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Bis(acetylacetonato)Ni(II)/$NaBHEt_3$-catalyzed hydrosilylation of 1,3-dienes, alkenes and alkynes

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ABSTRACT

The utility of commercially available Ni(II) salts, $Ni(acac)_2$ (acac = acetylacetonato) (**1a**) and its derivatives bis(hexafluoroacetylacetonato)nickel(II) (**1b**) and bis(2,2,6,6-tetramethyl-3,5-heptanedionato) nickel(II) (**1c**) as versatile hydrosilylation catalyst precursors is described. Complexes **1a-c** catalyze 1,4-selective hydrosilylation of 1,3-dienes in the presence of $NaBHEt_3$ at ambient temperature. The reactions exhibit good regioselectivity to give the branched isomers as major products. The catalytic system also catalyzes hydrosilylation of alkenes including industriary important siloxy-, amino-, and epoxy-substituted ones as well as both terminal and internal alkynes.

1. Introduction

Hydrosilylation reaction of carbon-carbon multiple bonds is one of the most important processes for the production of orgaosilicon compounds and for the curing of organosilicon materials [1]. For these reactions, precious metal complexes containing Pt, Rh, Ru *etc*., are widely used as catalysts. On the other hand, due to the low abundance and high cost of these metals [2], there is an emerging demand to develop inexpensive and environmentally benign earth-abundant metal catalysts. So far, several 3d metal catalysts containing Fe [3], Co [4] and Ni [5] have been revealed to be good candidates for non-precious metal surrogates. However, 3d metal complexes often exhibit diverse reactivity, and thus many side reactions simultaneously proceed during the catalytic reactions, leading to the formation of a complicated reaction mixture. In recent years, well-defined Fe catalysts with good selectivity have been developed. One notable example was reported by Chirik et al. using iron complexes bearing bis(imono)pyridine (PDI = 2,6-(2,6-$R_2C_6H_3N$ = $CMe)_2C_5H_3N$), $[Fe(PDI)(N_2)_2]$ (R = ^{i}Pr) and $[(PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$ (R = Et, Me), which exhibit higher reaction selectivity than platinum-based industrial catalysts [3c]. Another example is the bis(iminopyridine) Fe complex system, which demonstrated the first example of regio- and stereoselective hydrosilylation of 1,3-dienes [3a]. These examples successfully demonstrate the high capability of 3d metal complexes as a hydrosilylation catalyst although the systems still have room to be improved, such as high instability and complicated preparation method of the catalysts, etc.

The use of the commercially available Ni(II) salts, $Ni(acac)_2$ (acac = acetylacetonato) (**1a**) as a hydrosilylation catalyst has been reported in 1991 under rather harsh reaction conditions with low reaction selectivity [5d-f]. It is also reported that **1a** in conjunction with a proper reducing agent such as alkyl aluminum reagents AlR_3 [R_3 = Et_3, $Et_2(OEt)$], $LiAlH_4$, and BuMgBr effectively catalyzes 1,4-selective hydrosilylation of 1,3-dienes at ambient temperature, while the system is not applicable to normal α-alkene hydrosilylation reactions [5b,c]. Since simple and air stable **1a** is a promising catalyst precursor, it is of great interest to further investigate the capability of **1a** as a hydrosilylation catalyst. In this study, we found that **1a** and its derivatives bis(hexafluoroacetylacetonato)nickel(II) (**1b**) and bis(2,2,6,6-tetramethyl-3,5-heptandiono)nickel(II) (**1c**) (Fig. 1), serve as a good hydrosilylation catalyst precursor in the presence of $NaBHEt_3$.

Different from the previous systems, our system **1**/$NaBHEt_3$ catalyzes hydrosilylation not only of 1,3-dienes but also of α-alkenes at room temperature with a good selectivity. It was also revealed that the system catalyzed hydrosilylation of alkynes, furnishing monohydrosilylated products in moderate yields.

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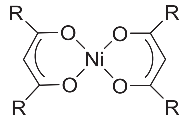


R = Me (**1a**), CF_3 (**1b**), *t*Bu (**1c**)

Fig. 1. Structures of 1a-c.

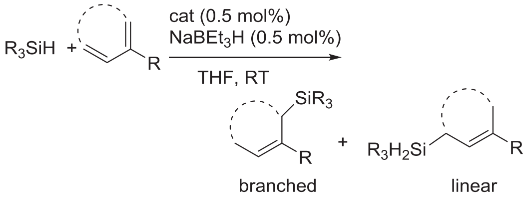
2. Results and discussion

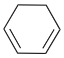
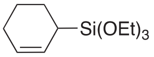
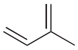
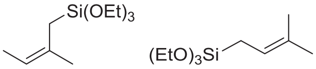
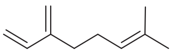
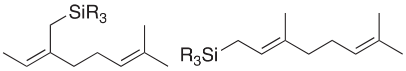
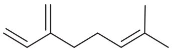
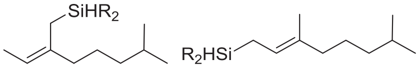
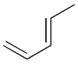
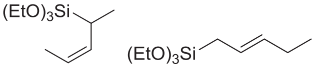
2.1. Hydrosilylation of 1,3-dienes

It was revealed that the **1a**/$NaBHEt_3$ system exhibits similar catalytic performance as the previous system **1a**/$AlEt_3$ in hydrosilylation reactions of various 1,3-dienes with $(EtO)_3SiH$. The reaction was performed at room temperature in THF using each 1.0 mmol of substrates and 0.5 mol% of **1a**/$NaBHEt_3$. Hydrosilylation of cyclohexadiene proceeded in a 1,4-fashion to form 3-triethoxysilylcyclohexene in 75% yield (Table 1, entry 1). Formation of $(EtO)_4Si$ (4%) was also observed, indicating the occurrence of substituent redistribution of $(EtO)_3SiH$ as a side reaction [6]. Isoprene hydrosilylation also proceeded in a 1,4-fashion, resulting in the formation of the corresponding hydrosilylated products as a mixture of two isomers, branched isomer, (*Z*)-2-methyl-1-triethoxysilyl-2-butene, and linear isomer, 3-methyl-1-triethoxysilyl-2-butene, within 2 h in 79% total yield (Table 1, entry 2). In this reaction, the branched isomer was obtained predominantly (branched:linear = 79/21), accompanied by the slight formation of $(EtO)_4Si$ (2%) and $(EtO)_3SiOSi(OEt)_3$ (4%). In this system, the order of substrate addition is critical for the reaction selectivity. When **1a** and $NaBHEt_3$ were initially mixed and then $(EtO)_3SiH$ and isoprene were successively added, substituent redistribution of the silane preferably proceeded to form a mixture of $(EtO)_4Si$ (12%), $(EtO)_3SiOSi(OEt)_3$ (6%), etc, as well as less amount of hydrosilylated products (61% total yield, branched:linear = 72/28). Superior results were obtained by the addition of silane and isoprene to the THF solution of **1a** and subsequent addition of $NaBHEt_3$. Therefore, all the reactions in Table 1 were performed following the latter procedure.

Myrecene was also hydrosilylated with $(EtO)_3SiH$ in 1 h, resulting in the formation of 1,4-adducts in 85% yields

Table 1
1a-**1c**/$NaBHEt_3$-catalyzed hydrosilylation of 1,3-dienes.[a]



Entry	Cat	R_3SiH +1,3-diene	Product yields[b] (Branched: Linear)
1	**1a**	$(EtO)_3SiH$ + 	 1 h, 75%[c]
2	**1a-c**	$(EtO)_3SiH$ + 	 **1a** (2 h): 79% (79: 21)[c] **1b** (1 h): 88% (81: 19)[c] **1c** (4 h): 76% (78: 22)[c]
3	**1a**	R_3SiH + 	 R_3 = $(EtO)_3$ (1 h): 85% (90: 10)[c] R_3 = $(EtO)_2Me$ (2 h): 81% (95:5) R_3 = Et_3 (3 h): 81% (95:5) R_3 = $(Me_3SiO)_2Me$ (10 h): 74% (90:10)
4	**1a**	R_2SiH_2 + 	 R_2 = Ph_2 (8 h); 82% (78:22)[d] R_2 = Et_2 (2 h): 65% (98:2)
5	**1a**	$(EtO)_3SiH$ + 	 2 h; 93% (15:85)

[a] Reaction conditions: catalyst/$NaBHEt_3$ (0.005/0.005 mmol), alkene (1.0 mmol), silane (1.0 mmol), in THF (5 mL) at room temperature.
[b] Isolated yield.
[c] $(EtO)_4Si$ (2–4%) was isolated as a byproduct.
[d] Ph_3SiH (6%) was isolated as a byproduct.