## A Convenient and Stereoselective Synthesis of (E)-Vinylseleno Zirconocenes and (E)-Vinylic Selenol Esters

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Abstract: The insertion of elemental selenium into the Csp<sup>2</sup>-Zr bond of alkenylchlorozirconocenes affords (E)-vinylseleno zirconocenes, which were trapped by acyl chlorides giving (E)-vinylic selenol esters in good yields.

Key words: hydrozirconation, vinylseleno zirconocenes, vinylic selenol esters

Recently transition metal selenolates have been widely used in synthesis of selenides due to their good nucleophilicity in aprotic solvents.<sup>1</sup> The following intermediates have been reported: ArSeZnCl,<sup>1</sup> ArSeCu,<sup>2</sup> ArSeSmI<sub>2</sub>,<sup>3</sup>  $Cp_2TiSeAr$ ,<sup>4</sup>  $Cp_2Zr(SeMe)_2$ ,<sup>5</sup>  $Cp_2Hf(SeMe)_2,^5$ and  $Cp_2ZrSe_2C_6H_4-o^6$  and they have complemented in reactivity the known main group metal selenolates, such as Ar-SeNa,<sup>7</sup> Me<sub>2</sub>AlSeMe,<sup>8</sup> ArSeTl.<sup>9</sup> Vinylic selenolates are important intermediates for vinylic selenides, whose promising potential could be anticipated by the combination of the special reactivity of selenium and particularly reactivity associated with the carbon-carbon double bond.<sup>10</sup> Herein we report the first example of vinylseleno transition metal complexes, and its application in facile synthesis of (E)-vinylic selenol esters. Although vinylic bromomagnesium selenolate<sup>11</sup> and vinylic lithium selenolate<sup>12</sup> have been reported, it is safe to say that vinylseleno transition metal complexes will complement in reactivity the main group metal selenolates.



Typical procedure: To the stirred suspension of 1.2 mmol Cp<sub>2</sub>Zr(H)Cl<sup>13</sup> in 8 ml THF (freshly distilled from sodium and benzophenone) under N2 atmosphere was added dropwise 1mmol phenylacetylene through a syringe. The mixture was stirred until it turned into a clear solution, then was added dropwise by a syringe into the stirred suspension of 1.2 mmol selenium powder in 2 ml THF(disposed as above), the mixture turned gradually from a dark yellow-green suspension into a deep red solution during 0.5 hours. Then 1 mmol CH<sub>3</sub>COCl was added dropwise through a syringe, and the mixture was continued to be stirred for 4 hours. The solvent was removed under reduced pressure, and the product was extracted from the residue with diethyl ether (4 x 10ml), filtered, concentrated under reduced pressure and further purified by flash chromatography on silica gel (light petroleum ether-diethyl ether (10:1) as the eluent), affording the product **3a**.

The outcomes were summarized in Table 1.

Table 1. Synthesis of (E)-vinylic selenol esters from alkynes, elemental selenium and acyl chlorides.



<sup>a</sup> Bt=benzotriazol-1-yl <sup>b</sup> Isolated yields.

It is noteworthy that in our experiments the insertion of elemental selenium into Csp<sup>2</sup>-Zr bond proceeds smoothly in THF at room temperature(about 10 °C) and usually completes in 30min., while Gautheron B. et al reported similar reactions between Se and t-Bu-zirconocene dimethyl or diphenyl in boiling heptane for several hours.<sup>5,6</sup>

Selenol esters<sup>14</sup> are synthetically useful compounds as precursors of acyl radicals and acyl cations. They can also be easily converted into the corresponding acids, esters, amides, ketones, aldehydes, and alkenyl selenides.<sup>15</sup> In particular, vinylic selenol esters are very versatile selenium derivatives which can serve as good electron acceptors to generate cleanly vinylic selenide anions under mild conditions<sup>12a</sup> and other applications.<sup>12b</sup> However, according to our knowledge, the only reported synthetic method of vinylic selenol esters involved demethylation of vinylic methyl selenides with excessive MeSeLi under severe conditions or sodium in DMA, followed by carbonylation of the produced vinylic selenide anions.<sup>12</sup> In comparison, our method is more attractive. It should be pointed out that apart from the 1-alkynes employed in Scheme 1, various internal alkynes, alkenes, functionalized alkynes and alkenes can proceed hydrozirconation reaction smoothly and stereoselectively,16 moreover, all the reagents in Scheme 1 are commercially available, as a result, the present method has provided a versatile, convenient route to various selenol esters other than (E)-vinylic selenol esters.

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- (17) Physical and spectroscopic data of (*E*)-3-(benzotriazol-1-yl) propenyl acetyl selenide(**3d**): yellowish solid, mp 69-70 °C (uncorrected). <sup>1</sup>H NMR(CCl<sub>4</sub>, Hexamethyldisilane as the internal standard):  $\delta$ 8.06-7.93(m, 1H), 7.62-7.13(m, 3H), 6.93(d, 1H, J = 15.6Hz), 6.03(dt, 1H, J = 15.6 and 6.0Hz), 5.24(d, 2H, J = 6.0Hz), 2.30(s, 3H). IR(KBr) v[cm<sup>-1</sup>]: 1736(C = O), 1358, 1320, 1268, 1236, 1164, 1108, 976, 946, 738, 576. MS(m/z):282(m<sup>+</sup>+1, <sup>80</sup>Se). Anal. Calcd. for C<sub>11</sub>H<sub>11</sub>N<sub>3</sub>OSe: C%, 46.98; H%, 3.91; N%, 15.00. Found: C%, 47.18; H%, 3.59; N%, 15.11.

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