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Cationic nitridoruthenium(VI) catalyzed hydrosilylation of ketones and aldehydes

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ABSTRACT

The first example of a ruthenium nitrido compound as hydrosilylation catalyst is described, using phenylsilane as reductant. A variety of ketones and aldehydes are reduced to alcohols with good to high isolated yields. Some mechanistic insight on this new system is provided on the basis of the available experimental findings.

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High oxidation state transition metal complexes are known for their activity in catalytic oxidation and oxygen atom transfer reactions.[1] Recently, a number of high valent rhenium and molybdenum complexes bearing terminal oxo- or imido-groups have been demonstrated to be efficient catalysts in a variety of reduction reactions,[2,3] such as hydrosilylation of ketones and aldehydes,[4] reduction of imines[5] and amides,[6] and hydrogenation of alkynes.[7] Besides the synthetic utility of these reactions, they also pose some very interesting mechanistic questions as related to σ-bond activation.[8,9]

So far this new type of catalysts for reductions are derived exclusively from high valent rhenium and molybdenum with a d^0 or d^2 electronic configuration, specifically those of Re(V), Re(VII), Mo(VI) and Mo(IV) compounds. In an effort to expand the scope of catalysts and further our understanding on the novel mechanisms, we have become interested in investigating the use of other high valent metals in catalytic reductions. Herein we report the hydrosilylation of carbonyl compounds catalyzed by a cationic nitrido Ru(VI) complex, **1** (see Fig. 1).[10] To the best of our knowledge, this is the first example of hydrosilylation catalyst based on high valent Ru(VI) with a terminal nitrido group.

The catalytic activity of RuN-salen compound **1** was examined using acetophenone as a representative substrate under different reaction conditions. Variations in solvents, silanes, and catalyst loading are summarized in Table 1. Among the solvents examined, non-polar toluene and benzene seem to be suitable for the reaction, although **1** is barely soluble in them. Since toluene has a higher boiling point than benzene (110 °C vs 80 °C), we suspect that the reaction temperature plays a key role for the difference observed in toluene and benzene. In fact, it is found that benzene can be equally effective as solvent when the reaction is carried out in a sealed NMR tube where the reaction temperature can be higher

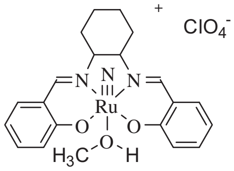

Figure 1. Cationic nitrido-ruthenium(VI) salen.

Table 1
Catalytic hydrosilylation of acetophenone[a]

Entry	Catalyst loading	Silane	Solvent	Time (h)	Conversion[b] (%)
1	5 mol %	$PhSiH_3$	Benzene	48	90
2	5 mol %	$PhSiH_3$	THF	48	67
3	5 mol %	$PhSiH_3$	CH_2Cl_2	48	68
4	5 mol %	$PhSiH_3$	CH_3CN	48	0
5	5 mol %	Et_3SiH	Toluene	48	50
6	5 mol %	Et_3SiH	Benzene	48	0
7	5 mol %	$PhSiH_3$	Toluene	4	99
8	1 mol %	$PhSiH_3$	Toluene	18	99

[a] Reaction conditions: 0.6 mmol acetophenone, 1.5 equiv of silanes, and RuN catalyst in refluxing solvents.
[b] Determined by NMR.

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than the normal boiling point of benzene. Tertiary silanes such as Et_3SiH are active for the hydrosilylation with a much slower rate when compared with primary silane $PhSiH_3$. The reaction also provides an excellent conversion when the loading of catalyst **1** is reduced to 1 mol %, albeit with a longer reaction time. No hydrosilylation reaction was observed at room temperature or without using a catalyst.

With the reaction conditions established, we then examined the scope of substrates of the hydrosilylation in this catalytic system. A variety of carbonyl compounds was investigated with $PhSiH_3$ (1.5 equiv) and 1 mol % of catalyst in refluxing toluene or benzene. The results are summarized in Table 2. It is found that all the substrates were efficiently converted to the corresponding silylethers, which were further converted to alcohols upon aqueous acidic workup. The reaction can be applied effectively to aliphatic ketones and alicyclic ketones with high isolated yields (entries 2 and 3). The conversion of benzaldehydes proceeds considerably faster, typically complete in less than two hours under same conditions (entries 4–6). Substituted benzaldehydes bearing electron-donating and electron-withdrawing groups also afforded the corresponding alcohols upon workup. Thus the present catalytic system represents a new method for the reduction of ketones and aldehydes, which is an extremely useful synthetic transformation.[11]

It should be noted that although the conversion is generally complete as judged from the disappearance of the starting carbonyl compounds, the isolated yields are sometimes modest due to the presence of side reactions. For example, in the crude reaction mixture of acetophenone reduction, ethylbenzene is detected as a minor product via further deoxygenative reduction.[12] This over-reduction could be significant for aryl ketones or aryl aldehydes, particularly if the reaction is allowed to run too long. It is also noted that small amount of acetophenone reappears after acidic workup, presumably through the intermediacy of silyl enol ether.[13] It is worth mentioning that the minor products profile is different from the $Re^{V}O$-catalyzed hydrosilylation, where ethylbenzene and di(phenylethyl)ethers are observed.[4c]

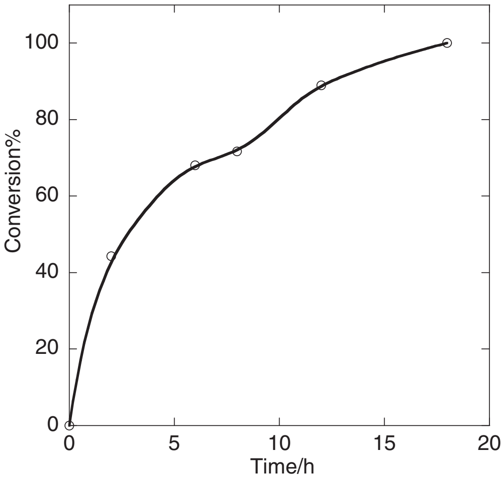
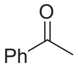
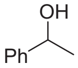
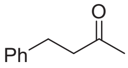
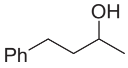
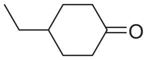
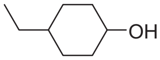
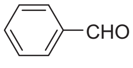
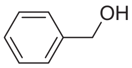
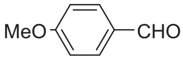
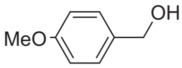
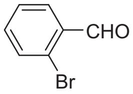
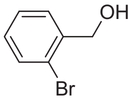


Figure 2. Time profile of the hydrosilylation of acetophenone with $PhSiH_3$ (1.5 equiv) and 1 mol % catalyst in refluxing toluene. The conversion (circles) is determined by NMR and the line is a smoothing function and not a kinetic fit.

Table 2
Hydrosilylation of various carbonyl compounds catalyzed by RuN[a]

Entry	Substrate	Product	Time	Yield[b] (%)
1			18 h	67
2			20 h	86
3			20 h	89
4			2 h	66
5			1.5 h	73
6			2 h	87

[a] Reaction conditions: 0.6 mmol ketone or aldehyde, 1.5 equivalent of $PhSiH_3$ and catalyst (1 mol %) in heated toluene or benzene.

[b] Isolated yields; complete consumption of starting carbonyl compounds was observed in all cases.

The catalytic mechanism is unclear at the moment. Low valent $Ru^{II/III}$ are well known as hydrosilylation/hydrogenation catalysts.[14] $Ru^{VI}N$ complexes easily undergo N–N coupling reactions to afford Ru^{III},[10] or they could be reduced by hydrosilanes to give low valent Ru species.[15] Therefore it is reasonable to postulate that the active species in the reaction is actually Ru^{III}. To probe this possibility, firstly a Ru^{III} compound, $[\mathrm{Ru(saldach)(H_2O)_2^+}][\mathrm{PF_6^-}]$[16] was prepared independently and subjected to same catalytic conditions. It was found that no hydrosilylation of acetophenone was observed within 48 h in refluxing toluene. Secondly, we investigated the reaction of compound **1** with $PhSiH_3$ in CD_3CN because of solubility consideration. It appeared that **1** can be reduced by $PhSiH_3$, rather slowly at room temperature, to give a dark greenish, paramagnetic species. The exact nature of this species is unknown; however, it is clear that it is different from the species in the catalytic reaction when carbonyl substrates are present, which is typically of a brown-reddish color. We also monitored the time profile of acetophenone hydrosilylation (Fig. 2), which shows no apparent induction period that may exist due to the reduction of RuN by hydrosilane before catalysis began. Based on these preliminary results, we postulate that the catalysis proceeds through a heterolytic cleavage of the SiH bond activated by coordination to the metal center, similar to that of monooxo Re^{V} based systems.[2] However, the different minor-product profiles in these two systems may indicate some differences in the reaction pathways. Further detailed studies are necessary to shed light on the reaction mechanism.

In conclusion, we have demonstrated that the air-stable, cationic $Ru^{VI}N$-salen is an efficient catalyst for the reduction of carbonyl compounds in the presence of a tertiary silane. The reaction proceeds smoothly with good to high yields. Research is ongoing to expand the scope of the reduction and to elucidate the reaction mechanism.

Acknowledgements

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