

Scope and Mechanistic Studies of Catalytic Hydrosilylation with a High-Valent Nitridoruthenium(VI)

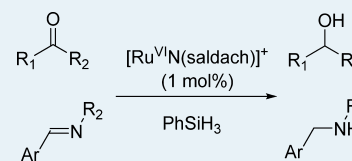
Srinivas Abbina, Shi Bian, Casey Oian, and Guodong Du*

Department of Chemistry, University of North Dakota, 151 Cornell Street Stop 9024, Grand Forks, North Dakota 58202, United States

Supporting Information

ABSTRACT: Hydrosilylation catalyzed by a high-valent nitridoruthenium(VI) compound, $[\text{RuN}(\text{saldach})(\text{CH}_3\text{OH})]^+[\text{ClO}_4]^-$ (**1**, where saldach is the dianion of racemic *N,N'*-cyclohexan-diyl-bis(salicylideneimine)) is described. Using phenylsilane as reductant, a variety of unsaturated organic substrates, including aldehydes, ketones, and imines, are effectively reduced to alcohols and amines, respectively, accompanied by the redistribution of PhSiH_3 at silicon. Mechanistic studies indicate that the catalysis proceeds via silane activation rather than carbonyl activation, and the silane is likely activated via multiple pathways, including a radical-based pathway.

KEYWORDS: hydrosilylation, ruthenium nitrido, aldehydes and ketones, imines, catalytic reduction, silane activation, radical mechanism



INTRODUCTION

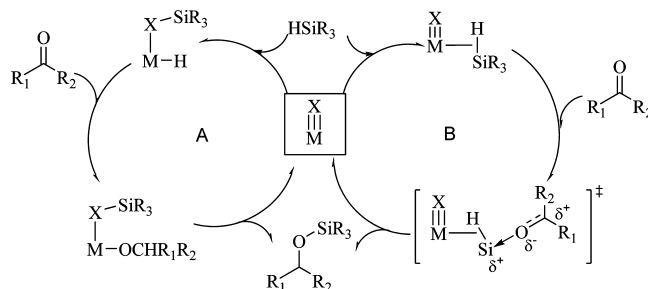
Reduction of unsaturated organic compounds is an important transformation in academic and industrial research. Particularly, catalytic hydrosilylation of carbonyl compounds, the addition of a Si–H bond across a C=O double bond, has been extensively studied.¹ Because of the mild nature and ease of handling of hydrosilanes, they are often used as a convenient alternative to hydrogenation,² especially in asymmetric synthesis.³ The field has been traditionally dominated by catalysts based on low-valent precious metals platinum, rhodium, and iridium.^{2,3} Oxidative addition of Si–H to low-oxidation-state, late transition metals is believed to be a key step in the reaction.⁴

Therefore, it is noteworthy that a high-valent *cis*-dioxo rhenium(V) compound, $\text{Re}(\text{O})_2\text{I}(\text{PPh}_3)_2$, was found to effectively catalyze the hydrosilylation of aldehydes and ketones.⁵ This represents a new reactivity mode for high-valent transition metals in reduction catalysis⁶ because such complexes are typically involved in catalytic oxidation and oxygen atom transfer reactions.^{7–9} Significant progress has been made in the use of high-valent complexes in catalytic reductions and the understanding of their reaction mechanisms.^{10,11} A number of catalysts have been identified, mostly high-valent rhenium (V, VII)^{12,13} and molybdenum (IV, VI)^{14–16} complexes bearing terminal oxo or imido groups. They have proved effective in a variety of reduction reactions, such as hydrosilylation of ketones and aldehydes^{17,18} and reduction of imines,¹⁹ esters,²⁰ amides,²¹ azides,²² nitriles,²³ nitro compounds,²⁴ and sulf-oxides.²⁵ Asymmetric reduction of ketones and imines has been achieved with good to excellent enantioselectivity.^{26,27} Furthermore, other sigma bonds, such as H–H and B–H, can be activated by high-valent transition metals, as hydrogenation of alkynes,^{28,29} and reduction with boranes^{30–33} have demonstrated. Because of their high oxidation state, these complexes are usually moisture- and air-stable, allowing the

reaction to be carried out conveniently on the benchtop under air. In addition to the synthetic utility of these reactions, the high-valent transition metal catalysts also provide a new paradigm in which important mechanistic questions can be addressed as related to σ -bond activation.^{34,35}

Several mechanisms have been proposed for the high-valent, transition-metal-catalyzed hydrosilylation. For the *cis*-dioxo $\text{ReO}_2\text{I}(\text{PPh}_3)_2$ catalyst, the Si–H bond adds across one of the two $\text{Re}=\text{O}$ bonds to afford a siloxy rhenium hydride, followed by carbonyl insertion and silylether elimination (Scheme 1,

Scheme 1. Proposed Mechanism of Oxo and Imido Re- and Mo-Catalyzed Hydrosilylation



path A).^{36,37} Depending on the substrates, the resting state of the catalyst may vary. Related MoO_2Cl_2 catalyst likely follows a similar mechanism.^{38,39} However, this unconventional pathway seems to be unique to catalysts bearing *cis*-dioxo groups, as Si–H addition to $\text{Re}=\text{O}$ is not observed for the monooxorhenium

Received: December 31, 2012

Revised: February 14, 2013

Published: February 21, 2013

catalysts, such as $\text{ReOCl}_3(\text{PPh}_3)_2$.⁴⁰ In these systems, silane activation is believed to proceed via a η^2 -silane σ -adduct, followed by heterolytic cleavage at the electrophilic rhenium center (Scheme 1, path B). The rhenium hydride formation step may not be needed if the reaction proceeds in a more concerted manner,^{41,42} resembling the situation in catalytic silane alcoholysis reactions.⁴³ As in the ionic hydrogenation mechanism, a carbonyl coordination step is not required.⁴⁴ Indeed, a nonhydride ionic hydrogenation mechanism is supported by a computational study.⁴⁵ On the ground of a stoichiometric labeling experiment, an alternative mechanism, in which the metal center simply activates the carbonyls as a Lewis acid, is suggested for imidomolybdenum catalysts, as well as the rhenium catalysts mentioned above.^{46,47} In another study, the expected Si–O elimination (the last step of path A in Scheme 1) from the intermediate is not observed.⁴⁸ The disparity in mechanistic understanding is perhaps not too surprising because hydrosilylation is often complicated and a universal mechanism is not expected for different catalysts and substrates. In any event, the roles of the multiply bonded terminal ligands and hydrides in silane activation remain unclear in catalysis.

Given the utility of this novel type of catalysts in reductions, we became interested in related transition metal compounds. We have recently communicated the application of a cationic nitride Ru(VI) complex, $[\text{Ru}(\text{VI})\text{N}(\text{saldach})(\text{MeOH})^+][\text{ClO}_4^-]$ (**1**, where saldach is the dianion of racemic *N,N'*-cyclohexan-diyl-bis(salicylideneimine)), Figure 1),⁴⁹ which is

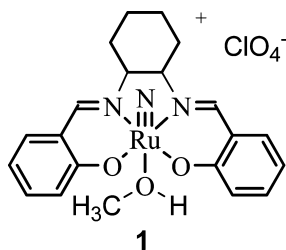


Figure 1. RuN catalyst.

isoelectronic with rhenium (V) and Mo(IV) with a d^2 electron configuration, in catalytic hydrosilylation of aldehydes and ketones.⁵⁰ Herein, we describe a detailed study of the $1/\text{PhSiH}_3$ system in catalytic reduction of various carbonyl compounds and imines. Furthermore, we present evidence that more than one pathway, including a radical pathway, is at play for the current hydrosilylation.

RESULTS AND DISCUSSION

As mentioned previously, high-valent transition metal catalysts can effectively reduce a variety of unsaturated organic substrates. We have shown that $\text{RuN}(\text{saldach})^+$ is an effective catalyst for the reduction of a few ketones and aldehydes by primary silane.⁵⁰ To extend the scope of the reaction, we have examined a number of different substrates, with particular attention on the hydrosilylation of carbonyl and imine compounds.

Reduction of Carbonyl Compounds. Using the standard conditions (~ 0.5 mmol substrate, 1.5 equiv of PhSiH_3 , 1 mol % catalyst **1**, ~ 120 °C in benzene), we carried out the hydrosilylation of a diverse set of representative aliphatic and aryl carbonyl compounds, including acyclic, cyclic, aryl, acyclic conjugated enone, and cyclic conjugated enone, etc.⁵¹ The

selected results are summarized in Table 1. As noted before, reduction of aldehydes was efficient, typically complete within 2 h, except for *p*-nitrobenzaldehyde, which is surprisingly sluggish (Table 1, entry 3). Substituents such as halo, hydroxyl, and nitro groups are tolerated, although there is evidence that the nitro group may be reduced further after the carbonyl reduction. The α,β -unsaturated cinnamaldehyde underwent 1,2-addition reaction of silane, leading to the corresponding alcohol in 74% yield (entry 6), and 1,4 addition product is not observed.

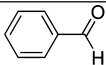
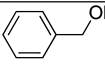
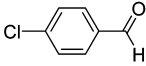
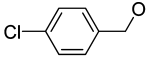
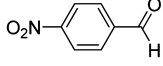
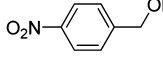
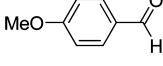
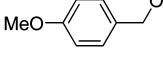
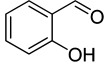
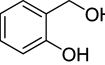
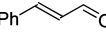
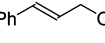
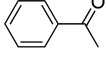
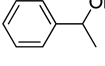
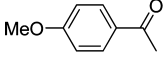
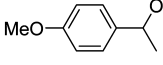
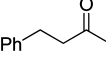
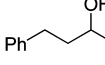
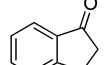
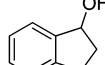
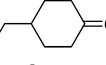
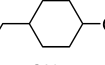
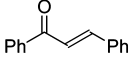
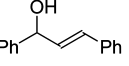
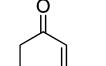
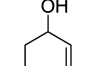
In comparison with aldehydes, the reduction of ketones was relatively slow, taking ~ 20 h to completion. In most of the cases, the corresponding alcohols are successfully isolated by column chromatography in good yields. Sometimes, deoxygenation of carbonyl to corresponding alkyl compounds can be observed. For example, 4-ethyl-anisole is isolated in 27% yield along with the desired alcohol in the reduction of 4-methoxyacetophenone (entry 8). On the other hand, α,β -unsaturated enones seem to be challenging substrates in the reaction. The acyclic *trans*-chalcone gave rise to a complex mixture, from which only $\sim 16\%$ expected 1,2-reduction product is isolated (entry 12). Other isolated products include 16% 1,4 reduction product and the deoxygenation product (18%). In the case of a cyclic enone, 3-methyl, 2-cyclohexenone, no 1,4-addition product was observed, and the desired unsaturated alcohol was identified by both GC/MS data and ^1H NMR spectroscopy, although the conversion is low (entry 13).

Reduction of Imines. Synthesis of amines from imines is an important transformation in pharmaceutical and agricultural chemistry that can be achieved with a stoichiometric reducing agent or catalytic hydrogenation.⁵² Alternatively, this can be done via catalytic hydrosilylation and a number of high-valent Re- and Mo-based systems have been shown to effect the reduction of imines. To expand the substrate scope of the $\text{Ru}^{\text{VI}}\text{N}-\text{PhSiH}_3$ system, we examined a number of imines under the standard reaction conditions employed for carbonyl compounds. The results are summarized in Table 2.

It is evident that the $\text{C}=\text{N}$ double bonds in imine react readily under these conditions, leading to the formation of the corresponding amines upon workup. The reactivity is comparable with that of ketones and slower than aldehydes. The imines derived from anilines are generally slower than imines derived from alkyl amines (Table 2, entries 1–4 vs 5–6). As expected, a similar level of functional group tolerance is observed. The reduction of imine derived from isopropyl amine, $\text{PhCH}=\text{N}^i\text{Pr}$, seems to stop after $\sim 33\%$ conversion, and prolonged reaction time failed to improve the conversion (entry 3). Similar reactivity was seen with an imine derived from 2,6-dimethyl aniline (entry 6). Apparently, the steric bulk near the imino nitrogen plays a significant role in the reduction reaction.

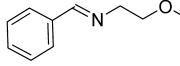
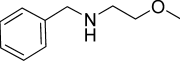
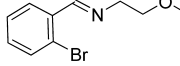
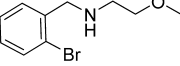
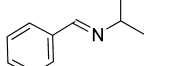
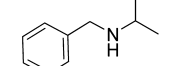
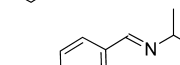
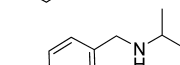
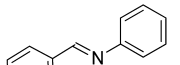
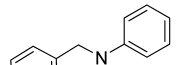
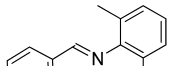
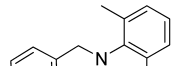
Product Profile. Although the desired reduction products, alcohols and amines, can generally be isolated in good yields, it has been noted that the initial reaction products are rather complex. For example, in the crude reaction mixture of an imine and PhSiH_3 , various products can be detected by GC/MS (Scheme 2). In the case of aldehydes and ketones, mono-, di-, and trialkoxy silanes are observed among the products, with the dialkoxysilane being dominant. The preference for dialkoxysilane formation has been observed in other catalytic hydrosilylations.^{15,53,54} This suggests that $\text{PhSiH}_2(\text{OR})$ is more active than PhSiH_3 in the reaction. Further reduction to

Table 1. Hydrosilylation of Carbonyl Compounds Catalyzed by RuN^a

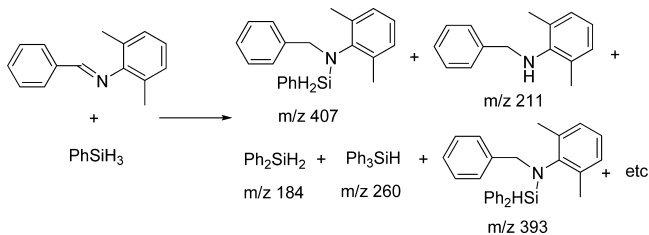
Entry	Substrate	Product	Time	Conversion ^b	% Yield ^c
1			40 min	100	73
2			2 h	100	76
3			26 h	100	78
4			1.5 h	100	73
5			2 h	100	84
6			1.5 h	100	74
7			18 h	100	67
8			13 h	100	36 ^d
9			20 h	100	86
10			8 h	83	65
11			20 h	100	89
12			20 h	100	16 ^e
13			20 h	54	-

^aReaction conditions: 0.3–0.8 mmol substrate, 1.5 equiv of PhSiH₃, and catalyst **1** (1 mol %) in heated toluene or benzene (~120 °C). ^bBased on NMR integration. ^cIsolated yields. ^d*p*-Ethylanisole was isolated in 27% yield. ^eOther products isolated include 1, 3-diphenylpropan-1-ol (15%) and 1, 3-diphenylpropan-1-one (16%).

Table 2. Hydrosilylation of Imines Catalyzed by RuN^a

Entry	Substrate	Product	Time	Conversion	% Yield ^b
1			12 h	100	85
2			24 h	100	58
3			24 h 48 h	33 33	- -
4			18 h	65	60
5			18 h 46 h	50 97	- 85
6			24 h 72 h	40 63	- 60

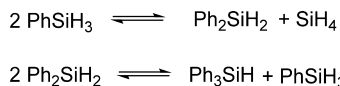
^aReaction conditions: 0.4–0.8 mmol imine, 1.5 equiv of PhSiH₃, and catalyst **1** (1 mol %) in heated toluene or benzene. ^bIsolated yields

Scheme 2. Products in Hydrosilylation of an Imine^a

^aThe top two species are the major products.

deoxygenation products is typically noted for ketones when longer reaction time is needed for complete conversion. After acidic workup, however, the majority of the species isolated are the corresponding alcohols or amines. In comparison, the Re^VO-catalyzed hydrosilylation of acetophenone was accompanied mostly by the formation of ethylbenzene and *dl*, *meso*-di(1-phenyl ethyl)ethers.¹³ The different product profiles suggest that these catalysts may have different features in the reaction.

Redistribution at Silicon. Very notable is the presence of silane redistribution products, mostly Ph₂SiH₂, with a small amount of Ph₃SiH (Scheme 3). SiH₄, the other possible

Scheme 3. Redistribution of PhSiH₃

redistribution product, has not been detected, supposedly because of its high volatility and reactivity. Sometimes, hydrosilylation products derived from Ph₂SiH₂ can be detected (see Scheme 2). In the literature, silane redistribution reactions have been observed in the presence of low-valent, late transition metal complexes, such as Ru, Rh,⁵⁵ Ir,⁵⁶ or others.⁵⁷ However, in high-valent transition-metal-catalyzed hydrosilylations with PhSiH₃, silane redistribution has been rarely reported.^{14,15,21} To further probe this reactivity with the present ruthenium catalyst, reaction in the absence of carbonyl substrate was carried out under similar conditions with a catalytic amount of **1**. The conversion of PhSiH₃ reached a plateau of ~25% after 24 h. Among the products, Ph₂SiH₂ can be easily identified by both ¹H NMR (5.1 ppm) and GC/MS (*m/z* 184; *t_R* = 13.55 min). A small amount of Ph₃SiH can be detected by GC/MS (*m/z* 260) in the crude mixture, along with silane dehydrocoupling product PhH₂SiSiH₂Ph (*m/z* 214). It is unclear how the redistribution occurs. One obvious choice is catalysis by low-valent Ru resulting from reduction by PhSiH₃; however, the observation that the redistribution stops before completion seems to suggest that high-valent Ru is important in the present redistribution.

Mechanistic Consideration. To probe the mode of activation with the RuN catalyst, stoichiometric reactions of **1** and substrates were studied. Treatment of **1** with a carbonyl substrate, PhCHO, showed no observable change in the NMR or UV-vis spectra. On the other hand, reaction between **1** and PhSiH₃ in CH₃CN is indicated by the facile color change from reddish brown to green. Although the reaction product was not isolated, ESI-MS analysis revealed predominantly a peak at *m/z* 422, in agreement with a Ru^{III}(saldach)⁺ species.⁵⁸ These observations do not support a Lewis acid-catalyzed carbonyl

activation pathway;⁴⁶ rather, a silane activation pathway is more likely, although it should be noted that the observation of Ru(VI) reduction by silane is not necessarily related to a silane activation pathway, and the possibility of Lewis acid catalysis cannot be completely ruled out.

The question is then how silane is activated in the reaction, as diverse pathways have been proposed for high-valent catalysts.^{10,11} Compared with isoelectronic Re(V) and Mo(IV), Ru(VI) is certainly more oxidizing, because complex **1** can abstract hydrogen from relatively weak C–H bonds via a hydrogen atom transfer mechanism.⁵⁹ It is thus conceivable that RuN abstracts hydrogen from silane in the initial step, generating a silyl radical, PhH₂Si•. This could explain the formation of disilane via combination of two silyl radicals. The radical pathway in catalytic hydrosilylation has been indicated for a titanium(IV)/silane system via a single electron transfer process.⁶⁰ In a high-valent-Mo-catalyzed hydrosilylation, radical mechanism could provide a feasible pathway on the basis of the computational studies.⁶¹

To investigate the possibility of radical involvement, the catalytic reduction of PhCHO (1 equiv) by PhSiH₃ (1.5 equiv) was carried out in the presence of 1 equiv of a silyl radical scavenger, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO).⁶² The hydrosilylation reaction slowed down, as shown in Figure 2, but still was able to finish. At the end of the reaction, 2,2,6,6-

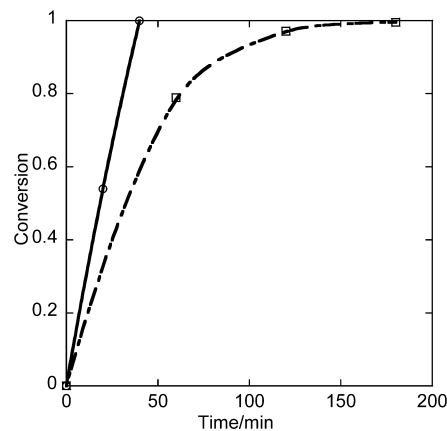
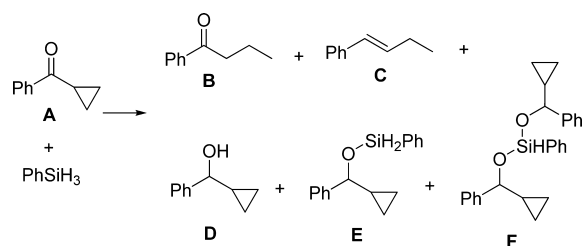


Figure 2. Time profile for the catalytic hydrosilylation of PhCHO in the absence (circle) and presence (square) of 1 equiv of TEMPO.

tetramethyl-1-piperidine, the reduction product derived from TEMPO, was detected in ~0.5 equiv (relative to PhCHO). Control experiment shows that TEMPO reacts with PhSiH₃ under similar conditions, but takes much longer (>48 h). These observations are suggestive of the involvement of a silyl radical in the catalytic reaction.⁶³

In addition, cyclopropyl phenyl ketone was employed in catalytic hydrosilylation as a mechanistic probe; formation of cyclopropyl ring-opening products indicates a radical mechanism.⁶⁴ Analysis of the crude reaction products showed again a complex mixture, but both direct hydrosilylation and ring-opening products were detected (Scheme 4). After hydrolysis, mono- and dialkoxy silanes (**E** and **F**) disappeared, and the major components are identified in a ratio of A/B/C/D = 2.4:1.0:1.7:5.2. The reappearance of the starting ketone (such as **A**) upon workup has been noted previously,⁵⁰ presumably through a silyl enol ether intermediate. The presence of cyclopropyl ring-opening products **B** (and **C**) clearly suggests the involvement of a radical pathway, but perhaps not as a

Scheme 4. Hydrosilylation Products Derived from Cyclopropyl Phenyl Ketone



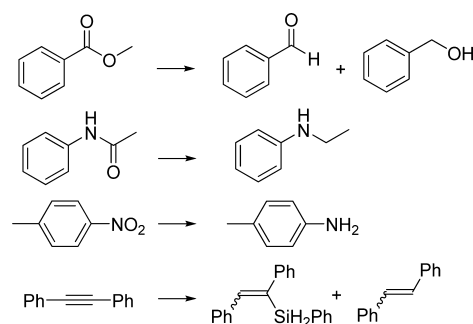
principal contributor.⁵⁸ As to the major pathway or pathways, a heterolytic cleavage of the SiH bond activated by coordination to the highly electrophilic RuN unit⁴⁹ can be surmised, similar to that of monooxo Re^V-based systems in Scheme 1B. However, a more detailed conclusion cannot be reached at this point.

The effect of electronic factors was further studied with a series of substituted benzaldehydes in competition reactions with PhCHO. Both electron-donating (4-OMe) and electron-withdrawing groups (4-Cl, 4-NO₂) seem to accelerate the reaction, lending further support for a radical contribution.⁶⁵ However, a linear free energy relationship between relative rates and σ^{\bullet} or other Hammett constants (σ and σ^+) could not be established, which may be a reflection of the presence of multiple pathways. Curiously, at competition conditions, reduction of *p*-nitro benzaldehyde is much faster, even faster than benzaldehyde.

Involvement of Ru^{III}. Low-valent Ru species have been studied extensively as hydrosilylation/hydrogenation catalysts.⁶⁶ In the present system, Ru^{VI}N can be easily reduced in the presence of PhSiH₃. Ru^{VI}N complexes could also undergo N–N coupling reactions to afford Ru^{III}.⁴⁹ A recent work has called attention to low-valent rhenium, which may be responsible for hydrosilylation with oxorhenium(V) catalysts.⁶⁷ It is also worth mentioning that the Brookhart's [(POCOP)-Ir^{III}H]⁺ system has been proposed to catalyze hydrosilylation of carbonyl compounds through an ionic mechanism featuring an η^1 -silane intermediate.⁶⁸ Thus, we investigated the possibility of Ru(III) as the actual catalyst. An independently prepared Ru(III)-saldach complex, [Ru(saldach)(H₂O)₂]⁺[PF₆]⁻,⁶⁹ did not exhibit much reactivity at similar conditions, but in situ generation for Ru(III) from Ru(VI)N and PhSiH₃ in C₆D₆ seemed to lead to decomposition. In addition, under catalytic conditions, the reaction mixture maintained an orange-brown color throughout, not the green color, characteristic of Ru^{III}, observed in the absence of carbonyl substrates.⁵⁸ Furthermore, ESI-MS analysis of the reaction mixture under catalytic conditions reveals the absence of mononuclear [Ru^{VI}N]⁺ or [Ru^{III}]⁺; instead, the majority of the Ru-containing species is observed at *m/z* 858 and 892, with correct isotopic patterns for a dinuclear form, possibly [(saldach)Ru]₂N, although its nature remains uncertain. These observations do not support Ru^{III} as the primary active catalyst, but it may still be involved in a minor pathway.

Reduction of Other Unsaturated Substrates. A wide variety of unsaturated substrates has been subjected to high-valent rhenium- and molybdenum-catalyzed reductions. To further examine the scope of the present Ru^{VI}N system, we tested a few less-active, unsaturated groups, including ester, amide, nitro, and alkyne. In these reactions, the desired reduction products can be observed (Scheme 5), but the

Scheme 5. Catalytic Reduction of Some Unsaturated Substrates



conversions are low (10–35%). It is also noted that the consumption of PhSiH₃ is considerably larger than the unsaturated substrates, although the products were not always tractable. In addition to Ph₂SiH₂, which is easily detected by both NMR and GC/MS, we suspect that phenylsilane oligomers/polymers were formed in these reactions, as indicated by the presence of broad but featureless signals between 4 and 6 ppm in ¹H NMR.⁶²

CONCLUSION

In summary, we have demonstrated that a high-valent nitridoruthenium(VI) compound, [RuN(saldach)-(CH₃OH)]⁺[ClO₄]⁻ (1), is an effective catalyst for hydrosilylation of unsaturated organic substrates, particularly aldehydes, ketones, and imines. The reaction mixture contains various species, including the redistribution products of PhSiH₃. This and other mechanistic studies indicate that the catalysis likely proceeds by silane activation via several pathways; in particular, evidence for a radical pathway is presented. Efforts are underway to improve the performance of this type of RuN-based catalyst and gain more insights into the mechanistic aspects.

EXPERIMENTAL SECTION

General. The ruthenium catalyst was prepared according to the literature.⁴⁹ Imine substrates were obtained by condensation of the corresponding carbonyl compounds and amines. All other reagents and reactants were obtained commercially and were used as received. All ¹H and ¹³C NMR spectra were recorded on a Bruker Avance-500 NMR spectrometer and referenced to the residue peaks in CDCl₃ (7.26) or C₆D₆ (7.16). UV–vis measurement was performed on a PerkinElmer Lambda 35 spectrophotometer. GC/MS analyses were performed on an HP 5890 GC/HP 5971/B MSD system with electron impact ionization (70 eV) and a DB5 column (30m × 0.53 mm i.d., 0.25 μ m thick; initial temperature, 50 °C; initial time, 1 min; ramp rate, 10 °C/min; final temperature, 310 °C; final time, 5 min). High-resolution mass spectrometry (HRMS) was performed using high-resolution time-of-flight G1969A instrumentation (Agilent, Santa Clara, CA).

Catalytic Hydrosilylation. In a typical procedure, RuN catalyst 1 (3–5 mg, 1 mol %), substrate (0.5–0.8 mmol, 1.0 equiv), C₆D₆ (0.30–0.35 mL), and PhSiH₃ (1.5 equiv) were charged into a J Young NMR tube, usually in that order. Trimethylphenyl silane or hexamethyl benzene was used as internal standard (5–20%). This was then mixed and heated in an oil bath at ~120 °C. The reaction progress was monitored by periodically taking ¹H NMR. The reduction for ketones is

typically complete within 1 day, and aldehyde substrates take only 2 h or less. After the reaction was complete or nearly complete, the reaction mixture was transferred to a round-bottom flask with diethylether and hydrolyzed with aqueous HCl or tetrabutylammonium fluoride (TBAF). Before and after the hydrolysis, a small sample was taken for GC/MS analysis. After hydrolysis, the organic layer was extracted with ether and then subjected to column chromatography on silica with an appropriate mixture of hexane/EtOAc as eluent. The reduction products were identified by ^1H NMR and GC/MS analysis in comparison with literature data or authentic samples.

■ ASSOCIATED CONTENT

■ Supporting Information

Experimental details and characterization data. UV-vis spectra of **1** and related species. ESI-MS analysis of catalytic reactions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: 1-701-777-2241. Fax: 1-701-777-2331. E-mail: gdu@chem.und.edu

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is supported in part by the ND EPSCoR through NSF Grant no. EPS-0814442 and the University of North Dakota. We thank Dr. A. Kubatova and R. Cochran for assistance with ESI-MS.

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