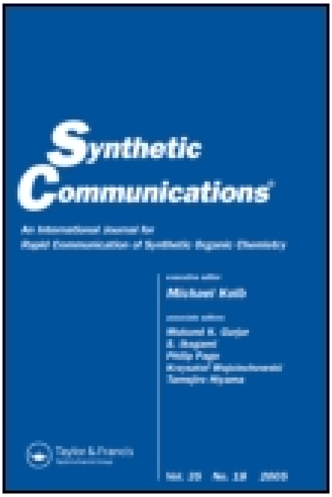

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Coupling Alkylation of (E)-α-Selanylvinylic Zirconium Compounds to Give Trisubstituted Alkenes

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COUPLING ALKYLATION OF (E)-α-SELANYLVINYLIC ZIRCONIUM COMPOUNDS TO GIVE TRISUBSTITUTED ALKENES

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Abstract: Hydrozirconation of internal acetylenic selenides afforded 1,1-bimetalloalkenes, (E)-α-selanylvinylzirconium, which can undergo sequential cross coupling reaction to form two carbon-carbon bonds in the same olefinic carbon leading to trisubstituted alkenes stereoselectively.

Many biologically active compounds occuring in nature possess the structual skeleton of trisubstituted alkenes.[1] Recently, many 1,1-, or 1,2-bimetalloalkenes are used widely in stereoselective synthesis of trisubstituted alkenes. In a previous paper, we have shown the first example of the hydrozirconation of 1-phenylselenoacetylenes to obtain (E)-2-selanylvinylzirconium compounds as a 1,2-bimetalloalkenes of selenium and zirconium, and also have studied their application for synthesis of (E)-disubstituted alkenes. As an extension of our studies, in this paper, we studied the reactivity of hydrozirconation of internal acetylenic selenides, in order to develop a new method for stereoselective synthesis of trisubstituted alkenes.

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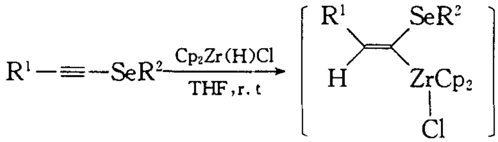
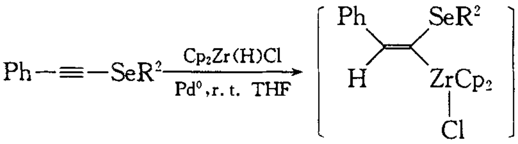
The results indicated that internal alkylacetylenic selenides **1** can undergo hydrozirconation easily, the reaction is a *cis* addition, but the regioselectivity is different from the hydrozirconation of 1-phenylselenoacetylenes, which obtained (E)-1-selanylvinylic zirconium compounds **2** (R^1=alkyl). (**Scheme 1**) Obviously the regiochemistry of this reaction is determined by electrochemical effect. Hydrostannation[2] and hydroboration[3] of internal alkylselenoacetylenes also have the same situations.



1 **2**

Scheme 1

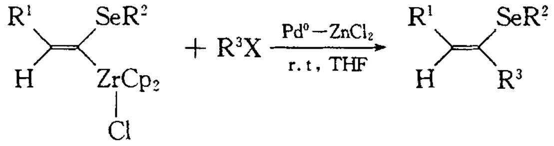
The above method can not be suitable to the hydrozirconation of phenylacetylenic selenides even extending the time or raising the temperature. Recently, it was reported that palladium-complexes can catalyze hydrostannation and hydroboration of alkynes.[4,5] Thus we tried to use the catalytic palladium method on hydrozirconation of phenylacetylenic selenides. The experimental results show that in the presence of 5%mmol $Pd(PPh_3)_4$, the hydrozirconation of phenylacetylenic selenides can be completed in an hour at room temperature(**Scheme 2**).



3 **4**

Scheme 2

The (E)-α-selanylvinylzirconium compounds **2** and **4** can not need to be isolated and in the presence of Pd(PPh_3)$_4$ and $ZnCl_2$ it can take cross-coupling reaction with alkyl halides directly. The experimental results show that intermediates 1,1-bimetalloalkenes cross coupled with alkyl halides to afford a convenient method for the synthesis of disubstituted vinylic selenides **5**. (**Scheme 3**)



(R^1=alkyl or Ph)

2 or **4** **5**

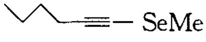
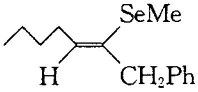
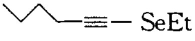
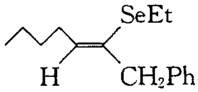
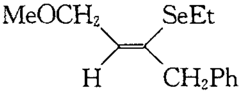
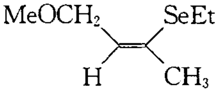
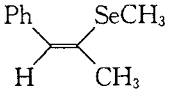
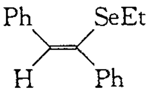
Scheme 3

The regio- and stereo- chemistry were established by ^1H NMR measurements. One olefinic proton of (Z)-disubstituted vinylic selenides **5a-d** was characteristically split into triplet with coupling contant J about 7.2 Hz, which indicates that the hydrozirconation of internal alkylselenoacetylenes with $Cp_2Zr(H)Cl$ proceeds with strong preference for the addition of the zirconium atom at carbon adjacent to the alkylseleno group.

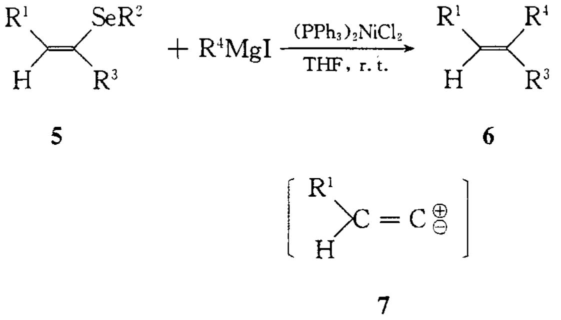
(Z)-Disubstituted vinylic selenides are also effective precursors for synthesizing stereodefined trisubstituted alkenes. We carried out the coupling reaction of (Z)-1-ethylseleno-1-phenyl-phenylethene **5f** with Grignard reagent R^4MgI in the presence of Ni(PPh_3)$_2Cl_2$ to provide (Z)-1-methyl-1-phenyl-phenylethene **6f** (**Scheme 4**).

As (E)-1-selanylvinylzirconium compounds **2** and **4** undergo a two-step cross-coupling reaction to form two carbon-carbon bonds on the same olefinic carbon and allow the synthesis of trisubstituted alkenes

Table 1 Hydrozirconation of internal acetylenic selenides with $Cp_2Zr(H)Cl$ followed by cross-coupling reaction

Entry	Internal alkylselenoacetylenes	Disubstituted vinylic selenides	Yield[a] (%)
5a			75
5b			78
5c	$MeOCH_2-\equiv-SeEt$		80
5d	$MeOCH_2-\equiv-SeEt$		85
5e	$Ph-\equiv-SeMe$ [b]		70
5f	$Ph-\equiv-SeEt$ [b]		62

a Isolated Yield. b in presence of $Pd(PPh_3)_4$.



6f $R^1=Ph, R^2=Et,$
$R^3=Ph, R^4=CH_3$
Yield: 63%

Scheme 4

stereoselectively, **2** and **4** can be regarded as the equivalent of the cation-anion synthon **7**. In summary, compared to other methods that have been reported, our method for the synthesis of stereodefined trisubstituted alkenes has the advantages of simple procedure, mild conditions and convenient isolation of products.

Experimental

IR spectra were obtained as films on shimadzu IR-440 spectrometer. ^1H NMR spectra (chemical shifts in ppm from internal TMS) were measured on a Bruker AM-300 spectrometer at 300 MHz with $CDCl_3$ as solvent. Mass spectra were recorded on Finnigan GC-MS 4021 or MHT8430 mass spectrometers.

A typical procedure for the preparation of 5a-d is as follows

To a solution of $Cp_2Zr(H)Cl$ (4 mmol) in THF (10 ml) was added alkylselenoacetylenes $R^1-\equiv-SeR^2$ (4 mmol) at room temperature under nitrogen, stirred for about half an hour at r. t, the precipitate dissolved, solution turned from yellow to green. To this mixture was then added $ZnCl_2$ (4 mmol), $Pd(PPh_3)_4$ (4×5% mmol), R^3X (4 mmol), at r. t stirred for about an hour. The mixture was treated with sat. aq Na_2CO_3 (15ml). The phase was separated, dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was purifed by flash chromatography on a 3ft×1 inch column (100—200 mesh) with light petroleum (bp. 30—60°C) as eluent to give **5**.

(Z)-1-methylseleno-1-benzyl-1-hexene (5a)

^1H NMR: δ=7.3—7.0(m,5 H),6.25(t,1 H),4.31(s,2 H),2.40(s,3 H),1.9—2.33(m,2 H),0.95—1.58(m,7 H). IRν(cm^{-1}):1630,807. MS m/z:268(M—1).

(Z)-1-ethylseleno-1-benzyl-1-hexene (5b)

^{1}H NMR: δ=7.25—7.0(m,5 H),6.27(t,1 H),4.33(s,2 H),2.75(q,2 H),1.87—2.25(m,3 H),2.0—2.32(m,2H),0.93—1.84(m,7 H). IRν (cm^{-1}):1631,808. MS m/z:282(M—1).

(Z)-1-ethylseleno-1-benzyl-3-methoxy-1-propene (5c)

^{1}H NMR: δ=7.20—6.95(m,5 H),6.29(t,1 H),4.32(s,2 H),3.88(d, 2 H),3.25(s,3 H),2.70(q,2 H),1.41(t,3 H). IRν(cm^{-1}):1609,775. MS m/z:269(M—1).

(Z)-1-ethylseleno-1-methyl-3-methoxy-1-propene (5d)

^{1}H NMR: δ=6.25(t,1 H),3.87(d,2 H),1.90(s,3 H),2.71(q,2 H), 1.42(t,3 H). IRν(cm^{-1}):1610,780. MS m/z:193(M—1).

General Procedure for the synthesis of 5e,5f. To a solution of $Cp_2Zr(H)Cl$ (4 mmol) in THF (10 ml) was then added $Pd(PPh_3)_4$ (4 × 5% mmol), stirred for 30 min to make $Cp_2Zr(H)Cl$ insert to $Pd(PPh_3)_4$ adequitly. To the solution injected Ph—≡—SeR^2(4 mmol), stirred at r.t for 1 hr, after the hydrozirconation, the following procedure was the same as the synthesis of **5a-d.**

(Z)-1-methylseleno-1-methyl-phenylethene (5e)

^{1}H NMR: δ=7.50—7.0(m,5 H),6.81(s,1 H),1.95(s,3 H),2.41(s,3 H). IRν(cm^{-1}):1660,1590,1544,805. MS m/z:211(M—1).

(Z)-1-ethylseleno-1-phenyl-phenylethene (5f)

^{1}H NMR: δ=7.80—7.0(m,10 H),6.78(s,1 H),2.74(q,2 H),1.48(t, 3 H). IRν(cm^{-1}):1650,1598,806. MS m/z:288(M—1).

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