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Chemoselective reduction of imines catalyzed by Ru(II) half-sandwich complexes: a mechanistic study

Noor U Din Reshi[(a)], Lakshay Kathuria[(a)], Ashoka G. Samuelson[(a)]*

Abstract

Ruthenium half-sandwich complexes ligated to in the reduction of N-benzylidineaniline using silyl hydrides as reductants has been examined. The chemoselective reduction of imines takes place under mild conditions to afford the corresponding amines in nearly quantitative yield. Mechanistic studies indicate that dissociation of the ancillary ligands generate the active catalyst in all the complexes studied, which is the same species generated by [Ru(*p*-cymene)$(Cl)_2]_2$ under the reaction conditions. This results in the formation of a single catalytic species irrespective of the starting half-sandwich complex. Detailed mechanistic studies involving trapping of intermediates, *in situ* studies using mass spectrometry and NMR spectroscopy were carried out using the active catalyst generated by [Ru(*p*-cymene)$(Cl)_2]_2$. The mechanism of the reaction is dependent on the number of the hydrogen atoms in the reducing silane. The reaction proceeds via Gade-Hoffman pathway or Zheng-Chan pathway when a dihydro or trihydrosilane is the reductant. However, the use of a monohydrosilane, leads to longer reaction times presumably due to a change in the reaction pathway.

Keywords:
Reduction
Hydrosilylation
Silyl hydrides
Ru(II) half-sandwich complexes
Imines

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Introduction

Amines are widely used in the synthesis of agrochemicals, natural products, pharmaceuticals, as well as biologically valuable fine chemicals.[1–4] They are present in different alkaloids, amino acids, and nucleotides. Several methodologies have been developed to synthesize amines. For example, the transition-metal catalyzed C-N bond formation especially using Pd-catalyzed Buchwald–Hartwig and Cu-catalyzed Ullman reactions has emerged as a useful method in amine synthesis.[5,6] The use of stoichiometric quantities of reductants such as lithium aluminium hydride and lithium borohydride for reducing imines, amides, cyanides, and nitroarenes is an alternative route to synthesize amines. However, these reductants are sensitive to air and moisture, incompatible to various functional groups and result in the formation of metal salt by-products.[7] Although the alkylation of ammonia using alkyl halides or alcohols is a simple method for preparation of amines, alkylation is difficult to control with alkyl iodides and bromides.[8]

The transition metal catalyzed hydrogenation, transfer hydrogenation, and reductive amination are also simple methods for amine synthesis. Although hydrogen is the ideal reducing agent, it is not suitable for many substrates due to high temperatures and high pressures required, and absence of chemoselectivity.[9–12] Reductive amination of carbonyl compounds using primary amines, via sequential condensation and catalytic reduction, constitutes a basic method for producing substituted amines, but it often requires drastic reaction conditions.[13–19] Transfer hydrogenation using silanes provides an attractive alternative method of reduction through hydrosilylation.

Hydrosilylation of imines has been performed under mild conditions in the presence of various metal catalysts; however, in comparison with the asymmetric hydrosilylation of prochiral ketones, the reaction of prochiral imines has been more challenging in achieving good enantioselectivity.[20] Most of the homogeneous transition metal catalysts for hydrosilylation of imines are based on platinum, rhodium, palladium, and titanium[21]. However, catalysts based on ruthenium, iridium, iron, zinc, nickel, palladium, and rhenium are also reported.[22] Catalysts based on Ru are widely used in reduction, more so in asymmetric hydrogenation and transfer hydrogenation of imines.[23–25] On the other hand, there are not many examples of ruthenium catalyzed hydrosilylation of imines.[26–30]

Dixneuf and co-workers reported $[RuCl_2(p\text{-cymene})]_2$ (**P**) as an efficient catalyst for the hydrosilylation of imines.[31] They obtained a variety of secondary amines in 69–97% yield from the corresponding imines using a catalyst loading of 1-2 mol%. The reaction was done in ethanol under ambient conditions at room temperature using PMHS as reductant which is an inexpensive by-product from the silicon industry. Furthermore, this strategy offered a very good chemoselectivity for reduction of the C=N bond and functional groups like -CN, $-NO_2$, C=O, and C=C were tolerated. Furthermore, the use of ethanol eliminated the need for a desilylation step which is usually involved in the hydrosilylation reactions to generate the product from the intermediate silylamine or silylether. This method was also applied successfully for hydrosilylation of difficult to reduce ketimines using 2 mol% of the catalyst at room temperature for 4–20 h.

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In this work, we examined the catalytic activity of ruthenium half sandwich complexes **1a**-**1g** and **2a**-**2e** (Figure 1) based on chiral 2-oxazolidinethiones and 2-thiozolidinethiones as ligands for their use in the hydrosilylation of imines. Initial mechanistic studies indicated that the catalytically active intermediate generated by these thione coordinated catalysts was similar to that generated by the achiral, Dixneuf catalyst, [Ru(*p*-cymene)(Cl)$_2$]$_2$. This resulted in the formation of a racemic amine when prochiral ketimines were reduced. The detailed reaction path adopted by [Ru(*p*-cymene)(Cl)$_2$]$_2$ to catalyse selective reduction of C=N bond was also studied.

Results and discussion

Synthesis

Our efforts to generate an enantioselective catalyst for the synthesis of amines led us to chiral half-sandwich ruthenium complexes shown below (see Fig. S1 for complete list). They could be readily made from chiral 2-oxazolidinethiones and 2-thiozolidinethiones which in turn were prepared using a literature procedure from natural amino acids and the cymene dimer [Ru(*p*-cymene)(Cl)$_2$]$_2$.[32]

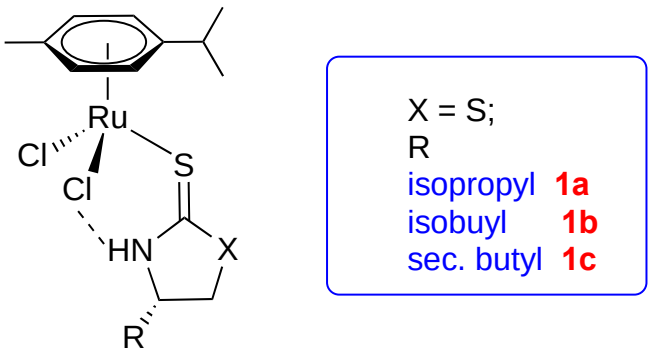
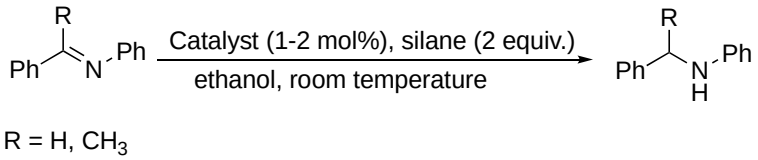


Figure 1. Ruthenium half sandwich complexes studied in this work (see also Fig. S1).

Reduction of imines

In order to test the catalytic activity of the complexes in the reduction of aldimines a test substrate N-benzylidineaniline was used. The optimization studies carried out using the representative complex **1a** showed that the best turn over frequency (TOF = 400 h^{-1}) was obtained using ethanol as the solvent. Moreover, the use of ethanol eliminated the need for the desilylation step to get amines.[31] Subsequently, all the complexes were tested using the optimized conditions. The complexes showed excellent catalytic activity under the optimized conditions and the catalytic activity was independent of the ancillary ligand resulting in the complete reduction of N-benzylidineaniline in 15 minutes (Scheme 1, R = H; Supporting Information Table S1).

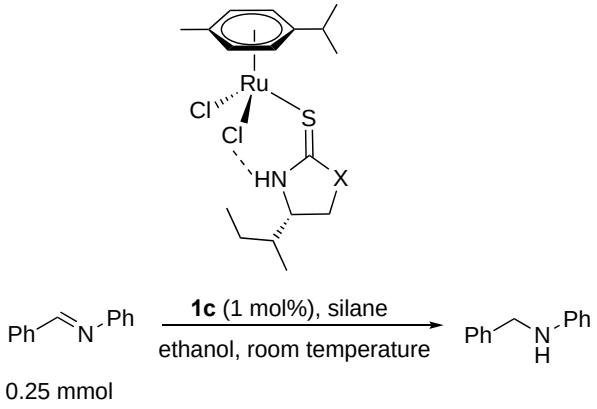
Scheme 1. Catalytic reduction of imines



R = H, CH_3

Further optimization of the reaction conditions involved different reagents and the optimum amounts of the reducing agent needed for the reaction. Interestingly, when 0.34 equiv. of imine was used, the reaction became significantly slower and the conversion decreased marginally to 90 % (Entry 3, Table 1). This decrease in the rate of the reaction could be due to a slower hydride transfer from intermediate sterically crowded hydride donors $(C_2H_5O)_nSiH_{3-n}Ph$ as compared to $PhSiH_3$. There was little effect on the conversion and the rate of reaction when a dihydrosilane (diphenylsilane) was used instead of phenylsilane (Entry 2, Table 1). However, the rate of the reaction decreased significantly when a monohydrosilane, triphenylsilane, was used (Entry 5, Table 1). The slower reactivity of monohyrdosilanes as compared to trihydrosilanes and dihydrosilanes could also be due to the operation of different mechanisms *vide infra*.

Table 1. Effect of varying the nature and amount of silane.



0.25 mmol

Entry	Silane	Silane (equiv.)	Time (min)	Conversion (%)[a]
1	$PhSiH_3$	2	15	100
2	Ph_2SiH_2	2	15	100
3	$PhSiH_3$	0.34	30	91
4	Ph_2SiH_2	0.5	30	92
5	Ph_3SiH	1	30	38
6	Ph_3SiH	1	60	91

[a] By ^1H NMR.

A primary reason for testing these chiral thione complexes as catalysts was to probe the asymmetric reduction of ketimines under the conditions used for reducing aldimines so effectively. Thus, all complexes afforded nearly quantitative yields in 2 h for the reduction of N,1-diphenylethan-1-imine using 2 mol% of any of these complexes (Scheme 1, R = CH_3; See Supporting Information Table S2). Surprisingly, the ee was zero with all the complexes. When the reaction was carried out at 0 ^oC, the reaction took 6 h to complete but the ee still remained zero (Table S2). Since the complexes showed very similar catalytic activity, only complex **1c** was tested as a catalyst for the reduction of various imines (See Supporting Information Table S4). However, no chirality induction was observed.

Although ruthenium(II) catalysts have been used for the hydrosilylation of alkenes[33], and ketones[26,34–36], this ruthenium(II) hydrosilylation of imines is very chemoselective similar to that observed by Dixneuf group which used the ruthenium dimer **P**. Thus, using this catalyst, acetophenone, and styrene could not be reduced. All observations regarding the effect of the nature of the substituent on the reactivity and chemoselectivity towards hydrosilylation are similar to that observed using $[(\eta 6\text{-cymene})RuCl_2]_2$ (**P**) as the catalyst strongly pointing to a common intermediate either **P** or one generated by **P** and the complexes studied by us.

Mechanistic studies

The extremely similar reactivity of Ru half-sandwich complexes of thiones and the complete absence of enantioselectivity led to a suspicion that these complexes generate a common intermediate under the reaction conditions. Confirmation of the common intermediate under the reaction conditions needed some more studies with the Ru half-sandwich complexes of thiones using NMR and mass spectrometry. The ^1H NMR spectrum of **1c** in $CDCl_3$ indicated the presence of a single compound. However, its ^1H NMR spectrum in CD_3OD showed the presence of $[(\eta^6\text{-cymene})RuCl_2]_2$ (**P**) , free ligand (**L**) and a new compound (**T**) and the ratio of **P**: **L**: **T** was estimated to be 1: 2: 4. The excellent catalytic activity of **P**, which does not contain the ancillary ligand, in the hydrosilylation of imines to the corresponding amines in ethanol is known.[31] As observed earlier, the catalytic reactivity pattern of Ru-thione complexes studied in this work matches that of **P**. Furthermore, the formation of **P** from **1c** in alcohols (deuterated methanol) points to its involvement in the reaction carried out in ethanol.

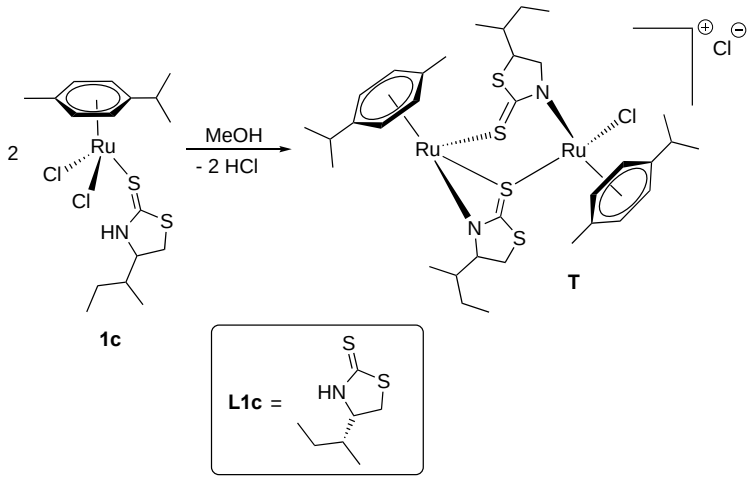
To test the hypothesis that **P** was the actual catalyst generated *in situ*, a test reaction was carried out using N-benzylidineaniline as the substrate and **1c (**1 mol%) as the catalyst in ethanol in the presence of added thione ligand (5 mol%) in ethanol before the addition of substrate and phenylsilane (2 equiv.). This led to a dramatic decrease in the catalytic activity and only 20 % of N-benzylidineaniline was reduced in 4 h. The suppression of the dissociation of the thione from ruthenium in complex **1c** by adding the ligand **L1c** decreases the amount of **P** and hence reduces the catalytic activity making the rate comparable to the corresponding complex.

The intermediate **T** is an unsymmetrical complex as indicated by the presence of four sets of peaks in the cymene region. The ratio of arene to ancillary ligand (**L**) in **T** is 1:1 as indicated

by the integration ratios of the corresponding peaks. It was impossible to elucidate the structure of the complex formed in methanol purely from the ^{1}H NMR spectrum although mass spectrometry was more helpful *vide infra*. However, Ru half-sandwich complexes of heterocyclic thiones are known to form dimers under similar conditions.[37–39] For example [Ru(η^6-cymene)Cl_2(2-mercaptobenzothiazole)] forms a dinuclear species in the mixture of methanol and water (10% methanol).[37] Taking a cue from these reports, the dinuclear species is assigned a plausible structure **T** (**Scheme 2)**. However, it is likely that **T** is a mere bystander as there was no chirality induction observed in the reduction of prochiral imines.

The positive-ion mode ESI-MS spectra of **1c** showed peaks at 410.0553 and 855.0792 that were assigned respectively to [**1c**-$(HCl_2)^-$]$^+$ and the dinuclear species [**T**-Cl^-]$^+$. The formation of **P** and the dissociation of the ancillary ligand from the Ru centre was indicated by the presence of peaks at 576.9561 and 294.0440 which were assigned respectively to **P**-**Cl**$^-$ and [(η^6-cym)Ru(OH)(CH_3CN)]$^+$. There was no indication of the loss of the arene ring in the ^{1}H NMR spectrum and ESI-MS spectrum. These observations were similar to those made with Ru-half-sandwich complexes of monodentate S coordinating ligands such as 2-mercaptobenzothiazole,[37] 2-mercapto-1-methylimidazole, and 4,5-diphenyl-2-mercaptoimidazole[39].

Scheme 2. Formation of dinuclear complex T from 1c in MeOH

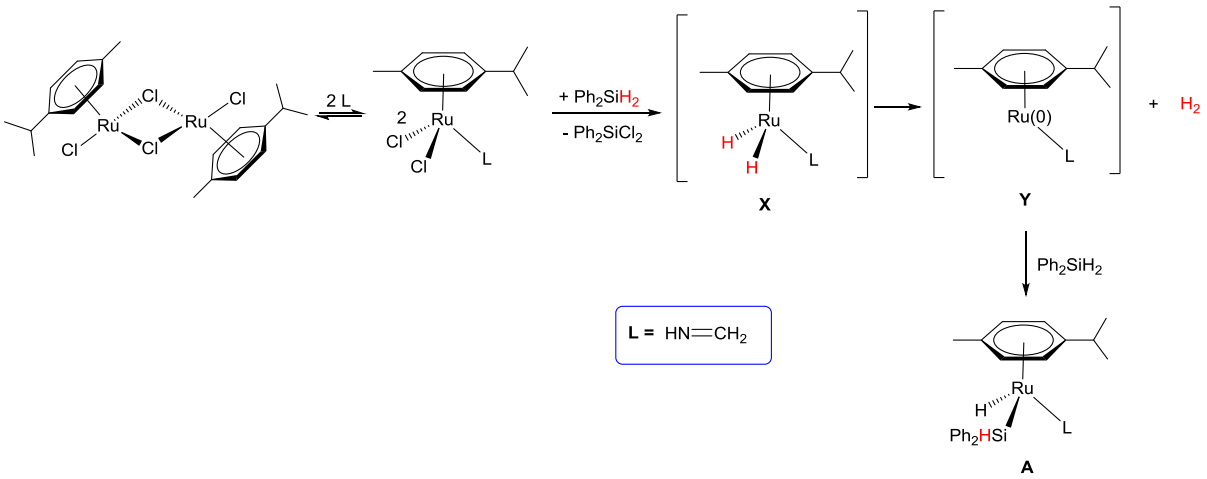


The achiral metal complex [(η^6 -cymene)$RuCl_2$]$_2$ (**P**) formed *in situ* was a better catalyst, all further mechanistic studies were carried out with **P**.

P (0.008 mmoles), trimethoxybenzene (0.75 mg, 0.0044 mmoles as internal standard) and $CDCl_3$ (0.4 mL) were loaded in an NMR tube. Diphenylsilane (0.026 mmoles) was added and the reaction was followed by ^{1}H NMR spectroscopy. A small amount of a gas was released immediately after the addition of diphenylsilane. The evolution of gas was also observed during the catalytic reactions on the addition of the silane to the solution containing the catalyst and substrate. Examination of the NMR spectrum recorded immediately after the addition of diphenylsialne showed a singlet at δ = 4.62 ppm, which can be assigned to dihydrogen. The release of dihydrogen can be rationalized by the reactions shown in **Scheme 3**. The reductive elimination of the dihydride species (Intermediate **X**) to furnish **Y** was

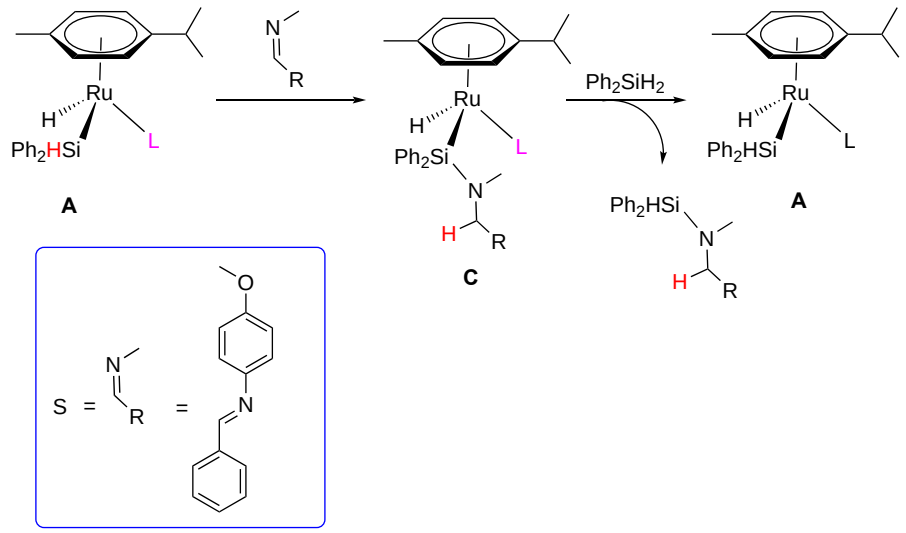
examined by DFT calculations using a slightly truncated model and found to be thermodynamically accessible (ΔG = 9.47 kcal/mol; L: $HN=CH_2$; see Supporting Information).

Scheme 3. Formation of A



A Ru-dihydride complex formed by the sigma bond metathesis can lose dihydrogen by the reductive elimination. The Ru(0) intermediate thus generated can oxidatively add a molecule of diphenylsilane to form species **A**. The presence of **A** was inferred from the ^{1}H NMR spectrum recorded immediately after the addition of diphenylsilane. The peaks at δ = -10.17 ppm and 5.74 ppm were assigned respectively to the Ru-H and Ru-SiH protons in **A**. Similar chemical shifts have been assigned to Ru-H and Ru-SiH protons.[33,40–45] The ^{1}H NMR spectrum also showed the presence of an unidentified Ru-cymene complex (**B**) besides **A**, and **P**. After 30 minutes, **P** and diphenylsilane completely disappeared from the ^{1}H NMR spectrum. The species **A** and **B** were present in the ratio **A**: **B** = 4.25:1 after 30 minutes and the total amount of **A** and **B** was estimated to be close to 95% of **P** used. After 30 minutes when dominant species present in the reaction mixture was **A**, the substrate imine **S** was added. (1 equiv. w.r.t **A**, 2.6 mg). After the addition of **S**, peak at δ = 5.74 ppm (SiH) started decreasing in intensity along with the peak at δ = 8.53 ppm (CH peak of imine). Concomitantly a peak appeared at δ = 4.37 ppm. The latter resonance might be assigned to the CH of the reduced amine. In 4 h, the peaks at δ = 5.74 and δ = 8.53 completely disappeared. The new species **C** was assigned the structure containing "Ru(H)(silylamine)" (**Scheme 4**). Interestingly, species **C** has a hydride peak at δ = -10.17 ppm. It indicated that the imine did not insert into the metal-hydride bond which is the path followed in the hydrosilylation of olefins catalyzed by the late transition metal complexes (Chalk-Harrod mechanism).[46]

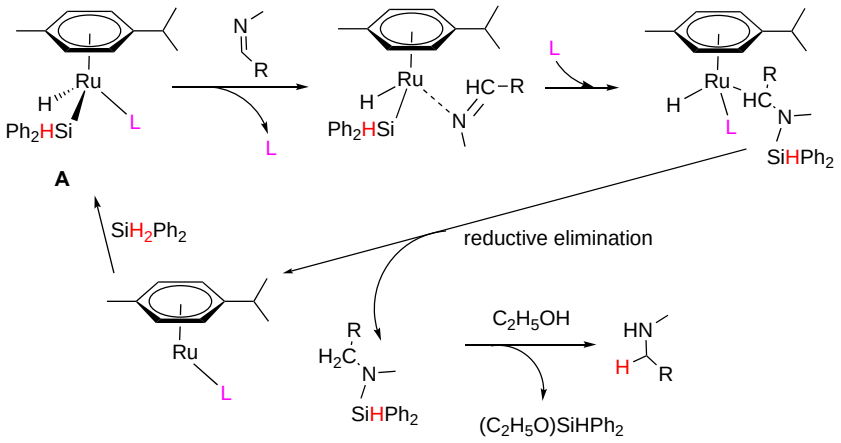
Scheme 4. Reaction of imine with A



When 5 µL of diphenylsilane was added to the NMR tube containing **C**, **A** was regenerated (**Scheme 4**). This can happen via the reductive elimination of silylamine from **C**, followed by the oxidative addition of diphenylsilane.

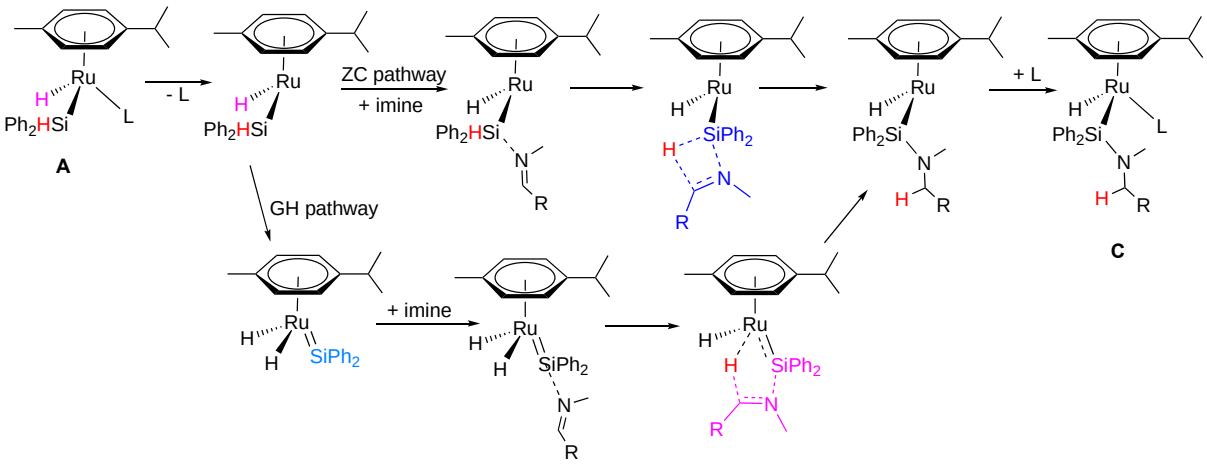
Scheme 5 shows one plausible mechanism for this reaction whereby the formation of **A** is followed by the insertion of the substrate into M−Si bond. The subsequent reductive elimination yields the respective silyl amine (Ojima mechanism).[47] Similar to many reports, the use of monohydrosilanes led to slower reaction rates relative to the use of dihydrosilanes or trihydrosilanes (**Table 1**).[48–53] The rate enhancement can be due to the effect of steric properties of silane. Tertiary silanes being sterically bulky is likely to transfer a hydride slower than a secondary silane which in turn should transfer hydride slower than a primary silane. However, the similar rates of primary and secondary silanes (Ph_3SiH < Ph_2SiH_2 = $PhSiH_3$) cannot be explained purely by steric factors. The Zheng-Chan mechanism (ZC mechanism) and the Gade-Hoffman silylene mechanism (GH mechanism) (**Scheme 6**) are not accessible to a tertiary silane.

Scheme 5. Ojima-like reaction mechanism



In the ZC pathway, the imine binds to the electrophilic Si center and the hydrogen atom on Si is transferred to the substrate via a four-membered transition state to form **C**. Whereas in GH pathway, the hydrogen atom on Si is transferred to ruthenium to form a dihydride silylene intermediate. The generation of silylene complexes by the double Si-H activation pathway has been proposed for many rhodium and ruthenium complexes during the hydrosilylation reactions.[50,54] After the substrate binds to the Si center, one of the hydride ligands is transferred to the substrate via a five-membered transition state to form C.

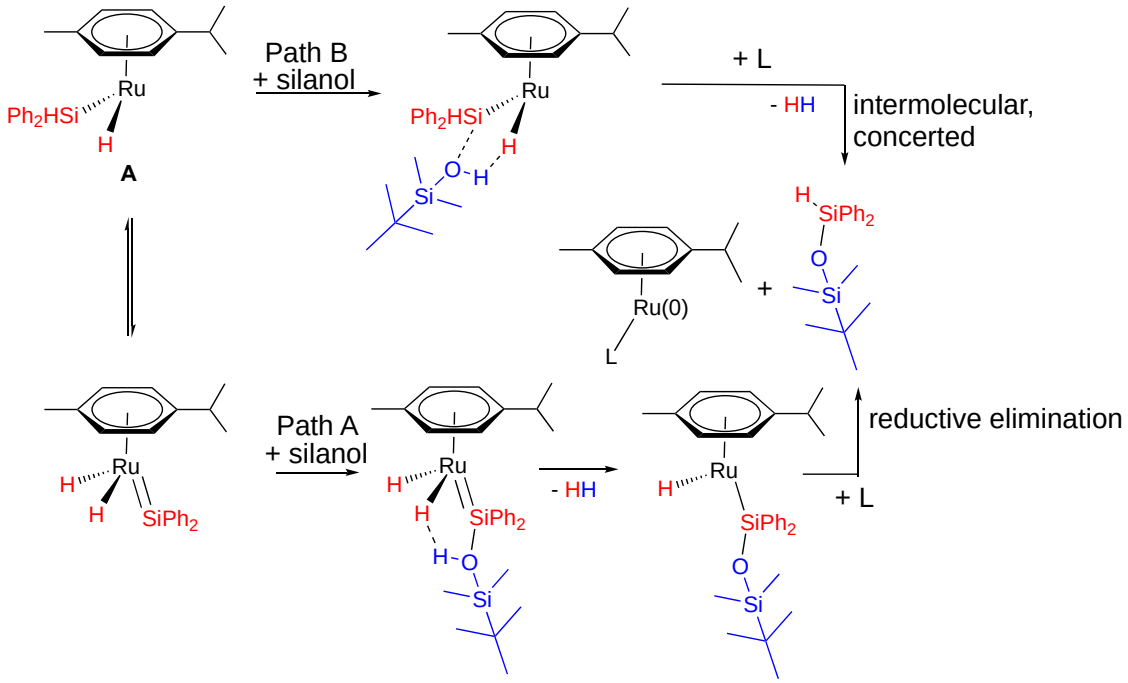
Scheme 6. Possible Zheng-Chan mechanism (top) and Gade-Hoffman mechanism (bottom) for the reaction



Since there was no direct experimental evidence for the formation of an intermediate silylene, a trapping experiment similar to that reported by Kuhn *et al.*[52,54] was performed to detect it. To 5 mg of **P** dissolved in 0.5 mL of $CDCl_3$, 25 µL (20.7 mg, 0.15 mmol) of *t*-$BuMe_2SiOH$ and 50 µL (50.1 mg, 0.27 mmole) of Ph_2SiH_2 were added. The reaction was monitored by ^1H NMR and ^{29}Si NMR spectroscopy. After 60 minutes, silanol completely disappeared from the ^1H NMR spectrum with the formation of *t*-$BuSiMe_2$-O-$SiHPh_2$. The disiloxane was

characterized by ^{1}H NMR and ^{29}Si NMR spectroscopy.[52] Disiloxane can be formed by the coordination of the silanol to the electrophilic Si centre of the Ru-silylene complex, which is followed by the loss of H_2 and reductive elimination (**Scheme 7**, **Path A**). Alternatively, disiloxane can be formed by the reaction of monohydride complex **A** with the silanol (**Scheme 7**, path B). In the latter case, a monohydrosilane is expected to show a similar reactivity as that of a dihydrosilane.[52] However, there was no reaction between the silanol and Ph_3SiH in presence of **P** (silanol: Ph_3SiH: **P**) up to 12 hr, hence the formation of disiloxane by the reaction of **A** with silanol (**Path B**) can be ruled out.

Scheme 7. Pathways for the formation of disiloxane

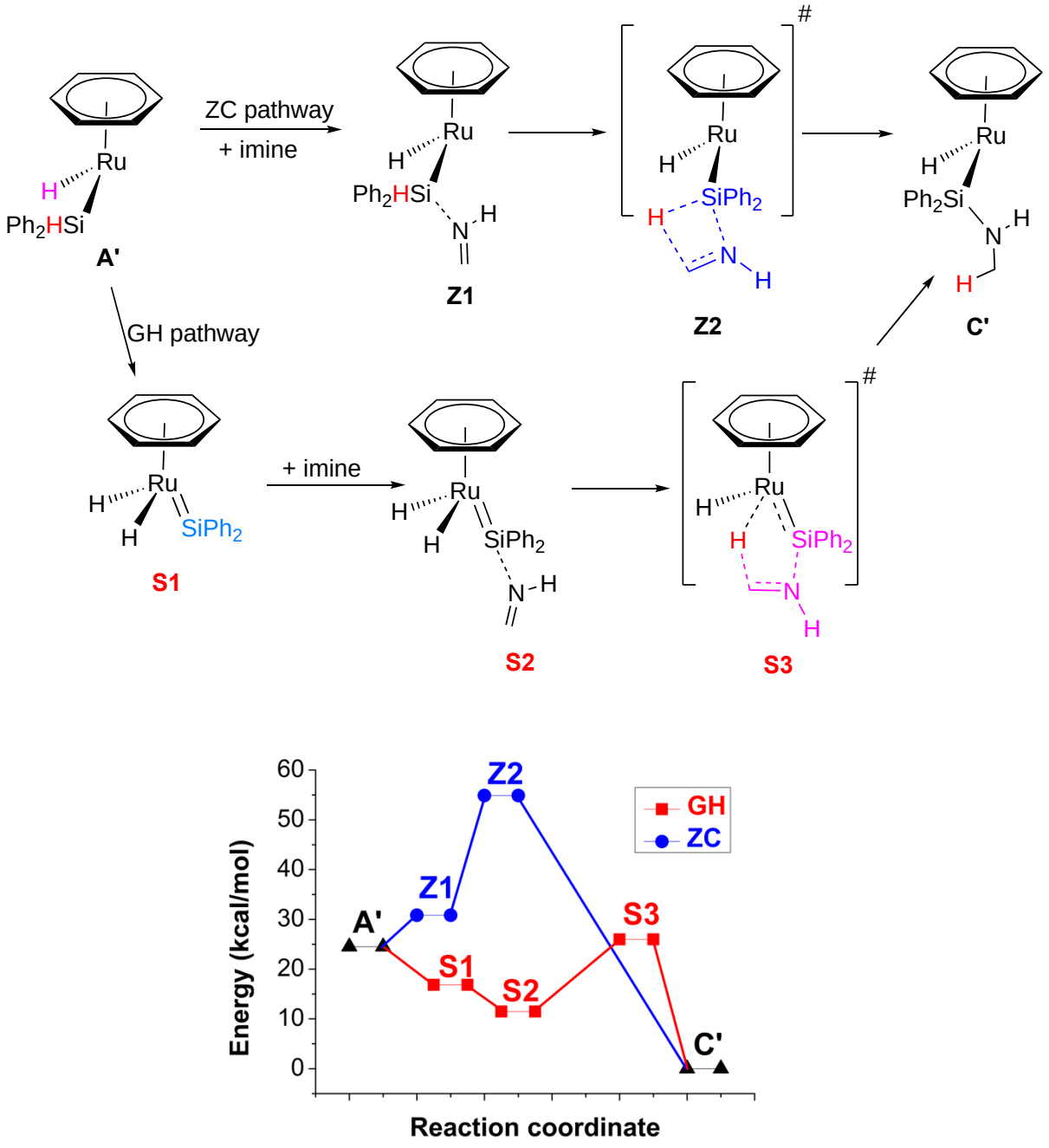


The formation of alkoxysilanes $Ph_{4-n}Si(OC_2H_5)_n$ which are reductively eliminated in the final step was also confirmed from the ^{1}H NMR spectra of crude catalytic reaction mixtures.

To further differentiate between ZC and GH mechanisms, the reaction was investigated using computational tools. The reaction intermediates, using a slightly truncated model of [Ru(p-cymene)H($SiHPh_2$)] which is probably the actual catalyst were examined using DFT calculations. Ph_2SiH_2 was used as the model silane and methanimine as the model imine. Key catalytic steps were calculated at the B3LYP/LanL2DZ(Ru)/6-311G (H,C,N,O,Si) level of theory. (**Scheme 8**). The imaginary frequency, which characterizes the transition state **Z2**, represents a vibrational motion, which leads to the breaking of Si-H bond and the formation of C-H bond. The corresponding transition state in the GH mechanism (**S3**) which is characterized by the imaginary frequency that leads to the transfer of hydride ligand to the unsaturated carbon was also located. Interestingly, **S3** is lower in energy relative to **Z2** by 28 kcal/mol. The hydride migration from silyl group to Ru in **A′** leads to the formation of silylene intermediate (**S1**) with a Ru=Si bond (2.24 Å) which is significantly shorter than Ru-

Si bond in **A′** (2.38 Å). Due to the very steep nature of the potential energy surface, all the efforts to locate the transition state connecting **S1** to **S2** failed. However, the large difference in the energies of **Z2** and **S3** is probably a decisive factor to favor the GH pathway.

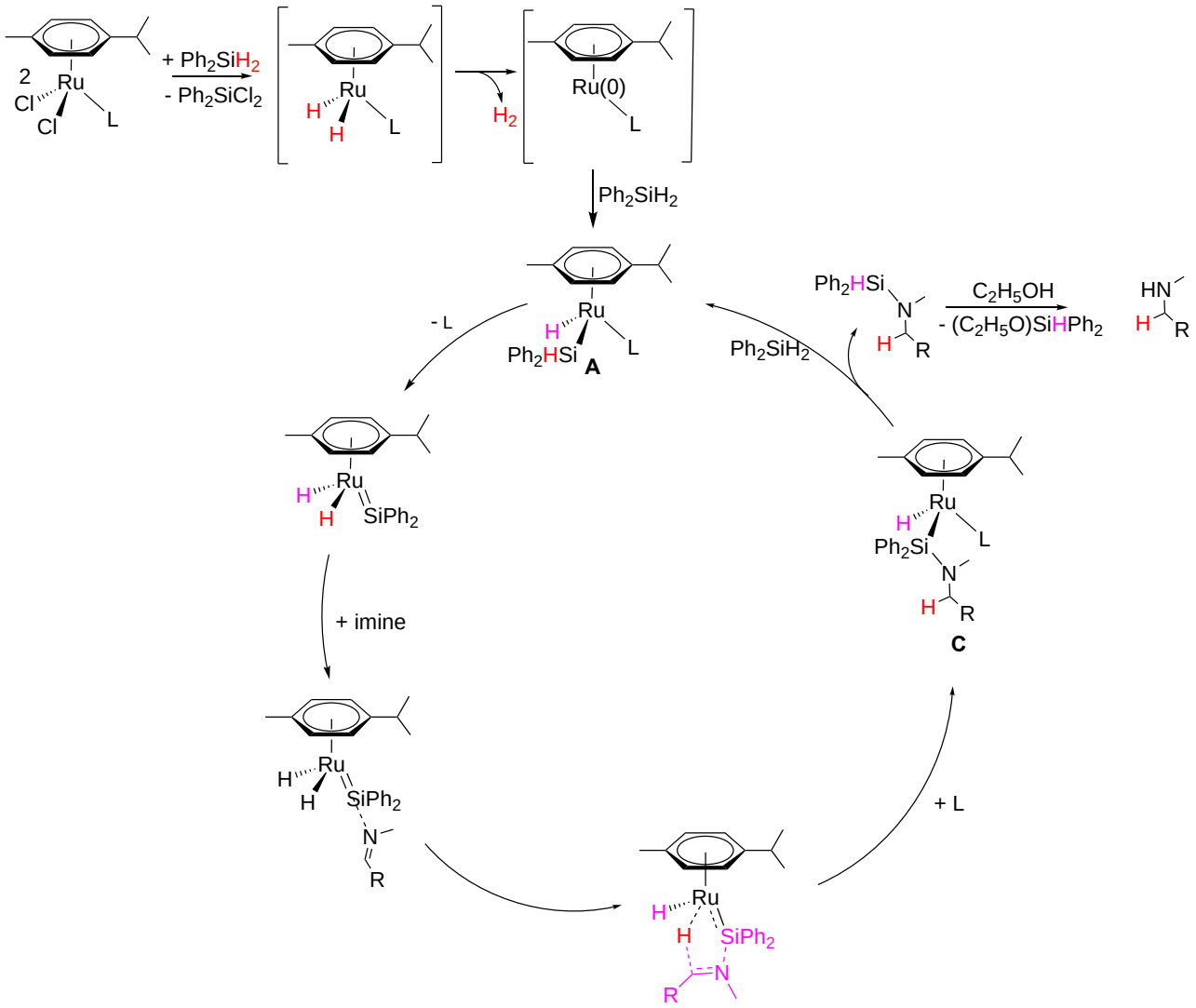
Scheme 8. Comparison of the computed free energy profiles (B3LYP/LanL2DZ(Ru)/6-311G (H,C,N,O,Si) of the ZC (blue) and GH pathway (red) using methanimine as substrate



Based on these observations this reaction proceeds through a silylene intermediate similar to the Gade-Hoffman mechanism (**Scheme 9**).[50,52] In the case of monohydrosilanes, such as

triphenylsilane where ZC and GH mechanisms are not accessible, the reaction can take place via a slower pathway (Ojima mechanism).

Scheme 9. Proposed mechanism



Conclusions

All half-sandwich complexes proved equally good in the chemoselective reduction of aldimines and ketimines. ^{1}H NMR spectroscopy suggested that the common catalyst generated by Ru-thione complexes is the same species generated by [Ru(*p*-cymene)(Cl)$_2$]$_2$. This helps one to understand the observations such as the drastic decrease in the catalytic activity by adding excess ligand, no enantiomeric excess in the reduction of prochiral substrates, and similar reactivity pattern of different Ru half-sandwich complexes to that of **P**. The rate enhancement observed with di and trihydrosilanes along with the results of various stoichiometric reactions can be explained by both ZC and GH pathways. Furthermore, the trapping experiment gave an indirect evidence for the formation of a silylene intermediate. However, ZC pathway could not be completely ruled out based on DFT calculations. In case

of a monohydrosilanes such as triphenylsilane where ZC and GH mechanisms are not accessible, the reaction can take place via a slower pathway presumably like the mechanism proposed by Ojima.

Experimental section

General remarks

All catalytic reactions and manipulations were carried under ambient conditions. HPLC grade ethanol was used. Analytical thin layer chromatography (TLC) was performed using precoated silica gel plates supplied by Merck (60 F254). After elution, the plates were visualized using UV radiation (254 nm). Preparative TLC was done using ChemLabs Silica gel GF 254. The NMR spectra were recorded on a Bruker AMX 400 spectrometer that operates at 400 MHz for ^{1}H and 100 MHz for ^{13}C NMR. Chemical shifts for ^{1}H NMR spectra are reported in ppm relative to the chloroform signal at δ 7.26 as a singlet.

Synthesis

Ru half-sandwich complexes of chiral 2-oxazolidinethiones and 2-thiozolidinethiones were prepared according to a literature procedure.[32] Aldimines were prepared similar to the reported procedure, by refluxing an equivalent mixture of amine and aldehyde in dry ethanol in the presence of a catalytic amount of acetic acid and molecular sieves.[55] Ketimines were prepared by refluxing an equivalent mixture of amine and ketone in dry xylene in presence of catalytic amount of *p*-tolunesulphonic acid and molecular sieves.[56] Both aldimines and ketimines were purified by recrystallization.

General procedure for reduction

The catalyst (0.0025 mmol) was dissolved in 5 mL of spectroscopic grade ethanol. 0.25 mmol of imine was added to this solution. This was followed by the addition of $PhSiH_3$ (0.5 mmol). Then the reaction mixture was stirred at room temperature. Aliquots from the reaction mixture were withdrawn at specified intervals. The volatiles were removed using a rotary evaporator. Then ^{1}HNMR spectra of the residues were recorded in $CDCl_3$. Conversion was calculated from the intensity ratios of the peaks arising from the reactant and product. The amines were purified by preparative thin layer chromatography using a mixture of hexane/ethyl acetate (2-5%) as the eluent. The enantiomeric excess was determined using optical activity measurements.

Characterization of A

^{1}H NMR ($CDCl_3$, 400 MHz): δ = -10.17 (1H, s, hydride), 1.41 (3H, d, J = 6.8 Hz, isopropyl), 1.44 (3H, d, J = 6.8 Hz, isopropyl), 2.29 (3H, s, methyl), 2.99 (1H, m, isopropyl), 4.85 (1H, d, J = 5.9 Hz, cymene), 5.30(1H, d, J = 5.9 Hz cymene), 5.54(1H, d, J=5.9 Hz, cymene),5.64 (1H,d,J=5.9 Hz, cymene), 5.74 (1H, s, SiH), 7-8 (10H, $SiHPh_2$).

Characterization of C

^{1}H NMR ($CDCl_3$, 400 MHz): δ = -10.17 (1H, s, hydride), 1.40 (3H, d, J = 7 Hz, isopropyl), 1.44 (3H, d, J = 7 Hz, isopropyl), 2.29 (3H, s, methyl), 2.98 (1H, m, isopropyl), 3.72 (3H, s, OCH_3), 4.84 (1H, d, J = 5.9 Hz, cymene), 5.30(1H, d, J = 5.9 Hz cymene), 5.54(1H, d, J=5.9 Hz, cymene),5.64 (1H,d,J=5.9 Hz, cymene), 7-8 (10H, $SiHPh_2$), 6-8 (10H Ph_2 of bound amine).

Characterization of *t*-BuSiMe$_2$-O-SiHPh$_2$[52]

^{1}H NMR (CD_2Cl_2, 400 MHz) δ (ppm) = 0.08 (s, 6H, $SiCH_3$), 0.90 (s, 9H, CCH_3), 5.53 (s, 1H, SiH), 7.36 (m, 6H, Ar-H),7.59 (m, 4H, Ar-H); ^{29}Si NMR (CD_2Cl_2, 79 MHz) δ = -22.5 (s, Ph_2HSiO), 15.0 (s, t-$BuMe_2SiO$).

Computational details

Geometry optimizations were carried out using the suite of programs available in the Gaussian09 (G09) package[57] using the DFT B3LYP method.[58] All optimizations and vibrational frequency calculations were performed in the gas phase without symmetry and geometry constraints. The 6–311G[59,60] basis set was used for main group elements and hydrogen. The LANL2DZ basis set with effective core potential (ECP) was used for Ru.[61–63] Transition states were located using the Berny algorithm.[64,65] The number of imaginary frequencies (N_{imag}) obtained for the optimized structures was used to characterize the geometry minima (N_{imag} = 0) and transition states (N_{imag} = 1). Intrinsic reaction coordinate calculations were carried out to confirm that the transition state structures connect the reactants and the respective products.[66]

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Conflict of Interest

There are no conflicts to declare

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