the reaction of **1a** (0.60 mmol) with 1 atm of H_2 was carried out in the presence of a catalytic amount of **2** (5 or 10 mol.%) in anhydrous 1,2-dichloroethane at 50 °C. Although the hydrogenolysis of **1a** took place smoothly at 50 °C with the aid of complex **2a** (10 mol.%), the reaction did not proceed in the absence of either complex **2a** or H_2 (Table 1; runs 1–3). The reaction of **1a** with H_2 proceeded in the presence of 5 mol.% of **2a** at 50 °C for 18 h to afford **3a** in 88% yield, and a longer reaction time (48 h) improved the yield of **3a** up to >95% (Table 1; runs 4 and 5). When an analogous Ru(η^2-H_2) complex [RuCl(η^2-H_2)(dppe)$_2$]PF_6 (**4b**) [13] was used in place of complex **4a**, the yield of **3a** did not significantly change (Table 1; runs 4 and 6). Employment of a dihydrogen complex [RuH(η^2-H_2)(dppe)$_2$]OTf (**4c**) with much lower acidity (pK_a = 15.0) [15] did not induce the hydrogenolysis effectively (Table 1; run 7). On the other hand, when [RuCl(η^2-H_2)(dppp)$_2$]OTf (**4d**) [dppp = 1,3-bis(diphenylphosphino)propane] with higher acidity (pK_a = 4.3) [9b,16] derived from [RuCl(dppp)$_2$]OTf (**2d**) and H_2 was used as catalyst, the yield of **3a** was slightly lower compared with that from **4a** (Table 1; runs 4 and 8). This is compatible with the previous findings that treatment of **2d** with 1 atm of H_2 in solution at ambient temperature gives a mixture of complexes **2d** and **4d** in a ratio of about 9:1 [9b,16], whereas complex **2a** is completely transformed into complex **4a** under the same conditions [9b,13]. New dihydrogen complexes [RuCl(η^2-H_2)(diphosphine)$_2$]OTf containing typical chiral diphosphine ligands such as BINAP [17] and CHIRAPHOS [18] prepared here (vide infra) were also found to be effective for this catalytic reaction (Table 1; runs 9 and 10). Noteworthy is the remarkable catalytic activity of the dihydrogen complex (**4e**) containing BINAP (Table 1; run 9), although we could not determine the pK_a [19]. Hydrogenolysis of 1-triethylsilyloxy-1-cyclohexene (**1b**) and 1-*t*-butyldimethylsilyloxy-1-cyclohexene (**1c**) also occurred in the presence of **4a** or **4e** under the same conditions, but the reactions were slower than that of **1a** probably due to the steric factors of the bulky substrates (Table 1; runs 11–16) [20].

Table 1
Hydrogenolysis of silyl enol ethers catalysed by Ru(η^2-H_2) complexes under 1 atm of H_2[a]



run	silyl enol ether	Ru(η^2-H_2) complex	GLC yield of **3a** (%)
1[b]	**1a**	[RuCl(η^2-H_2)(dppe)$_2$]OTf (**4a**)	>95
2[c]	**1a**	——	<3
3[b,d]	**1a**	[RuCl(η^2-H_2)(dppe)$_2$]OTf (**4a**)	11[f]
4	**1a**	[RuCl(η^2-H_2)(dppe)$_2$]OTf (**4a**)	88
5[e]	**1a**	[RuCl(η^2-H_2)(dppe)$_2$]OTf (**4a**)	>95
6	**1a**	[RuCl(η^2-H_2)(dppe)$_2$]PF_6 (**4b**)	83
7	**1a**	[RuH(η^2-H_2)(dppe)$_2$]OTf (**4c**)	16
8	**1a**	[RuCl(η^2-H_2)(dppp)$_2$]OTf (**4d**)	56
9	**1a**	[RuCl(η^2-H_2)(BINAP)$_2$]OTf (**4e**)	>95
10	**1a**	[RuCl(η^2-H_2)(CHIRAPHOS)$_2$]OTf (**4g**)	70
11	**1b**	[RuCl(η^2-H_2)(dppe)$_2$]OTf (**4a**)	55
12[b]	**1b**	[RuCl(η^2-H_2)(dppe)$_2$]OTf (**4a**)	64
13	**1b**	[RuCl(η^2-H_2)(BINAP)$_2$]OTf (**4e**)	75
14	**1c**	[RuCl(η^2-H_2)(dppe)$_2$]OTf (**4a**)	30
15[b]	**1c**	[RuCl(η^2-H_2)(dppe)$_2$]OTf (**4a**)	44
16	**1c**	[RuCl(η^2-H_2)(BINAP)$_2$]OTf (**4e**)	48

[a] All the reactions were carried out in the presence of catalyst (5 mol %) and silyl enol ether (0.60 mmol) in anhydrous 1,2-dichloroethane (5 mL) at 50 °C for 18 h under 1 atm of H_2.
[b] Reaction was carried out in the presence of catalyst (10 mol %) for 8 h.
[c] In the absence of catalyst under 1 atm of H_2.
[d] Under 1 atm of N_2.
[e] Reaction was carried out for 48 h.
[f] **3a** was obtained from the stoichiometoric reaction of **4a** (10 mol %) with **1a**.

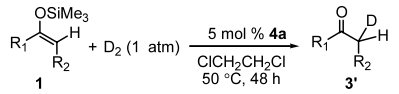
2.2. The hydrogenolysis of silyl enol ethers with D_2 gas

The experiment employing D_2 gas in the hydrogenolysis unequivocally demonstrated the proton transfer from H_2 to silyl enol ethers. Thus, treatment of **1a** with 5 mol.% of **2a** under 1 atm of D_2 at 50 °C for 48 h in anhydrous 1,2-dichloroethane resulted in the formation of α-monodeuterated **3a′** in very high GLC yield (Table 2; run 1). The same procedure was applied for other trialkylsilyl enol ethers (**1b** and **1c**), 1,1-disubstituted trimethylsilyl enol ether (**1d**), and 1,1,2,2-tetrasubstituted trimethylsilyl enol ethers (**1e** and **1f**). Reactions of bulky trialkylsilyl enol ethers (**1b** and **1c**) were sluggish under the same conditions, but α-monodeuterated ketone **3a′** being obtained with high selectivities (Table 2; runs 2 and 3). Similar treatment of other trimethylsilyl enol ethers (**1d**, **1e**, and **1f**) with D_2 afforded the corresponding α-monodeuterated ketones **3d′**, **3e′**, and **3f′** (Table 2; runs 4–6). Incorporation of deuterium at the α-position of **3a′** and **3d′**–**3f′** was fully characterized by ^{1}H-NMR and GC–MS analysis (see Section 3).

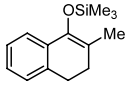
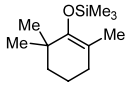
2.3. Synthesis of chiral dihydrogen complexes [RuCl(η^2-H_2)((S)-BINAP)$_2$]OTf (4e) and [RuCl(η^2-H_2)((R,R)-CHIRAPHOS)$_2$]OTf (4g) toward asymmetric protonation of prochiral silyl enol ethers

We intended to extend the novel catalytic reaction to the asymmetric protonation of prochiral silyl enol ethers with H_2 assisted by new acidic Ru(η^2-H_2) complexes containing chiral diphosphines. Protonation of [RuHCl((*S*)-BINAP)$_2$] (**5e**) [21] with trifluoromethanesulfonic acid (HOTf) gave the dihydrogen complex [RuCl(η^2-H_2)((*S*)-BINAP)$_2$]OTf (**4e**) in high yield. This complex was also prepared from the reaction of [RuHCl((*S*)-BINAP)$_2$] (**5e**) with a hydride acceptor Me_3SiOTf under 1 atm of H_2 (Scheme 2). The existence of the η^2-H_2 moiety in complex **4e** was confirmed by

Table 2
Hydrogenolysis of silyl enol ethers catalysed by [RuCl(η^2-H_2)(dppe)$_2$]OTf (**4a**) under 1 atm of D_2



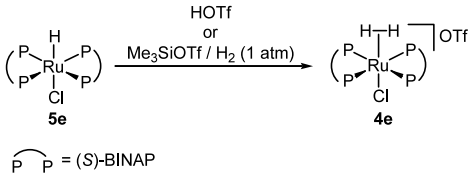
1 3'

run	silyl enol ether	yield of ketone (**3'**) (%) [b]	content of α–monodeuterated ketone (**3'**) (%)
1	 **1a**; $SiR_3 = SiMe_3$	>95	95
2	**1b**; $SiR_3 = SiEt_3$	72	94
3	**1c**; $SiR_3 = SiBu^tMe_2$	40	95
4	**1d** (R^1 = Ph, R^2 = H)	>95	99
5	 **1e**	>95	93
6	 **1f**	>95	85

[a]All the reactions were carried out in the presence of [RuCl(h_2-H_2)(dppe)$_2$]OTf (**4a**) (5 mol.%) and silyl enol ether (0.60 mmol) in anhydrous 1,2-dichloroethane (5 ml) at 50 °C for 48 h under 1 atm of D_2. [b]Determined by GLC.

variable-temperature T_1 measurement and the observation of a large $^1J_{HD}$ for the corresponding isotopomer. The broad signal at −9.11 ppm exhibited a minimum T_1 value of 21 ms (400 MHz in CD_2Cl_2) at 243 K. The deuterio derivative *trans*-[RuCl(η^2-HD)((*S*)-BINAP)$_2$]OTf (**4e**-d_1) was prepared by the reaction of **5e** with a stoichiometric amount of trifluoromethanesulfonic acid-d_1 (DOTf) in CD_2Cl_2 at room temperature. A $^1J_{HD}$ coupling constant of 21.5 Hz in CD_2Cl_2 at 20 °C was observed for complex (**4e**-d_1). These values of the minimum T_1 and $^1J_{HD}$ are compatible with the η^2-H_2 bonding to the metal [3].

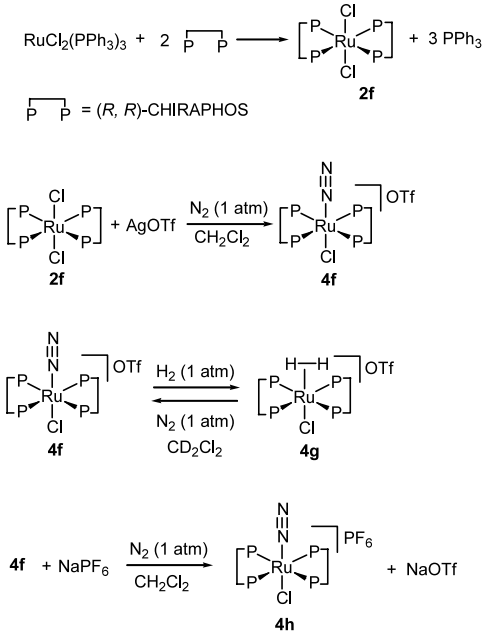
Dihydrogen and dinitrogen ruthenium complexes containing CHIRAPHOS ligands [RuCl(η^2-H_2)((*R*, *R*)-CHIRAPHOS)$_2$]OTf (**4g**) and [RuCl(N_2)((*R*, *R*)-CHIRAPHOS)$_2$]OTf (**4f**) were synthesized by the following procedures (Scheme 3). At first, [RuCl$_2$((*R*, *R*)-CHIRAPHOS)$_2$] (**2f**) was prepared from the reaction of [RuCl$_2$(PPh$_3$)$_3$] with two equivalents of (*R*, *R*)-CHIRAPHOS in toluene at reflux temperature [22]. Subsequent treatment of complex **2f** with AgOTf in dichloromethane under 1 atm of N_2 afforded the dinitrogen complex **4f** in high yield. The dinitrogen complex **4f** was converted to [RuCl(N_2)((*R*, *R*)-CHIRAPHOS)$_2$]PF_6 (**4h**) by anion exchange with $NaPF_6$. The molecular structure of **4h** was unambiguously determined by X-ray analysis (see Section 3). The N_2 stretching absorption at 2155 cm^{-1} for **4f** indicates that the back-bonding from the metal to the N_2 ligand is weak. In fact, the coordinated N_2 on the Ru atom was



Scheme 2.

readily replaced by dihydrogen to form the dihydrogen complex **4g**. The existence of the η^2-H_2 moiety in complex **4g** was confirmed by variable-temperature T_1 measurement. A minimum T_1 value of 15 ms (400 MHz in CD_2Cl_2) at 273 K was obtained for the broad signal at −12.6 ppm, assignable to the η^2-H_2 coordination [3].

Catalytic asymmetric protonation of silyl enol ethers with 1 atm of H_2 was investigated by using both **4e** and **4g** under various reaction conditions (Scheme 4). However, treatment of **1e** (0.20 mmol) in the presence of a catalytic amount of **4e** or **4g** (0.010 mmol, 5 mol.%) at 25 °C for 48 h in anhydrous dichloromethane under 1 atm of H_2 afforded **3e** in 41 or 13% GLC yield, respectively, with no enantioselectivity. Change of the solvent from dichloromethane to THF or toluene did not induce any asymmetric reaction. The protonation of *tert*-butyldimethylsilyl enol ethers with HCl is known to occur at the sp^2 carbon bearing the methyl group (*C*-protonation) [23]. Thus, we expected that if **1g** is used as substrate in place of **1e**, some asymmetric induction may be realized. However, the reaction of **1g** with H_2 in the presence of a catalytic amount of **4e** (5 mol.%) under the same reaction conditions proceeded quite slowly to give **3e** in 20% GLC yield with no enantioselectivity. Furthermore, the stoichiometric protonation of **1e**



Scheme 3.

with one equivalent of **4e** at −78 °C for 3 h in anhydrous dichloromethane under 1 atm of H_2 afforded **3e** in >95% yield, but no enantioselectivity was observed. These results indicate that H^+ of activated H_2 on the ruthenium is transferred not to the sp^2 carbon, but to the oxygen atom of silyl enol ethers (*O*-protonation).

2.4. The reaction mechanism for the hydrogenolysis of *1a* catalysed by *4a*

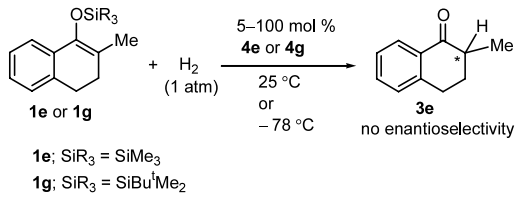
In order to obtain further information about the reaction mechanism, we investigated the following stoichiometric or catalytic reactions. When dihydrogen complex **4a** was reacted with one equivalent of **1a** under 1 atm of N_2 in $ClCD_2CD_2Cl$ at room temperature in an NMR tube, ^1H-, $^{29}Si\{^1H\}$-, and $^{31}P\{^1H\}$-NMR analysis of the reaction mixture showed the almost quantitative formation of Me_3SiH, **2a** (>95 mol.%), **3a** (>95 mol.%), and a small amount (<5 mol.%) of monohydride complex $[RuHCl(dppe)_2]$ (**5a**; ^1H-NMR ($ClCD_2CD_2Cl$): δ −18.5 (s), $^{31}P\{^1H\}$-NMR: δ 61.6 (s)) [24]. Furthermore, treatment of lithium enolate **6a**, which was prepared in situ from **1a** and MeLi, with one equivalent of $[RuCl(\eta^2\text{-}D_2)(dppe)_2]OTf$ (**4a′**) under 1 atm of D_2 in anhydrous THF at room temperature led to the formation of α-monodeuterated **3a′** in >95% GLC yield and a monodeuteride complex $[RuDCl(dppe)_2]$ (**5a′**) in 85% isolated yield (Scheme 5). In this case, the nucleophilic reaction of **6a** on the coordinated D_2 causes the heterolytic cleavage of the D_2 to form **3a′**, while D^- remains at the ruthenium atom as **5a′**. Noteworthy is that the reaction of $[RuHCl(dppe)_2]$ (**5a**) [13] with equimolar Me_3SiOTf ($^{29}Si\{^1H\}$-NMR δ 46.0) under 1 atm of H_2 in anhydrous C_6D_6 at room temperature rapidly produced the dihydrogen complex **4a** and Me_3SiH in quantitative NMR yields (Scheme 6). This finding indicates that the cationic complex **2a** may initially form from the reaction of complex **5a** with Me_3SiOTf as a hydride acceptor, which is immediately transformed into the dihydrogen complex **4a** under H_2.

In sharp contrast, the catalytic hydrogenation of trimethylsilyl enol ethers by using typical homogeneous catalysts such as Wilkinson complex $[RhCl(PPh_3)_3]$ under the same reaction conditions led to the formation of the corresponding saturated trimethylsilyl ethers. For example, treatment of **1d** in the presence of 5 mol.% of $[RhCl(PPh_3)_3]$ under 1 atm of H_2 in anhydrous C_6H_6 at 50 °C for 24 h afforded (1-phenyl-1-trimethylsilyloxy)ethane in >95% GLC yield [25]. Furthermore, the reaction of 2-cyclohexen-1-one in the presence of a catalytic amount of **2a** under 1 atm of H_2 at 50 °C for 18 h did not produce **3a** at all, indicating that the hydrogenolysis of **1a** does not proceed via 2-cyclohexen-1-one, which might be formed from dehydrosilylation of **1a** [26].

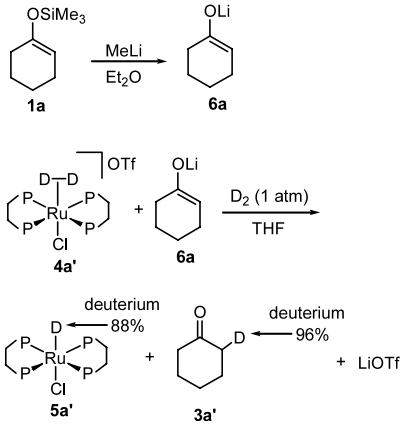
Based on the above results, we propose a mechanism for the novel hydrogenolysis of a silyl enol ether **1a** catalysed by dihydrogen complex **4a** as a typical example (Scheme 7). The reaction is initiated by the nucleophilic attack of the oxygen atom of the enol ether on the coordinated H_2 on the ruthenium atom. This induces the heterolytic cleavage of the H_2 and results in the formation of **3a** and Me_3SiOTf together with **5a**. The following reaction of Me_3SiOTf with **5a** under 1 atm of H_2 regenerates the starting dihydrogen complex **4a** via **2a**, concurrent with theformation of Me_3SiH. It is presumed that a delicate balance of the acidity of dihydrogen complex **4a** and the nucleophilicity of the hydride complex **5a** might realize this novel catalytic hydrogenolysis of silyl enol ethers. However, we cannot exclude the possibility that the concerted transfer of a proton and a hydride of the activated H_2 to the oxygen atom and the silicon atom of the enol ether, respectively, gives rise to the formation of **3a** and Me_3SiH. It is to be noted that this reaction mechanism is comparable to that of the heterolytic cleavage of H_2 catalysed by [Cp*RuH(dppm)] (dppm = bis(diphenylphosphino)methane), where tetramethylpiperidine and an acridinium salt work as proton and hydride acceptors, respectively [6a].

2.5. Stoichiometric asymmetric protonation of prochiral lithium enolate *6e*

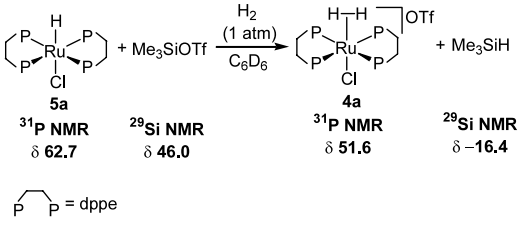
Treatment of lithium enolate **6e**, which was prepared in situ from the reaction of **1e** and MeLi, with one



Scheme 4.



Scheme 5.

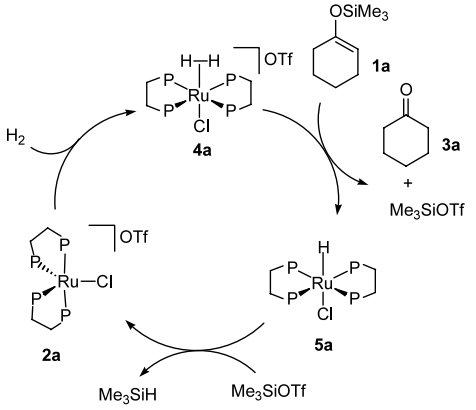


Scheme 6.

equivalent of complex **4e** in anhydrous dichloromethane under 1 atm of H_2 at -78 °C gave **3e** in $>95\%$ GLC yield with 75% ee (*S*), together with the formation of **5e** in 69% isolated yield (Scheme 8). In this stoichiometric protonation, the enantiomeric excess of **3e** critically depended upon the nature of the solvent. When THF, diethyl ether, or toluene was used in place of dichloromethane, no or much lower enantioselectivities ($<1\%$ ee, $<1\%$ ee, and 5% ee (*S*), respectively) were observed under similar reaction conditions. On the other hand, the stoichiometric protonation of **6e** with **4g** at -78 °C under similar reaction conditions afforded **3e** in $>95\%$ GLC yield with lower enantioselectivity ($<10\%$ ee); thus, **4g** was less effective for the asymmetric protonation of **6e** compared with **4e**. These results indicate that the reaction mechanism is different between silyl enol ethers (**1e** and **1g**) and lithium enolate (**6e**). We believe that the high enantioselectivity attained by the protonation of lithium enolate (**6e**) with a stoichiometric amount of **4e** is realized by the protonation of the coordinated H_2 at the sp^2 carbon bearing the methyl group (*C*-protonation) in place of the *O*-protonation (*vide supra*).

2.6. Conclusion

Novel catalytic hydrogenolysis of trialkylsilyl enol ethers with H_2 has been found to be catalysed by acidic dihydrogen complexes of ruthenium such as [RuCl(η^2-H_2)(dppe)$_2$]OTf (**4a**) and [RuCl(η^2-H_2)((*S*)-BINAP)$_2$]OTf (**4e**). In this reaction, H_2 is heterolytically cleaved into H^+ and H^- on the ruthenium centre and transferred to the enol oxygen and the trialkylsilyl silicon atom, respectively, to form a ketone and a silane. Furthermore, employment of a stoichiometric amount of a chiral dihydrogen complex **4e** results in the enantioselective protonation of a prochiral lithium enolate with H_2 to give a chiral ketone with high enantioselectivity (up to 75% ee). This provides a new approach to the enantioselective protonation of prochiral enolates [27].



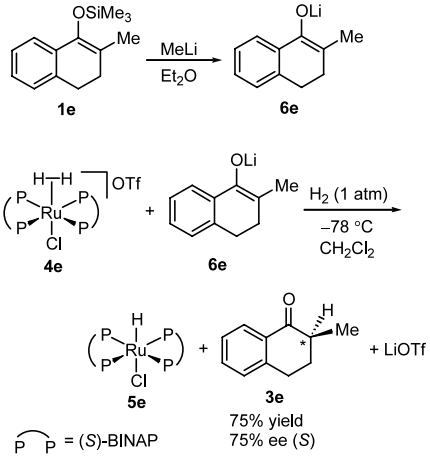
Scheme 7.

3. Experimental

3.1. General considerations

Preparation of complexes was performed under 1 atm of N_2 or Ar dried by passage through $CaCl_2$ and P_2O_5. Reaction of trialkylsilyl enol ethers with dihydrogen was carried out under 1 atm of H_2 dried by passage through $CaCl_2$ and P_2O_5. D_2 (99.9%) was obtained from Takachiho Chemical Industrial Co. (Japan). Solvents were dried by refluxing over Na–benzophenone ketyl (THF, toluene, benzene, and hexanes), P_2O_5 (dichloromethane, 1,2-dichloroethane), and distilled just before use. Unless otherwise noted, all manipulations were done by use of Schlenk techniques. Schlenks and flasks were dried thoroughly in an oven at 150 °C for 3 h just before use.

NMR spectra were recorded on a JEOL JNM-LA-400 spectrometer. IR spectra were recorded on a Shimadzu FTIR-8100M spectrometer. Quantitative GLC analyses were performed on a Shimadzu GC-14A instrument equipped with a flame ionization detector using a 25 m × 0.25 mm CBP-10, 14% cyanopropylphenylpolysiloxane in fused silica capillary column. GC–MS analyses were carried out on a Shimadzu GC–MS QP-5000 spectrometer. Elemental analyses were performed on a Perkin–Elmer 2400 series II



Scheme 8.

CHN analyzer. Optical rotation was measured on a JASCO DIP-360.

Trimethylsilyl enol ethers (**1a**, **1d**, and **1h**), triethylsilyl chloride, *t*-butyldimethylsilyl chloride and Me_3SiOTf were purchased from Tokyo Chemical Industry Co. (Japan) and distilled under reduced pressure. Other silyl enol ethers (**1b** [28], **1c** [29], **1e** [30], **1f** [31] and **1g** [32]) were prepared by the method described in the literatures. (*S*)-BINAP [17], *n*-BuLi and MeLi were purchased from Kanto Chemical Co., Inc. (Japan). 2-Methyl-1-tetralone (**3e**) and (*R*, *R*)-CHIRAPHOS [18] were purchased from Aldrich Chemical Company, Inc. Me_3SiH was obtained from Trichemical Co. Ltd (Japan). Amounts of the solvent molecules in the crystals were determined by both elemental analyses and ^{1}H-NMR spectroscopy.

3.2. Preparation of [RuCl(η^2-H_2)((*S*)-BINAP)$_2$]OTf (**4e**)

To a solution of [RuHCl((*S*)-BINAP)$_2$] (**5e**) (1.152 g, 0.83 mmol) in dichloromethane (10 ml) and THF (10 ml) was added 80 μl of HOTf by syringe under 1 atm of H_2. The reaction mixture was stirred at room temperature (r.t.) for 30 min, during which the yellow solution turned to a red solution. Addition of hexanes (50 ml) to the reaction mixture afforded a pale red solid **4e**, which was collected by filtration, washed with hexanes (20 ml × 3), and dried under reduced pressure. Yield: 82% (1.050 g, 0.68 mmol). ^{1}H-NMR (CD_2Cl_2): δ −9.11 (br, 2H), 5.2–8.8 (m, 64H); a minimum T_1 value of 21 ms (400 MHz) at 243 K was obtained for the broad signal at −9.11 ppm upon changing the temperature from 233 to 303 K. ^{31}P{^{1}H}-NMR (CD_2Cl_2): δ 2.5 (t, $J = 27$ Hz), 26.3 (t, $J = 27$ Hz). Anal. Calc. for $C_{89}H_{66}ClF_3O_3P_4SRu$: C, 69.73; H, 4.34. Found: C, 69.74; H, 4.38%.

Complex **4e** was also prepared form the reaction of **5e** with Me_3SiOTf under 1 atm of H_2. To a solution of **5e** (138 mg, 0.10 mmol) in dichloromethane (10 ml) was added Me_3SiOTf (22 mg, 0.10 mmol) by syringe under 1 atm of H_2. The reaction mixture was stirred at r.t. for 30 min under 1 atm of H_2. The color of the solution turned from yellow to red during the reaction. Addition of hexanes (50 ml) to the reaction mixture afforded a pale red powder, which was collected by filtration and washed with hexanes (20 ml × 3). The resultant powder was recrystallized from THF–hexanes to give a pale red solid of **4e** (49 mg, 0.032 mmol) in 32% yield.

3.3. Preparation of [RuCl(η^2-HD)((*S*)-BINAP)$_2$]OTf (**4e**-d_1)

The Ru(η^2-HD) complex (**4e**-d_1) was prepared in situ by the following procedure. To a solution of **5e** (28 mg, 0.020 mmol) in CD_2Cl_2 (0.75 ml) was added a mixture (20 mg) of HOTf and D_2O (1/1, wt.%) at r.t. under 1 atm of N_2. ^{1}H-NMR spectra of the reaction mixture showed the formation of **4e**-d_1. ^{1}H-NMR (CD_2Cl_2): δ −9.01 (tq, $^2J_{PH} = 7.2$ Hz, $^1J_{HD} = 21.5$ Hz).

3.4. Preparation of [$RuCl_2$((*R*, *R*)-CHIRAPHOS)$_2$]·CH_2Cl_2 (**2f**·CH_2Cl_2)

A solution of [$RuCl_2(PPh_3)_3$] (910 mg, 0.95 mmol) and (*R*, *R*)-CHIRAPHOS (812 mg, 1.90 mmol) in toluene (20 ml) was stirred at reflux temperature for 3 h under 1 atm of N_2. After evaporation of the solvent, the residue was washed with hexanes (20 ml × 3) and extracted with CH_2Cl_2. Addition of hexanes to the concentrated CH_2Cl_2 solution afforded 2f·CH_2Cl_2 (821 mg, 0.74 mmol) in 78% yield as yellow crystals. ^{1}H-NMR ($CDCl_3$): δ 0.72 (br s, 12H), 2.81 (br s, 4H), 6.83–7.51 (m, 40H). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 46.8 (s). Anal. Calc. for $C_{56}H_{56}Cl_2P_4Ru·CH_2Cl_2$: C, 61.69; H, 5.27. Found: C, 61.83; H, 5.31%.

3.5. Preparation of [RuCl(N_2)((*R*, *R*)-CHIRAPHOS)$_2$]OTf (**4f**)

A solution of **2f** (821 mg, 0.74 mmol) and AgOTf (210 mg, 0.82 mmol) in CH_2Cl_2 (20 ml) was stirred at r.t. for 30 min under 1 atm of N_2. After evaporation of the solvent, the residue was extracted with CH_2Cl_2 (10 ml). Addition of Et_2O to the concentrated CH_2Cl_2 solution of product under 1 atm of N_2 afforded **4f** (739 mg, 0.63 mmol) in 86% yield as pale yellow crystals. IR (KBr): $\nu(N_2)$, 2155 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 0.36 (q, 6H, $J = 7$ Hz), 0.65 (q, 6H, $J = 7$ Hz), 2.37 (br m, 2H), 3.00 (br m, 2H), 6.71–7.48 (m, 40H). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 37.7 (t, $J = 22$ Hz) and 51.0 (t, $J = 22$ Hz). Anal. Calc. for $C_{57}H_{56}ClF_3N_2O_3P_4RuS$: C, 58.69; H, 4.84; N, 2.40. Found: C, 58.91; H, 5.13; N, 2.51%.

3.6. Conversion of **4f** into [RuCl(η^2-H_2)((*R*, *R*)-CHIRAPHOS)$_2$]OTf (**4g**)

In an NMR tube was placed **4f** (15.0 mg, 0.013 mmol) under 1 atm of N_2. Dry CD_2Cl_2 (0.60 ml) was then added by syringe under 1 atm of N_2. The reaction mixture was stirred at r.t. for 5 min under 1 atm of H_2. ^{1}H and ^{31}P{^{1}H}-NMR spectra of the reaction mixture showed the complete conversion of **4f** into **4g**. ^{1}H-NMR (CD_2Cl_2): δ −12.6 (br, 2H), 0.37 (q, 6H, $J = 6$ Hz), 0.80 (q, 6H, $J = 6$ Hz), 1.78 (br m, 2H), 3.16 (br m, 2H), 6.69–7.55 (m, 40H); a minimum T_1 value of 15 ms (400 MHz) at 273 K was obtained for the broad signal at −12.6 ppm upon changing the temperature from 233 to 303 K. ^{31}P{^{1}H}-NMR (CD_2Cl_2): δ 36.1 (t, $J = 24$ Hz) and 64.9 (t, $J = 24$ Hz).

3.7. Reaction of **1a** with H_2 in the presence of **2a** in an NMR tube (Scheme 1)

In an NMR tube was placed **2a** (16.3 mg, 0.015 mmol) under 1 atm of H_2. A solution of **1a** (28 mg, 0.16 mmol) in anhydrous $ClCD_2CD_2Cl$ (0.8 ml) was then added by syringe. The reaction mixture was kept at 50 °C for 8 h under 1 atm of H_2. The ^{1}H-NMR analysis of the mixture revealed that **3a** was obtained in >95% yield. The quantitative formation of Me_3SiH was confirmed by ^{1}H and ^{29}Si{^{1}H}-NMR spectra of the reaction mixture. Me_3SiH: ^{29}Si{^{1}H}-NMR (C_6D_6): δ −16.4. (**1a**: ^{29}Si{^{1}H}-NMR (C_6D_6): δ 14.6).

3.8. Reaction of **1a** in the presence of a catalytic amount of **4a** under 1 atm of H_2

A typical experimental procedure for the reaction described in Table 1 is as follows. In a 20 ml flask were placed **2a** (32.5 mg, 0.030 mmol) and naphthalene (30 mg) as an internal standard for GLC analysis under 1 atm of N_2. Anhydrous 1,2-dichloroethane (5 ml) was added, and then the mixture was magnetically stirred at r.t. for 5 min. After the N_2 atmosphere was replaced by 1 atm of H_2, **1a** (102 mg, 0.60 mmol) was added by syringe. The reaction mixture was stirred at 50 °C for 18 h in the flask attached with a balloon (3 l) containing 1 atm of H_2. The yield of **3a** was determined by GLC.

3.9. Reaction of trimethylsilyl enol ethers (**1a**–**1f** and **1g**) in the presence of a catalytic amount of **4a** under 1 atm of D_2

A typical experimental procedure for the reaction of **1a** with D_2 catalysed by **4a** (Table 2; run 1) is described below. In a 20 ml flask were placed **2a** (32.5 mg, 0.030 mmol) and naphthalene as an internal standard for GLC under 1 atm of N_2. Anhydrous 1,2-dichloroethane (5 ml) was added, and then the mixture was magnetically stirred at r.t. for 5 min. After the N_2 atmosphere of the reaction mixture was replaced by 1 atm of D_2, **1a** (102 mg, 0.60 mmol) was added by syringe. The reaction mixture was stirred at 50 °C for 48 h in the flask attached with a balloon (3 l) containing 1 atm of D_2. The formation of **3a**′ was observed by GLC (>95% yield). No other products than **3a**′ and Me_3SiD were observed by NMR, GLC and GC–MS. For the isolation of **3a**′, the solvent was removed under reduced pressure and the residue was extracted with Et_2O (10 ml). The Et_2O solution was distilled at atmosphere pressure to give a colorless liquid **3a**′ (b.p. 155 °C). The presence of D at the α-position of **3a**′ was confirmed by ^{1}H-NMR and GC–MS. ^{1}H-NMR ($CDCl_3$): δ 1.74 (m, 2H), 1.87 (m, 4H), 2.34 (br t, 3.05*H*; O=CC*H*$_2$CH$_2$). This result indicates the 95% deuterium content at the α-position of **3a**′. GC–MS *m*/*z* (relative intensity) 99 [M^+, 20], 98 [M^+-1, 2].

The presence of D at the α-position of **3d**′ (>95% GLC yield) was confirmed by ^{1}H-NMR and GC–MS. ^{1}H-NMR ($CDCl_3$): δ 2.62 (t, 2.00*H*; O=C–C*H*$_3$, $^1J_{HD}$ = 2.4 Hz), 7.47 (t, 2H), 7.68 (t, 2H), 7.96 (d, 1H). This result indicates the >99% deuterium content at the α-position of **3d**′. GC–MS *m*/*z* (relative intensity) 121 [M^+, 30], 120 [M^+-1, 10].

The presence of D at the α-position of **3e**′ (>95% GLC yield) was also confirmed by ^{1}H-NMR and GC–MS. ^{1}H-NMR ($CDCl_3$): δ 1.26 (s, 3H), 1.90 (m, 1H), 2.20 (m, 1H), 2.63 (m, 0.07*H*; O=C–C(CH$_3$)*H*–CH$_2$–), 2.99 (m, 2H), 7.22 (d, 1H), 7.29 (t, 1H), 7.44 (t, 1H), 8.03 (d, 1H). This result indicates the 93% deuterium content at the α-position of **3e**′. GC–MS *m*/*z* (relative intensity) 161 [M^+, 64], 160 [M^+-1, 9].

The presence of D at the α-position of **3f**′ (>95% GLC yield) was also confirmed by ^{1}H-NMR and GC–MS. ^{1}H-NMR ($CDCl_3$): δ 0.99 (s, 3H), 1.05 (s, 3H), 1.18 (s, 3H), 1.6–2.0 (m, 6H), 2.68 (m, 0.15*H*; O=CC*H*(CH$_2$)–CH$_2$–). This result indicates the 85% deuterium content at the α-position of **3f**′. GC–MS *m*/*z* (relative intensity) 141 [M^+, 22], 140 [M^+-1, 1].

3.10. Stoichiometric reaction of **4a**′ and **6a** under D_2 atmosphere (Scheme 5)

A solution of **6a** was prepared by the lithiation of **1a** (17.5 mg, 0.10 mmol) with MeLi (0.10 ml of 1.02 N diethyl ether solution, 0.10 mmol) in Et_2O (1 ml) at r.t. for 2 h under 1 atm of N_2. A solution of complex **4a**′, which was prepared from **2a** (110 mg, 0.10 mmol) in dry THF (10 ml) under 1 atm of D_2, was added to the above solution at 0 °C under 1 atm of D_2. The mixture was warmed up to r.t. and stirred at r.t. for 1 h under 1 atm of D_2. The GLC analysis based on naphthalene (10 mg) as an internal standard showed the formation of **3a**′ in >95% yield. For the isolation of **3a**′, the solvent was removed under reduced pressure and the residue was extracted with Et_2O (10 ml). The Et_2O solution was distilled at atmosphere pressure to give a colorless liquid **3a**′ (b.p. 155 °C). ^{1}H-NMR ($CDCl_3$): δ 1.74 (m, 2H), 1.87 (m, 4H), 2.34 (br t, 3.04*H*; O=C–C*H*$_2$–CH$_2$). This result indicates the 96% deuterium content at the α-position of **3a**′. GC–MS *m*/*z* (relative intensity) 99 [M^+, 22], 98 [M^+-1, 1]. On the other hand, the remained residue was recrystallized from CH_2Cl_2–Et_2O to give deuteride complex **5a**′ (79 mg, 0.085 mmol) in 85% yield. ^{31}P{^{1}H}-NMR (C_6D_6): δ 62.7 (s); ^{1}H-NMR (C_6D_6): δ −17.6 (m, 0.12*H*; Ru*H*), 2.04 (br, 4H), 2.65 (br, 4H), 6.87–7.70 (m, 40H). The ^{1}H-NMR spectrum of **5a**′ indicates the 88% deuterium content as deuteride of **5a**′.

3.11. Stoichiometric reaction of **5a** with Me_3SiOTf under H_2 atmosphere (Scheme 6)

In an NMR tube was dissolved **5a** (28.0 mg, 0.03 mmol) in anhydrous C_6D_6 (1.0 ml) under 1 atm of H_2. Then, Me_3SiOTf (9.0 mg, 0.04 mmol) was added by syringe. The $^{31}P\{^1H\}$-NMR spectrum of the reaction mixture showed that **4a** was formed in $>95\%$ yield. **4a**: $^{31}P\{^1H\}$-NMR (C_6D_6): δ 51.6 (s); ^1H-NMR (C_6D_6): δ -11.5 (br, 2H), 2.01 (br, 4H), 2.48 (br, 4H), 6.76–7.70 (m, 40H). On the other hand, the complete consumption of Me_3SiOTf ($^{29}Si\{^1H\}$-NMR δ 46.0) and the formation of Me_3SiH ($^{29}Si\{^1H\}$-NMR δ -16.4) was confirmed by ^1H and $^{29}Si\{^1H\}$-NMR spectra of the reaction mixture.

3.12. Asymmetric protonation of **6e** with **4e** (Scheme 8)

A solution of **6e** was prepared by lithiation of **1e** (25.0 mg, 0.10 mmol) with MeLi (0.10 ml of 1.02 N diethyl ether solution, 0.10 mmol) in anhydrous Et_2O (3 ml) at r.t. for 2 h under 1 atm of N_2. A solution of complex **4e** (150 mg, 0.10 mmol) in anhydrous CH_2Cl_2 (5 ml) was then added to the above solution of **6e** at -78 °C under 1 atm of H_2. The mixture was stirred at -78 °C for 4 h under 1 atm of H_2. Then the reaction mixture was gradually warmed up to r.t. and stirred at r.t. for 12 h. The GLC analysis showed the formation of **3e** in $>95\%$ yield. The solvent was removed under reduced pressure and the residue was extracted with Et_2O (5 ml × 3). The Et_2O solution was purified by TLC (SiO_2, hexane–EtOAc = 7/3 as an eluent) to afford **3e** as a pale yellow liquid (12 mg, 0.075 mmol) in 75% isolated yield. On the other hand, the remained residue was recrystallized from CH_2Cl_2–Et_2O to give **5e** as a yellow solid (95 mg, 0.069 mmol) in 69% yield. The absolute configuration of (*S*)-**3e** was determined by its optical rotation [33]. $[\alpha]^{18}D$ 30 (*c* 0.40, dioxane). The 75% ee value of (*S*)-**3e** was determined by GLC (carrier gas, helium; column temperature, 120 °C; split ratio, 20:1) on a cyclodextrin phase (Chiraldex GT-A, 30 m). The retention time of (*R*)-**3e**, 22.87 min (12.6%); the retention time of (*S*)-**3e**, 24.01 min (87.4%).

3.13. An X-ray crystallographic study

A single crystal of $[RuCl(N_2)((R, R)\text{-CHIRAPHOS})_2]PF_6$ (**4h**) obtained by anion exchange of **4f** with $NaPF_6$ was sealed in Pyrex glass capillaries under N_2 atmosphere and used for data collection. Diffraction data were collected on a Rigaku AFC-7R four-circle automated diffractometer at 20 °C. Orientation matrixes and unit cell parameters were determined by least-squares treatment of 25 reflections with $27.0 < 2\theta < 28.7°$ for **4h**. No significant decay was observed for three standard reflections monitored every 150 reflections during the data collection. Intensity data were corrected for Lorentz-polarization effects and for absorption (scans). Details of crystal and data collection parameters are summarized in Table 3. Structures solution and refinements were carried out by using the TEXSAN program package [34]. The positions of heavy atoms were determined by Patterson methods and subsequent Fourier syntheses (DIRDIF PATTY) [35]. All non-hydrogen atoms except for carbon atoms of phenyl rings of **4h** were refined anisotropically by full-matrix least-squares techniques (based on *F*). All hydrogen atoms were placed at the calculated positions and included in the final stage of refinement with fixed parameters. The ORTEP drawing of **4h** is shown in Fig. 1. Selected bond lengths and angles are listed in Table 4.

Table 3
Crystallographic data of $[RuCl(N_2)((R, R)\text{-CHIRAPHOS})_2]PF_6$ (**4h**)

Formula	$C_{56}H_{56}ClF_6N_2P_5Ru$
Formula weight	1162.45
Crystal system	Orthorhombic
Space group	$P2_12_12_1$(#19)
Crystal color	Yellow
a (Å)	15 107(3)
b (Å)	23.838(4)
c (Å)	14.838(3)
V (Å^3)	5343(1)
Z	4
D_{calc} (g cm^{-1})	1.445
F(0 0 0)	2384
μ_{calc} (cm^{-1})	5.53
No. of unique data	6778
No. of data used ($I > 3\sigma(I)$)	3251
No. of parameters refined	427
R	0.057
R_w	0.058
Goodness-of-fit indicator	1.45
Maximum residuals (e Å^{-3})	0.64

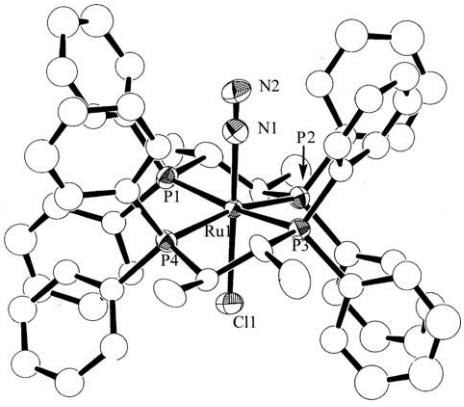


Fig. 1. ORTEP drawing of $[RuCl(N_2)((R, R)\text{-CHIRAPHOS})_2]PF_6$ (**4h**). PF_6^- anion and hydrogen atoms are omitted for clarity.

Table 4
Selected bond lengths and angles in $[RuCl(N_2)((R, R)\text{-CHIRAPHOS})_2]PF_6$ (**4h**)

Bond lengths (Å)			
Ru(1)–Cl(1)	2.399(3)	Ru(1)–P(4)	2.423(4)
Ru(1)–P(1)	2.427(4)	Ru(1)–N(1)	1.96(1)
Ru(1)–P(2)	2.421(4)	N(1)–N(2)	1.02(1)
Ru(1)–P(3)	2.421(4)		
Bond angles (°)			
Cl(1)–Ru(1)–P(1)	94.0(1)	P(2)–Ru(1)–P(3)	98.8(1)
Cl(1)–Ru(1)–P(2)	84.9(1)	P(2)–Ru(1)–P(4)	167.0(1)
Cl(1)–Ru(1)–P(3)	92.4(1)	P(3)–Ru(1)–P(4)	81.8(1)
Cl(1)–Ru(1)–P(4)	82.1(1)	P(1)–Ru(1)–N(1)	86.1(4)
Cl(1)–Ru(1)–N(1)	178.6(4)	P(2)–Ru(1)–N(1)	96.4(4)
P(1)–Ru(1)–P(2)	82.1(1)	P(3)–Ru(1)–N(1)	87.4(4)
P(1)–Ru(1)–P(3)	173.6(1)	P(4)–Ru(1)–N(1)	96.5(3)
P(1)–Ru(1)–P(4)	98.8(1)	Ru(1)–N(1)–N(2)	178.0(1)

4. Supplementary material

Crystallographic data for this structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 211323 (compound **4h**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2, 1EZ, UK (Fax: +44-1223-336-033, or e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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