Hydrovinylation of Alkenes Catalyzed by the Ruthenium−Hydride Complex Formed in Situ from $(PCy_3)_2(CO)RuHCl$ and $HBF_4{\cdot}OEt_2$

Chae S. Yi,* Zhengjie He, and Do W. Lee

Department of Chemistry, Marquette University, Milwaukee, Wisconsin 53201-1881

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*Summary: A ruthenium−hydride complex, generated in situ from the reaction of $(PCy_3)_2(CO)RuHCl$ (**1**) with $HBF_4{\cdot}OEt_2$, was found to be an effective catalyst for the hydrovinylation of alkenes. For example, the reaction of styrene with ethylene in the presence of **1**/$HBF_4{\cdot}OEt_2$ (0.5 mol %) at room temperature produced the hydrovinylation product in 93% isolated yield. Both terminal alkenes and dienes were found to give the hydrovinylation products. Higher reaction temperature was required for the phenyl-substituted internal alkenes, in which cases the isomerized products were obtained.*

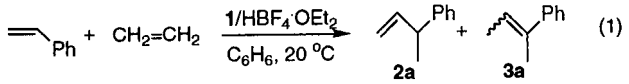
Introduction

The transition-metal-catalyzed hydrovinylation of alkenes has been shown to be a versatile method for forming new carbon−carbon bonds.[1−4] Since the regioselective addition of a vinyl group to an internal olefinic carbon is commonly observed for aryl-substituted olefins, much research has been focused on the development of an enantioselective process by using chiral metal catalysts. For example, Wilke first achieved a highly enantioselective hydrovinylation of styrene by using chiral Ni−phosphine complexes.[2] Rajanbabu recently employed Ni catalysts with chiral MOP ligands to achieve highly stereoselective hydrovinylation of aryl-substituted olefins.[3] Several other metal-catalyzed hydrovinylation reactions have also been reported,[4] but generally limited scope, disparate enantioselectivity, and undesirable reaction temperature still remain as drawbacks for most of these Ni- and Pd-catalyzed reactions.

The development of a ruthenium-based hydrovinylation reaction would be highly desirable, since chiral ruthenium−diphosphine catalysts have been shown to be effective for asymmetric reactions of alkenes.[5] However, commonly available ruthenium−hydride complexes do not exhibit high catalytic activity toward hydrovinylation of alkenes, and as a result, only a few articles have been published on the ruthenium-catalyzed hydrovinylation reactions.[6] While studying the ruthenium-mediated cross-coupling reactions of alkenes and alkynes,[7] we recently reported an effective hydrovinylation of alkynes using a cationic ruthenium−carbene complex as a catalyst.[8] We also found that the addition of $HBF_4{\cdot}OEt_2$ to the ruthenium−hydride complex $(PCy_3)_2(CO)(Cl)RuH$ (**1**) substantially enhanced the catalyst activity toward hydrogenation of alkenes.[9] Herein we report a highly effective hydrovinylation of alkenes by using a ruthenium catalyst generated in situ from the reaction of **1** and $HBF_4{\cdot}OEt_2$.

Results and Discussion

An initial activity study showed that the ruthenium−hydride complex formed in situ from **1**/$HBF_4{\cdot}OEt_2$ was found to exhibit uniquely high catalytic activity for the hydrovinylation of alkenes among the selected ruthenium−phosphine complexes. For example, the treatment of styrene (104 mg, 1.0 mmol) with ethylene (6.4 mmol) in the presence of **1** (3.6 mg, 0.5 mol %) and $HBF_4{\cdot}OEt_2$ (1.5 μL, 2.0 equiv) in benzene (2 mL) cleanly gave the product **2a** in 93% isolated yield (98% GC yield) after 6 h at room temperature (eq 1). Only a trace



(1)

amount of the isomerized product **3a** (<2% by GC) was detected in the crude reaction mixture. The reaction at 0 °C was found to be quite slow, giving <10% of **2a** after 6 h under otherwise identical reaction conditions. Also, the presence of an acid was found to be essential for the catalytic activity, because no hydrovinylation product was formed with the complex **1** alone under similar reaction conditions.

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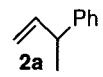
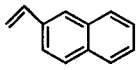
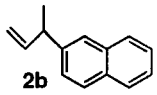
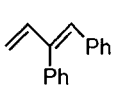
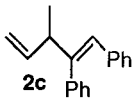
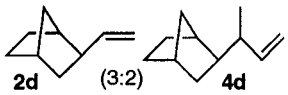
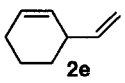
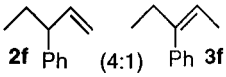
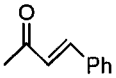
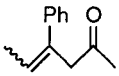
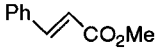
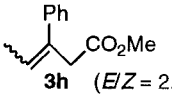
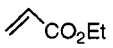
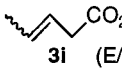
Table 1. Hydrovinylation of Alkenes Catalyzed by 1/HBF_4·OEt_2[a]

entry	alkene	product (s)	1 (mol%)	time (h)	temp (°C)	% yield[b]
1		 **2a**	0.5	6	20	98 (93)
2		 **2b**	0.5	8	20	94 (89)
3		 **2c**	1.0	6	75	92 (90)
4		 **2d** (3:2) **4d**	0.25	1	20	95[c]
5		 **2e**	2.0	6	50	94[c]
6		 **2f** (4:1) **3f**	2.0	15	50	55-60
7		 **3g** (*E*/*Z* = 3:1)	3.0	15	75	65
8		 **3h** (*E*/*Z* = 2.5:1)	2.0	24	50	65-70
9		 **3i** (E/Z = 2.5:1)	1.0	6	75	70[d]

[a] Reaction conditions: 1.0 mmol of alkene; 6.4 mmol of ethylene; 0.25−3 mol % of **1** and 1−2 equiv of HBF_4·OEt_2; 2 mL of C_6H_6. [b] The product yield was determined by GC using C_6Me_6 as an internal standard. The numbers in parentheses are the isolated product yields containing 1−2% of the isomerized products. [c] Products were isolated by a trap-to-trap vacuum distillation and contained 10−15% of the solvent. [d] Approximately 5% of $CH_3CH_2CH{=}CHCO_2Et$ was also formed.

The scope of the hydrovinylation reaction was examined by using the in situ formed **1**/HBF_4·OEt_2 as the catalytic system (Table 1). Both terminal alkenes and dienes were found to be effective for giving the hydrovinylation products **2**. In most cases, the products resulted from the regioselective addition of the vinyl group adjacent to either phenyl or other electron-withdrawing groups. A similar regioselectivity pattern has been commonly observed in nickel-catalyzed hydrovinylation of olefins.[3,4] For the norbornene case, a mixture of 1:1 and 1:2 coupling products was obtained at room temperature (entry 4). A higher reaction temperature was required for phenyl-substituted internal alkenes, and in these cases, an *E*/*Z* mixture of the isomerized products **3** was obtained (entries 6−8). It is interesting to note that, even for the internal alkenes with an electron-withdrawing group, the isomerized products **3** were formed apparently from the preferential addition of the vinyl group adjacent to the phenyl group (entries 7 and 8). In contrast, an *E*/*Z* mixture of the linear coupling product **3i** was obtained for ethyl acrylate, apparently formed from the addition of the vinyl group to the terminal olefinic carbon (entry 9). These results indicated that the presence of an aryl group is important for the regioselective addition of the vinyl group. Previously, the η^3-benzyl complex has been suggested as a key intermediate species in metal-catalyzed hydrovinylation reactions.[1]

We previously reported that the stoichiometric reaction of **1** with HBF_4·OEt_2 led to a mixture of the ruthenium−hydride complex and $Cy_3PH^+BF_4^-$.[9] We found that this isolated mixture exhibited activity similar to that of the in situ formed **1**/HBF_4·OEt_2 toward the hydrovinylation reaction.[10] The following results also implicate the ruthenium−hydride species. For example, the hydrovinylation of styrene with $CD_2{=}CD_2$ led to the product **2a** with an extensive deuterium incorporation at both vinyl and methyl positions. The extensive H/D exchange on the methyl group is consistent with a rapid and reversible olefin insertion/β-H elimination sequence via a metal−hydride species. The formation of the isomerized products **3**, especially at an elevated temperature, was also indicative of the involvement of the ruthenium−hydride species. For the 1-phenylpropene case, a mixture of **2f** and **3f** was obtained at 50 °C under the reaction conditions specified in Table 1, while only **2f** was formed at room temperature, albeit with a lower rate (10% yield after 24 h). The ruthenium−hydride complexes have been well-known to catalyze alkene isomerization reactions.[11]

(10) The isolated mixture was found to be stable in the solid state but slowly decomposed in C_6H_6 solution into a novel tetrameric species.[9]

In summary, the in situ formed **1**/HBF_4·OEt_2 was found to be an effective catalytic system for the hydrovinylation of alkenes under mild reaction conditions. The feasibility of the asymmetric version of the reaction is currently being explored by using chiral ruthenium−hydride complexes.

Experimental Section

General Information. All reactions were carried out in a nitrogen-filled glovebox or by using standard high-vacuum and Schlenk-line techniques, unless otherwise noted. Tetrahydrofuran, benzene, hexanes, and Et_2O were distilled from the purple solutions of sodium and benzophenone immediately prior to use. The NMR solvents were dried from activated molecular sieves (4 Å). All organic alkene substrates were received from commercial sources and used without further purification. The ruthenium complex **1** was prepared according to the reported procedure.[8] The ^1H and ^{13}C spectra were recorded with a GE GN-Omega 300 MHz FT-NMR spectrometer. Mass spectra were recorded with a Hewlett-Packard HP 5970 GC/MS spectrometer. The GC spectra were recorded with a Hewlett-Packard HP 6980 spectrometer equipped with a capillary column (30 m × 0.23 mm × 0.25 μm; 5% PHME siloxane).

General Procedure of the Hydrovinylation Reaction of Alkene. In a nitrogen-filled glovebox, complex **1** (0.25−3 mol %) was charged with 2 mL of benzene in a 25 mL Schlenk tube equipped with a Teflon stopcock. The reaction tube was brought out of the box, and HBF_4·OEt_2 (0.15 mmol) was added via syringe under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 30 min, during which time the solution turned red-brown. The tube was cooled in a liquid-nitrogen bath, and an alkene was added under a stream of nitrogen gas. Excess CH_2=CH_2 (6.4 mmol) was condensed into the reaction tube via a vacuum line, and the reaction mixture was stirred under the conditions specified in Table 1. The reaction tube was opened to air at room temperature, and the reaction mixture was filtered through a small pipet packed with 5 cm of silica gel (Aldrich, 60 Å) to remove the metal catalyst. The organic product was isolated after passage through another silica-packed pipet column (hexane/Et_2O) and solvent removal from a rotary evaporator.

Selected spectroscopic data for **2c**: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.36−6.90 (m, Ph), 6.49 (s, =CHPh), 6.02 (ddd, J = 16.8, 9.6, 6.6 Hz, CH_2=C*H*), 5.12 (m, =CH_2), 3.34 (pseudo-pentet, J = 6.6 Hz, C*H*CH_3), 1.26 (d, J = 6.6 Hz, CH*C*H_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 146.5 (=*C*HPh), 141.9 (CH_2=*C*H), 141.8 and 140.7 (Ph_{ipso}), 137.3 (PhCH=*C*Ph), 129.0, 128.3, 127.8, 126.8, 126.2, and 126.0 (Ph carbons), 113.9 (=CH_2), 46.6 (*C*HCH_3), 18.5 (CH*C*H_3); GC-MS m/z 234 (M^+).

Selected spectroscopic data for **2f**: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.40−7.15 (m, Ph), 5.97 (ddd, J = 17.5, 9.9, 7.8 Hz, CH_2=C*H*), 5.04 (m, =CH_2), 3.15 (pseudo-q, J = 7.2 Hz, C*H*CH_2), 1.76 (m, J = 7.2 Hz, C*H*$_2CH_3$), 0.88 (t, J = 7.2 Hz, CH_2C*H*$_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 142.2 (CH_2=*C*H), 138.2, 128.3, 127.6, and 126.0 (Ph carbons), 114.0 (=CH_2), 51.7 (*C*HCH_2), 28.2 (*C*H_2CH_3), 12.1 (CH_2*C*H_3); GC-MS m/z 146 (M^+).

Selected spectroscopic data for (*E*)-**3g**: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.41−7.20 (m, Ph), 6.09 (q, J = 7.5 Hz, =C*H*CH_3), 3.60 (s, C*H*$_2COCH_3$), 2.11 (s, CH_2COC*H*$_3$), 1.82 (d, J = 7.5 Hz, =CHC*H*$_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 206.7 (*C*OCH_3), 142.2 (=*C*PhCH_2), 133.8, 128.4, 126.9, and 125.8 (Ph carbons), 126.8 (=*C*HCH_3), 45.5 (*C*H_2COCH_3), 29.2 (CO*C*H_3), 14.7 (=CH*C*H_3); GC-MS m/z 174 (M^+).

Selected spectroscopic data for (*Z*)-**3g**: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.41−7.18 (m, Ph), 5.70 (q, J = 7.5 Hz, =C*H*CH_3), 3.44 (s, C*H*$_2COCH_3$), 2.06 (s, CH_2COC*H*$_3$), 1.67 (d, J = 7.5 Hz, =CHC*H*$_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 207.4 (*C*OCH_3), 144.3 (=*C*PhCH_2), 134.6, 128.8, 128.2, and 126.8 (Ph carbons), 126.1 (=*C*HCH_3), 54.1 (*C*H_2COCH_3), 29.6 (CO*C*H_3), 15.0 (=CH*C*H_3); GC-MS m/z 174 (M^+).

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