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A Ruthenium-Based Catalyst System for Hydrovinylation at Room Temperature

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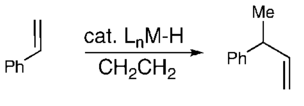
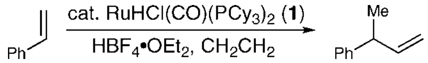
*Summary: A catalytic amount of RuHCl(CO)(PCy$_3$)$_2$ (**1**) activated with AgOTF or AgSbF$_6$ at room temperature was found to be an effective catalyst system for the hydrovinylation of vinylarenes. Vinylarenes with both electron-donating and electron-withdrawing substituents reacted with ethylene at room temperature to provide the desired 3-arylbutenes in moderate to excellent yield (60−99%) under mild reaction conditions.*

Stereoselective carbon−carbon bond formation is one of the most important types of bond construction in chemistry. However, there have been surprisingly few methods developed to construct these bonds directly from prochiral olefins, even though reactions such as these could have a potentially large impact on the fine chemical and pharmaceutical industry. Transition metal-catalyzed carbon−carbon coupling reactions have attracted considerable interest and continue to gain importance due to the demand for efficient syntheses. Metal-catalyzed hydrovinylation, the addition of a vinyl group and a hydrogen across an alkene, is depicted in eq 1 for styrene and ethylene and has been shown to be a useful, regioselective tool to generate new carbon−carbon bonds.[1]



(1)

A number of very active nickel complexes[2] have been developed to achieve hydrovinylation of styrenes with high stereoselectivity. Other available transition-metal catalysts based on cobalt,[3] palladium,[4] and iridium[5] have been used for the hydrovinylation reaction. All reactions suffer from limited substrate scope, and many exhibit various problems related to the high reaction temperatures and product isomerization (e.g., 3-phenyl-1-butene to 2-phenyl-2-butene) and/or oligomerization of styrene or ethylene. In 1965, Alderson, Jenner, and Lindsey achieved the first transition-metal-catalyzed hydrovinylation of an alkene by using hydrated Rh and Ru chloride catalysts to effect the codimerization of ethylene at high pressures.[6] Unfortunately, most other ruthenium complexes show little to no activity as catalysts in these reactions.[7] However, Yi and co-workers reported that a pentavalent ruthenium hydride complex, RuHCl(CO)(PCy$_3$)$_2$ (**1**), when treated with HBF$_4$·OEt$_2$ and heated, catalyzed the hydrovinylation reaction of styrene and ethylene with good yield and selectivity (eq 2).[8] The ruthenium hydride complex **1** is convenient to use, as it can be isolated and stored and is moderately tolerant to air and water.



(2)

Presumably, HBF$_4$·OEt$_2$ acts as a strong acid to protonate a dissociated tricyclohexylphosphine ligand, which opens a coordination site on the ruthenium metal and allows styrene to associate with the metal center, which then undergoes reductive elimination to produce the desired compound (Scheme 1a).

Our efforts have recently focused on the development of a cationic ruthenium complex to catalyze the hydrovinylation reaction (Scheme 1b). We envisioned that selective removal of the chloride from **1** would produce a cationic catalyst that may be stabilized by use of a weakly coordinating anion (e.g., OTf, SbF$_6$).[9] This method of activation would remove the need to use a strong acid to activate the catalyst and hopefully also remove the need to heat the reaction mixture above room temperature, thereby allowing a more versatile protocol which may be amenable to milder reaction conditions and hence a larger substrate scope. Another advantage of this process is the continued presence of two phosphine ligands on the metal center throughout the catalytic process. These ligands could presumably be replaced with a chelating chiral bis(phosphine) to deliver a chiral, nonracemic catalyst. Chelating ligands cannot be utilized with the known nickel and palladium catalysts, as they block an open coordination site needed for olefin coordination in these systems. In this paper, we report highly effective, mild, and

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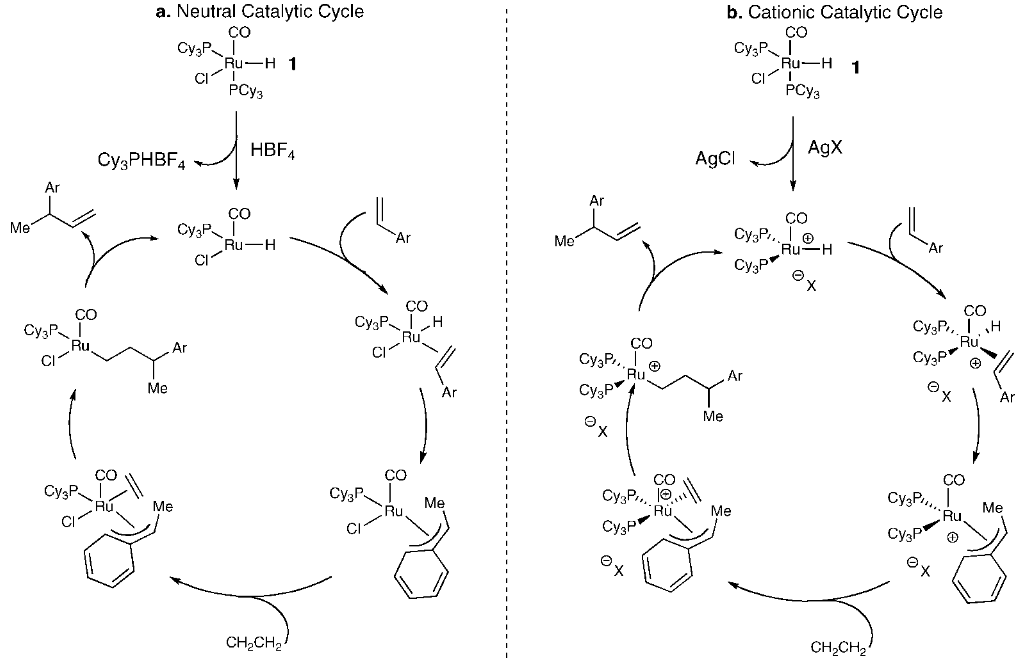
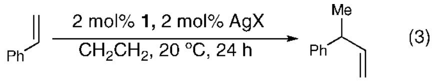
Scheme 1. Catalytic Cycles of the Hydrovinylation Reaction



acid-free reaction conditions for the hydrovinylation of vinylarenes using a cationic ruthenium catalyst based on **1**.

We initially screened a variety of silver salts in combination with **1**, for the hydrovinylation of styrene under a 1 atm pressure of ethylene. For example, treatment of styrene with ethylene in the presence of **1** and $AgSbF_6$ in CH_2Cl_2 gave 3-arylbutene in 35% yield after 24 h at room temperature (eq 3). Utilizing the triflate counterion (OTf) increased the yield to 52%. Other anions, including ClO_4 and BF_4, were less effective.

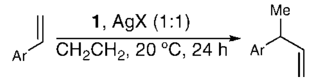


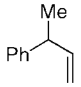
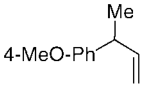
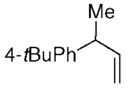
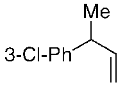
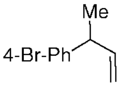
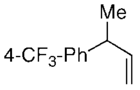
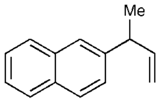
(3)

X = SbF_6, 35%
X = OTf, 52%

The scope of this reaction protocol was examined further by the reaction of ethylene with a variety of vinylarenes, catalyst **1**, and either AgOTf or $AgSbF_6$ (Table 1). All reactions were allowed to proceed for 24 h for the sake of comparison, although some reactions were complete in significantly less time. In some instances, lowering the catalyst loading to 0.5 mol % helped to increase the yield (entries 1 and 2). In the case of 4-methoxystyrene (entry 2), only polymerization resulted when 2 mol % of **1** was used with the SbF_6 counterion. Lowering the catalyst loading to 0.5 mol % produced 45% of the hydrovinylation adduct without signs of polymerization. Finally, replacing $AgSbF_6$ with AgOTf dramatically increased the yield of the desired product to 99%. There are both electronic and steric effects noticeable in these reactions; however, in most cases very good yields are still possible (entries 5−7). Gratifyingly, we never observed olefin isomerization of the products.

Table 1. Hydrovinylation of Vinylarenes Catalyzed by 1/AgX[a]



Entry	Product	**1** (%)	X	Yield (%)[b]	ref.[c]
1		0.5	OTf	98	10b
		2.0	OTf	52	
2		0.5	OTf	99	10b
		0.5	SbF_6	45	
3		0.5	OTf	67	10a
		2.0	OTf	81	
4		2.0	SbF_6	60	10b
5		0.5	OTf	60	10c
		2.0	SbF_6	96	
6		0.5	OTf	18	10d
		2.0	SbF_6	75	
7		0.5	OTf	23	10b
		2.0	OTf	88	

[a] Reaction conditions: 0.48 mmol of alkene; 0.0024 mmol of **1**/AgX (1:1); atmosphere of ethylene; 2 mL of CH_2Cl_2. [b] The product yield was determined by GC using 1-methylnaphthalene as an internal standard. [c] The products were identified by comparison with reported spectroscopic data (^1H, ^{13}C NMR) from the indicated references.[10]

Ruthenium hydride catalyst **1** can be made in one step, isolated, and stored. Complex **1** requires only treatment with a nonacidic Ag salt to become an active catalyst, rather than the strong Brønsted or Lewis acids required in other systems.

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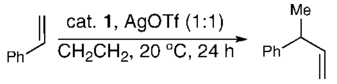
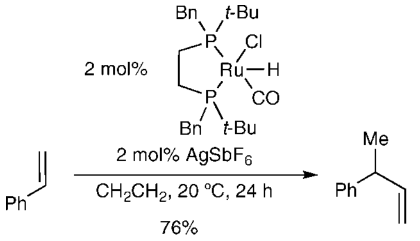
Table 2. Effect of Catalyst Concentration



entry	styrene concn (M)	amt of **1** (%)[a]	**1** concn (M)	yield (%)[b]
1	0.96	0.5	0.0048	60
2	0.96	0.25	0.0024	74
3	0.24	0.5	0.0012	98
4	0.24	2.0	0.0048	52
5	0.24	1.0	0.0024	75

[a] Catalyst loading. [b] Yield by GC.

The system works under mild conditions, at room temperature, and at atmospheric pressure. The possibility now exists to use chelating, bidentate phosphine ligands in this reaction process.



(4)

To this end, we applied our conditions to a reaction employing a catalyst with chelating, bidentate phosphine ligands; 1,2-bis(boranato(*tert*-butyl)benzylphosphino)ethane[11] was used in place of PCy_3 to yield 76% of the desired 3-arylbutene after 24 h (eq 4).

As several (but not all) reactions exhibited an increase in yield with a lowering of catalyst loading, we briefly examined the effect of concentration of the catalyst on the yield of the hydrovinylation of styrene with ethylene (Table 2). Because the yield increases with a decrease in catalyst concentration, it appears that bimolecular decomposition is a plausible mode of deactivation in this system.[12] Further studies are necessary to fully explore this effect, which will aid in future catalyst development.

In summary, a mild and acid-free ruthenium hydride catalytic system was found to be effective for the hydrovinylation of substituted vinylarenes at room temperature. This ruthenium-based catalytic system has an appealing reactivity profile, providing a useful level reactivity in favor of the desired hydrovinylation reaction while being selective enough to deliver the desired products in excellent yields without promoting deleterious side reactions such as oligomerization and isomerization.

Experimental Section General Considerations. All reactions were manipulated under argon and kept away from light, unless otherwise noted. Dry dichloromethane was used from a solvent purification system (neutral alumina, copper(II) oxide). All vinylarene substrates are commercially available and were used without further purification. Ruthenium complex **1** was prepared according to the reported procedure.[8b] The GC spectra were recorded with a Agilent 6850 Series II equipped with a CHIRALDEX B-PH fused silica capillary column (30 m × 0.25 mm × 0.12 μm).

Typical Reaction Procedure. In a nitrogen-filled glovebox, a 10 mL reaction flask equipped with a stir bar was charged with complex **1** (0.0024 mmol) and AgOTf (0.0024 mmol). The reaction mixture was removed from the glovebox, purged with argon, and charged with CH_2Cl_2. The reaction mixture was stirred for 3 h at room temperature followed by the addition of styrene (0.48 mmol) under a stream of argon. Ethylene was bubbled into the reaction flask, and a balloon was filled to maintain an atmosphere of ethylene, recharging the balloon after 12 h. The reaction mixture was stirred for 24 h and then opened to air and filtered through a small pipette packed with silica gel (silicycle 60 Å ultrapure) to remove the metal catalyst. The product was then passed through another silica-packed pipet column (hexanes), and the solvent was removed via rotary evaporator.

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