## The First Example of Transition-Metal-Catalyzed Hydroselenation of Acetylenes

Hitoshi Kuniyasu, Akiya Ogawa,\* Ken-Ichiro Sato, Ilhyong Ryu, and Noboru Sonoda\*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

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Abstract: A variety of transition metal complexes catalyzed the regioselective hydroselenation of acetylenes. In particular, the palladium acetate-catalyzed reaction afforded the Markovnikov adducts with high selectivity.

Addition of heteroatom-hydrogen bonds to carbon-carbon multiple bonds catalyzed by transition-metal complexes is one of the most challenging subjects in organic chemistry. Along this line, the hydrosilylation,<sup>1</sup> hydrostannation,<sup>2</sup> and hydroboration<sup>3</sup> have been well-documented. However, there are few reports of a similar activation of heteroatom-hydrogen bond in which hydrogen is more electropositive than the heteroatom.<sup>4</sup> We report herein the first example of transition-metal-catalyzed hydroselenation of acetylenes to give vinyl selenides<sup>5</sup> with high regioselectivity as shown in eq 1.



To a mixture of 1-octyne (1a) (1.0 mmol) and palladium acetate  $[Pd(OAc)_2]$  (0.02 mmol) in benzene (0.5 mL) was added benzeneselenol (1.0 mmol) under Ar atmosphere. Brown precipitates immediately deposited. After the mixture was heated at 80 °C for 15 h, the palladium complex precipitated was removed through Celite and the resultant mixture was purified by preparative TLC (silica gel) to give 2-phenylseleno-1-octene (2a) (62%) as the major product together with 2,2-bis(phenylseleno)octane (3a) (13% based on 1a), 2-phenylseleno-2-octene (4a) (7%, E/Z = 30/70), and 1-phenylseleno-1-octene (5a) (<3%) (eq 2).



In the presence of AcOH (0.02 mmol) as a catalyst or in the absence of catalyst under otherwise identical conditions, the addition scarcely proceeded. While the free-radical addition of selenols to terminal acetylenes was reported to provide the *anti*-Markovnikov adducts,<sup>6</sup> the present  $Pd(OAc)_2$ -catalyzed reaction afforded the Markovnikov adducts as the major product. Accordingly, these methods are regiocomplementary for the synthesis of vinyl selenides from terminal acetylenes and benzeneselenol (Scheme 1).



The results of the hydroselenation of some terminal acetylenes with benzeneselenol were shown in eq 3.



Both hydroxy and ester groups in acetylenes (1b and 1c) did not affect the reaction. When the enyne 1c was used as a substrate, the hydroselenation took place chemoselectively at the triple bond and the formation of cyclization products were not confirmed. The reaction of PhSeH with phenylacetylene (1d), however, permitted the formation of the regioisomer 5d as the major product, probably because the free-radical addition to 1d proceeded competitively in this reaction system.<sup>7</sup> To elucidate the stereochemistry of this Pd(OAc)<sub>2</sub>-catalyzed hydroselenation, the reaction of PhSeD (containing 88% d determined by <sup>1</sup>H NMR spectrum) to 1-octyne (1a) was carried out at 80 °C for 15 h (eq 4). The *E/Z* ratio of 2a' was tentatively determined as *E/Z* = 19/81 from the ratio of two vinyl protons of <sup>1</sup>H NMR spectroscopy.<sup>8</sup> This observed preponderance of Z isomer clearly indicates that the *cis* addition proceeded at least to a considerable extent.



Although it may be premature to discuss the reaction mechanism, a possible reaction path for this Pd(OAc)<sub>2</sub>-catalyzed hydroselenation is envisioned in Scheme 2. The reaction is initiated by the substitution of acetoxy ligands on palladium for PhSe group with generation of acetic acid, followed by coordination of acetylene to the palladium complex and regioselective insertion of the triple bond into Pd-Se bond. The resulting *cis* vinylpalladium intermediate is trapped by PhSeH or AcOH with retention of the stereochemistry to produce the Markovnikov adduct with regeneration of the catalyst.



Scheme 2. A Possible Reaction Path for the Pd(OAc)<sub>2</sub>-Catalyzed Hydroselenation of Terminal Acetylene

Table 1 summarized the results of the hydroselenation of 1a with PhSeH using other transition-metal catalysts. A variety of transition metal catalysts, namely, platinum, palladium, rhodium, and nickel complexes, exhibited the catalytic activities for this reaction. When Pt(PPh<sub>3</sub>)<sub>4</sub> was employed as a catalyst, 4a was obtained in good yield. It has already reported that the stoichiometric reaction of PhSeH with Pt(PPh<sub>3</sub>)<sub>4</sub> gave the Pt(PPh<sub>3</sub>)<sub>2</sub>(SePh)(H).<sup>9</sup> Thus, when the reaction of a mixture of 2a and 4a (2a:4a = 80:20) with 2 mol% of Pt(PPh<sub>3</sub>)<sub>4</sub> and 30 mol% of PhSeH was carried out at 80 °C for 15 h, the ratio was changed to 2a:4a = 7:93. This fact may suggest that 2a is a kinetic product and isomerizes to 4a promoted by the Pt-H species in this reaction system.

catalyst	2a	3a	<b>4a</b>	5a	catalyst	2a	3a	4a	5a
Pt(PPh <sub>3</sub> ) <sub>4</sub>	9%	•	81%	•	Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl <sub>2</sub>	15%	-	7%	15%
Pd(PPh <sub>3</sub> ) <sub>4</sub>	2%	•	48%		Ni(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	13%	-	-	-
PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	3%	•	72%	•	PdCl <sub>2</sub>	34%	16%	24%	-
PdCl <sub>2</sub> (PhCN) <sub>2</sub>	4%	-	68%	-					

Table 1. Hydroselenation of 1-Octyne (1a) in the Presence of Several Transition Metal Catalysts<sup>a</sup>

<sup>a</sup>Reaction conditions: catalyst (0.02 mmol), 1a (1.0 mmol), and PhSeH (1.0 mmol), PhH (0.5 mL), 80 °C, 14-16 h. Yields were determined by GLC or <sup>1</sup>H NMR.

Although organic selenide have been widely accepted as catalyst poisons,<sup>10</sup> this paper clearly reveals that benzeneselenol can be successfully employed in transition-metal-catalyzed reaction.<sup>11</sup> Our efforts are continuing with emphases on the scope and mechanism of these catalytic transformations.

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