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From vinyl sulfides, sulfoxides and sulfones to vinyl zirconocene derivatives

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Abstract—An easy and straightforward new method for the preparation of sp^2 zirconocene derivatives from a wide range of heterosubstituted alkenes such as vinyl sulfides, sulfoxides and sulfones is described. In all cases, a complete isomerization of the stereochemistry is observed and only the *E*-isomer is obtained. The reactivity of the resulting vinylic organometallic can be increased by a transmetalation reaction into organocopper, organozinc or organopalladium species and, therefore, several carbon–carbon formation were easily realized.

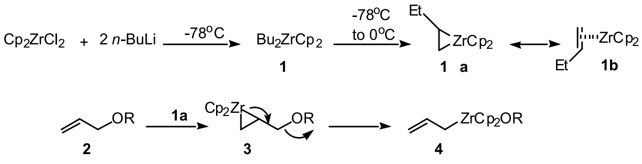
1. Introduction

Although numerous methods for the preparation of sp^2 organometallic derivatives are known in the literature and widely used in synthesis,[1] there are still some very challenging synthetic transformations such as the preparation of vinylic organometallics from oxygen- and sulfur heterosubstituted alkenes. As the importance of the sulfoxide and sulfone moieties stem from their application in carbon–carbon bond formations, including asymmetric synthesis, and this in turn derive from key aspects of their properties and reactivity, outstanding applications were found in organic synthesis.[2] In these applications, sulfoxides and sulfones are, therefore, mostly synthetic tools, which must be disposed of at the end of the sequence.[3] As a potentially very interesting transformation, the preparation of organometallic derivatives from vinyl sulfoxides or sulfones should be synthetically very useful since further functionalization will increase the complexity of the carbon skeleton. The only reported example was the transformation of vinyl phenyl sulfide into vinyl lithium derivatives via reductive metalation.[4] This method involves the reductive lithiation of alkenyl phenyl sulfides by means of either a stoichiometric amount of radical anion lithium *p*,*p*′-di-*tert*-butylbiphenylide (LDBB) or an excess of lithium metal in the presence of a catalytic amount of *p*,*p*′-di-*tert*-butylbiphenyl (DBB; 5% mol).[5] Such transformations failed on vinyl alkyl sulfides.[5,6] Although conceptually simple, the transformation of sulfur heterosubstituted alkenes into organometallic derivatives was not addressed (except for vinyl aryl sulfide) and was therefore a very interesting challenge to solve.

In this paper, we would like to report in full our results concerning these transformations.[6]

Over the past two or three decades, organozirconium derivatives have emerged as being synthetically useful reagents or intermediates in organic synthesis and their incredible efficiency, coupled to their unique ability to promote unusual transformations have aroused the imagination of chemists.[7] As particular example, we were recently interested by a side product, originally described by Negishi,[8] obtained when the diallyl ether **2** (R=C_3H_5) was treated with the zirconacyclopropane **1a** (easily prepared by the treatment of Cp_2ZrCl_2 with two equiv of *n*-BuLi in THF, and also called Negishi Reagent).[9] Instead of producing the desired zirconabicycle, the reaction gave the allylzirconocene derivative **4** via the addition product **3** followed by a β-elimination as described in Scheme 1.

This originally unwanted side reaction has proved to be a synthetically useful route to allylzirconocene derivatives, as nicely demonstrated by Hanzawa and Taguchi.



Scheme 1.

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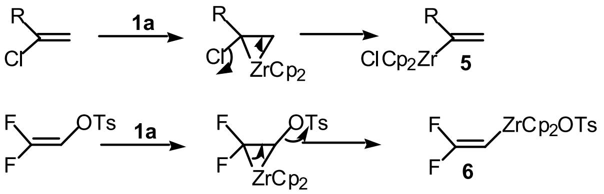
Therefore, several allylic,[10] allenic,[11] γ[12]- and γ,γ-alkoxy allylic[13] zirconium species were prepared.[14] So, although the direct insertion of organometallic derivatives into the carbon-ether bond is impossible, a two-step mechanism allows their easy preparations. This strategy was also developed for the selective cleavage of allylic ether derivative.[15] However, this concept of addition-β-elimination was only sporadically used for the preparation of vinyl zirconium derivatives. The initial report, published by Takahashi et al., was the preparation of **5** by reaction of 2-chloroalkene derivatives[16] with **1a**. Recently, Ichikawa and Minami successfully applied this strategy[17] for the synthesis of fluorinated vinyl zirconium moieties **6** (Scheme 2).



Scheme 2.

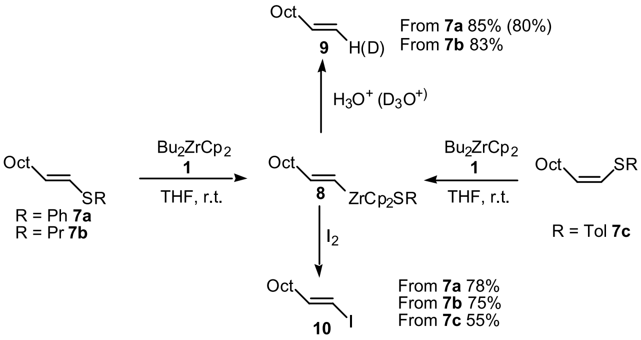
In both cases, a good leaving group was used (halide or tosyloxy groups) for the β-elimination reaction and no information on the stereochemical outcome of this reaction was disclosed.[18] On the other hand, when the difluoroolefin bears a substituent with a lower leaving-group propensity than that a fluorine (i.e., OPh or OMEM), the preferential elimination of fluoride occurs in low yield (respectively, 17 and 32% yield).[17]

2. Results and discussions

So, we reasoned that the combined addition–β-elimination mechanism could be an interesting way to prepare specific vinylic organometallic derivatives from sulfur-heterosubstituted olefins. Indeed, from the mechanistic interpretation given in Scheme 2, the combination of an olefinic moiety (complexation with **1a**) with a vinylic heteroatom (leaving group present in the β-position of the zirconacyclopropane) should lead to the corresponding sp^2 organometallic derivatives via an addition–elimination sequence.

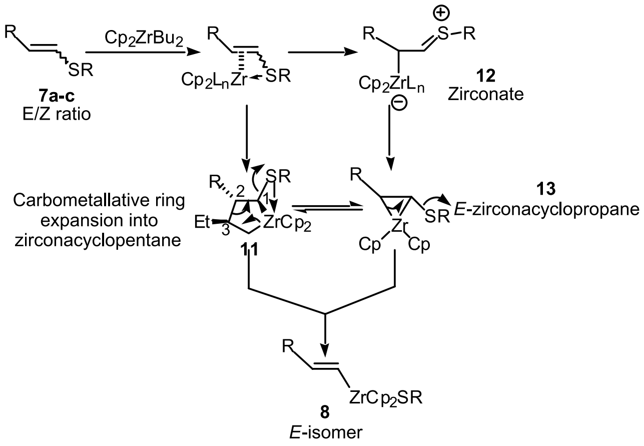
Our first attempt was directed to the preparation of vinylic zirconocene from vinyl phenyl sulfide; when **7a** was added to a slight excess of **1a**, generated by thermal decomposition of **1** in THF, and stirred at room temperature for few hours, the expected vinyl zirconocene **8** was obtained in excellent yield as determined by its hydrolyzed product **9**.

The formation of a discrete organometallic was first checked by deuteriolysis and iodinolysis to give **9** and **10** in 80 and 78% yields, respectively (Scheme 3). The reaction also proceeds efficiently from the alkyl vinyl sulfide **7b**, and **9** and **10** are respectively obtained in 83 and 75% yields after hydrolysis or iodinolysis. Thus, no difference has been found in this reaction between alkyl and aryl sulfide. When the same reaction was now performed on the *Z*-isomer of the aryl vinyl sulfide **7c**, followed by the addition of iodine, only the *E*-vinyl iodide **10** was obtained. So, whatever be the stereochemistry of the initial vinyl sulfide, the reaction is >99% stereoselective but not stereospecific, producing only the *E*-vinyl zirconium in good overall yields. No, stereoisomerization of **7c** into **7a** was observed in the process, which indicates that zirconocene **1a** is not a catalyst for the isomerization of thioenol ether. This isomerization can be explained by a carbometallative ring expansion between **1a** and **7a–c** to lead to the corresponding five-membered ring zirconacycle **11** which may produce the three-membered zirconacyclopropane **13**, since facile equilibration among three- and five-membered zirconacycle have been already discussed for skeletal rearrangements.[19] If we consider the ligand exchange described in Scheme 2, the addition–β-elimination should lead to different geometrical isomers of the corresponding vinyl zirconium derivatives **8** when starting from the *E*- or *Z*-isomers of vinyl sulfides (**7a** and **7c**, respectively). Therefore, more complicated intermediates are most probably involved during the complexation between the thioenol ethers **7a–c** and the zirconocene **1a** since we have a complete isomerization reaction. Our first hypothesis was that the initial step proceeds via a dipolar zirconate species[20] represented by **12**, followed by an isomerization reaction leading to the *trans* zirconacyclopropane **13**.[21] Then, after a β-elimination step, the corresponding *E*-vinyl zirconium should be obtained. Although this mechanistic interpretation was attractive, a stereochemical problem remains for the elimination reaction since an angle of 180° (*anti*-elimination) or 0° (*syn*-elimination) is usually required for an elimination reaction. In this case, an angle of 120° is expected in the zirconacyclopropane **13** (Scheme 4).



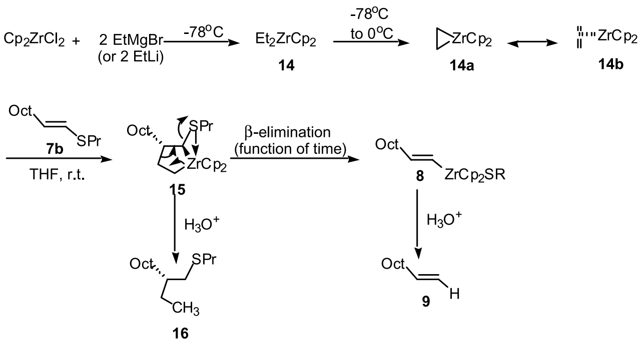
Scheme 3.

Now, if we consider the carbometallative ring expansion to produce the corresponding five-membered zirconacycle **11**, the carbon–heteroatom bond of the sp^3 metallated center C_1 should isomerize to produce the most stable intermediate. Such isomerization could be due to an interaction between the sulfur moiety and the zirconium atom,[22] which would produce a weakness of the C_1–Zr bond and would facilitate the isomerization. Thus, whatever the stereochemistry of the starting material, a conformation is always possible in which C_1–SR is antiperiplanar to C_2–C_3 in **11**. The elimination reaction or decarbozirconation, occurs in a concerted way to give the *E*-vinyl zirconium **8**. Unfortunately, neither the zirconacyclopentane nor the zirconacyclopropane have been trapped as intermediates. On the other hand, Cp_2ZrEt_2 **14** is known to give zirconocene-ethylene complex $Cp_2Zr(CH_2{=}CH_2)$ **14a** in a similar way to **1a**, but



Scheme 4.

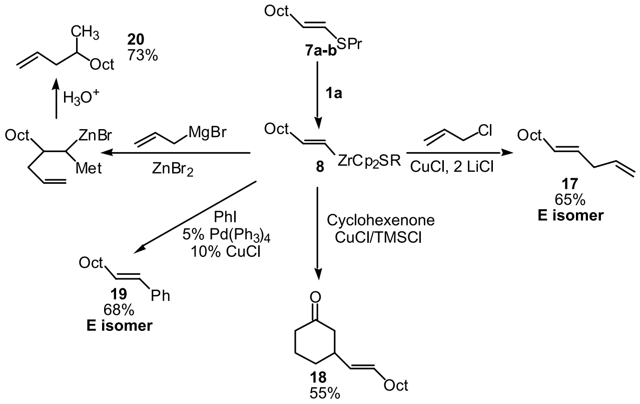
the behavior of the ethylene ligand is very different, in most cases, from the butene moiety of the zirconocene–butene complex **1b**.[23] Indeed, the ethylene ligand reacts with various unsaturated compounds and as it is usually incorporated in the reaction products, we were interested to see if it could be also incorporated into the vinyl sulfide **7b**. Cp_2ZrEt_2 was easily prepared by treatment of 2 equiv. of EtMgBr (and by also 2 equiv. of EtLi to check that there is no salt effects) with Cp_2ZrCl_2 to furnish **14**, which was then treated with **7b** at room temperature. The addition product **15** is rapidly observed by analysis by gas chromatography of aliquots after hydrolysis, which is followed by the elimination reaction to give the vinyl zirconium species **8** and ethylene. Both of the intermediates and the product were trapped by hydrolysis (Scheme 5). Although the formation of the vinyl zirconium **8** is slower in this particular case (only 2–3 h were necessary for the formation of **8** from **7b** and **1a**), we can clearly see that the addition product **15** undergoes a subsequent β-elimination reaction to give the expected product **8** (Table 1).



Scheme 5.

Table 1. Apparition of **9** after β-elimination of **15** followed by hydrolysis

Reaction time	**16** (%)	**9** (%)
20 min	90	10
2 h	70	30
3 h	50	50
10 h	30	70



Scheme 6.

Thus, from these mechanistic studies, we believe that the unique formation of the *E*-isomer results from a carbometallative ring expansion into zirconacyclopentane followed by an elimination reaction.

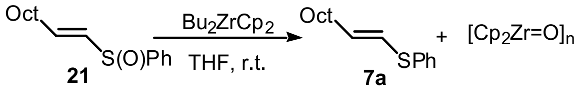
The scope of the reaction can be broader since vinyl zirconocenes can be transmetallated into more reactive species as described in Scheme 6.[24]

Indeed, addition of a catalytic amount of copper chloride in the presence of lithium chloride[25] leads to the corresponding *E*-vinyl copper derivative. The latter reacts either via a S_N2' process with allyl chloride (**17** in 65% yield) or in a 1,4-addition manner with cyclohexanone in the presence of TMSCl[26] (**18** in a non-optimized 55% yield). The palladium-catalyzed cross-coupling reaction of **8** with aryl iodide opens a new route to further functionalization as shown by the formation of **19** in 68% yield. Finally, the transmetalation of the vinyl zirconium **8** to zinc bromide followed by the addition of allylmagnesium bromide leads to new bismetallated species (**20** after hydrolysis in 73% yield).[27]

We were then interested to extend this methodology to the transformation of vinyl sulfoxides into vinylic organometallic derivatives. Indeed, the stereogenic sulfur atom in sulfoxides is configurationally stable at room temperature and thus sulfoxides may be chiral based on this property alone.[28] Therefore, reactions of chiral sulfoxides found extensive applications in Asymmetric Synthesis.[29] However, in most cases, once the new chiral centers are created, sulfoxides have to be removed in subsequent chemical steps. Although the replacement of sulfoxide moiety in vinyl sulfoxide by hydrogen atom can be performed by using different metals such as Na/Hg or activated zinc,[30] the transformation of vinyl sulfoxide into vinylic organometallic derivatives was unknown.

When *E*-vinyl sulfoxide **21** was treated with 1.5 equiv. of **1a** in THF at −78 °C and warning up the reaction mixture to room temperature, we obtained the corresponding sulfides **7a** instead of the expected vinyl zirconium derivative **8**. Therefore, vinyl sulfoxides are reduced with **1a** into the corresponding vinyl sulfide with concomitant formation of the insoluble polymer $[Cp_2Zr{=}O]_n$ (Scheme 7).

Low-valent group 4 organometallic derivatives such as



Scheme 7.

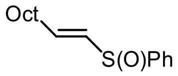
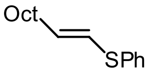
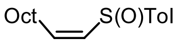
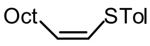
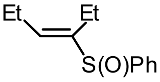
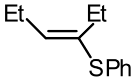
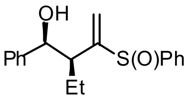
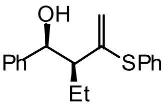
bis(trimethyl)phosphine zirconium derivatives are know to reduce CO_2 into CO and Cp_2ZrO polymer.[31] Thus, Bu_2ZrCp_2 **1** is also a very mild reducing agent of sulfoxides into sulfides with formation of the easily removable $[Cp_2ZrO]_n$ by simple filtration at the end of the sequence. As shown in Table 2, the scope of the reaction is relatively broad.

Diaryl, aryl–vinyl, aryl–alkyl sulfoxides were reduced in 1 to 2 h at room temperature in good to excellent yields (entries 1–6). Trisubstituted vinyl sulfoxides undergo also the transformation in good isolated yield. Whatever the stereochemistry of the vinyl sulfoxide (compare entries 2 and 3), the reduction occurs into the corresponding vinyl sulfide without isomerization of the double bond. Finally, even sulfoxide bearing two stereogenic centers on its carbon skeleton as in entry 5 can be reduced without any change in the stereochemical purity of the substrate. In this particular case, 2 equiv. of **1a** were used.

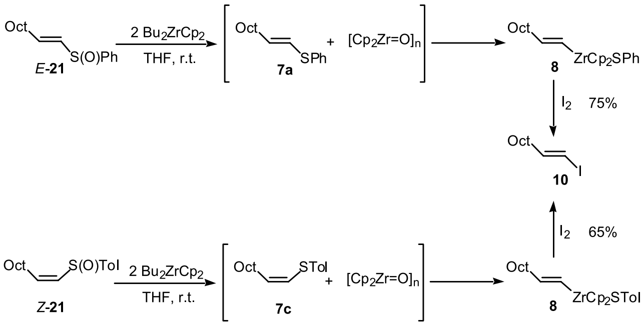
However, our main research goal was the preparation of vinyl zirconocene derivatives from vinyl sulfoxides and not its reduction. As sulfoxides can be easily transformed into sulfides and sulfides can be further transformed into vinylic organometallics, the expected vinylic organometallic derivatives have been obtained in a single-pot operation from sulfoxides by treatment with 2 equiv. of Bu_2ZrCp_2 as described in Scheme 8.

The first equivalent of **1a** reduces the vinyl sulfoxides *E*- and *Z*-**21** into the vinyl sulfide **7a** and **7c**, respectively, without any isomerization of the double bond and then, the second equivalent of **1a** transforms the vinyl sulfides **7a**,**c** into the corresponding organometallics with a complete isomerization of the double bond as discussed in Schemes 3 and 4. Reaction of *E*-**8** with iodine led in both cases to the *E*-vinyl iodide **10** in good overall yields.

Table 2. Reduction of sulfoxides into sulfides with Bu_2ZrCp_2

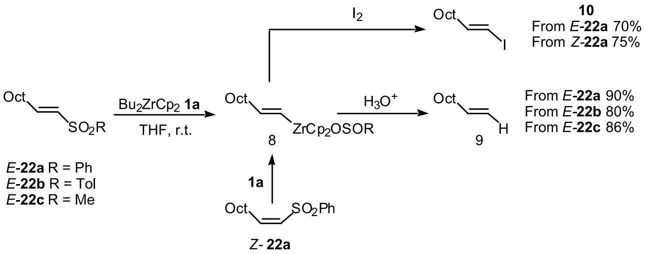
Entry	Sulfoxides	Sulfides	Yield[a]%
1	PhS(O)Ph	PhSPh	95
2			80
3			81
4			85
5	$C_{12}H_{25}S(O)Tol$	$C_{12}H_{25}STol$	73
6			92

[a] Yield of isolated products after purification by column chromatography.



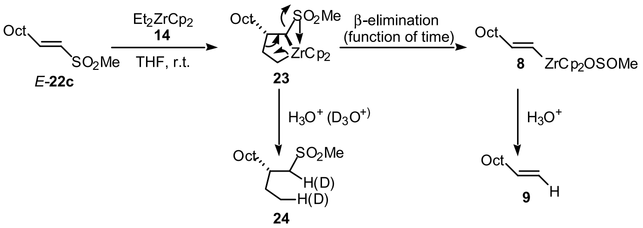
Scheme 8.

Finally, we turned our attention to vinyl sulfones. Indeed, although sulfones were extensively used for the creation of carbon–carbon bonds, the transformation into vinylic organometallic derivatives was simply unknown. To date, the available method for the replacement of sp^2 sulfone falls roughly into three categories: those resulting in replacement of the sulfone by hydrogen (reductive desulfonylation),[32] those in which the sulfone removal is accompanied by a C–C bond formation (alkylative desulfonylation)[33] and finally those in which the sulfone is a good leaving group towards β-elimination reaction with formation of the sulfinate moiety (RSO_2^-).[34] When *E*-**22a–c** were treated with Bu_2ZrCp_2 **1a** in THF at room temperature, a very fast reaction was observed which lead to the expected alkenes **9** in excellent isolated yields after hydrolysis, whatever the nature of the group on the starting sulfone (R=Ph, Tol, Me, Scheme 9). By reaction with iodine, *E*-**10** was isolated from *E*-**22a** in 70% yield.



Scheme 9.

When the *Z*-vinyl sulfone **22a** is treated with **1a**, a complete isomerization also occurs as determined by the reaction of the resulting vinyl organometallic derivatives with iodine. Only the *E*-isomer of **10** was isolated with good chemical yield. In order to probe the formation of zirconacyclopentane **23** as reactive intermediates, the same reaction between *E*-**22c** and Et_2ZrCp_2 **14** was repeated (as described in Scheme 4 but with sulfone instead of sulfide). Here again, the addition product **23** was rapidly formed at room temperature as determined by its hydrolyzed or deuteriolysis products **24** and **24**(*d*), respectively. Then, **23** disappear over time in favor of **8** (Scheme 10).



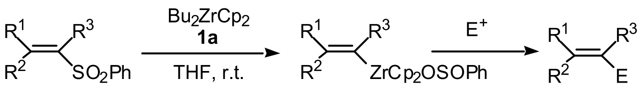
Scheme 10.

In order to extend the scope of the reaction, several polysubstituted vinyl sulfones were prepared and transformed into the corresponding vinylic organometallic derivatives as described in Table 3.

When β,β-disubstituted vinyl sulfones were treated with zirconocene **1a**, the expected products **25**, **27** and **29** were obtained in reasonably good yields (Table 3, entries 1, 3 and 5, respectively). The presence of an organometallic species was proved by trapping experiments either with MeOD (Table 1, entry 2 of unknown stereochemistry) or with iodine (Table 3, entry 4). Two geometrical isomers were obtained for the vinyl iodide **28** starting from two isomers for the corresponding vinyl sulfones. α,β-Disubstituted vinyl sulfones also undergo the transformation but only when one of the substituents is an aromatic group (either in α- or β-position as described in Table 3, entries 6–8). Only the *E*-isomer is obtained in these three cases. When the two substituents are alkyl groups, the reaction leads to several isomers, most probably due to subsequent isomerization of the resulting olefin (Table 3, entry 9). Interestingly, among all the isomers formed, no terminal double bond was detected. Finally, when cyclohexenyl sulfone was treated with **1a**, only a 40% yield of the cyclic organometallic was formed after iodinolysis (Table 3, entry 10).

From this study, we can deduce that β,β′-disubstituted—as well as α,β-disubstituted vinyl sulfones (but only when one substituent is aromatic) undergo the transformation but surprisingly not when substituents are alkyl groups. Apparently, the phenyl group induces a particular stabilization of the zirconacycle intermediate that leads to a complete stereoselective formation of the *E*-vinyl zirconium whereas in its absence, an isomerization occurs and, therefore, a loss of stereoselectivity.

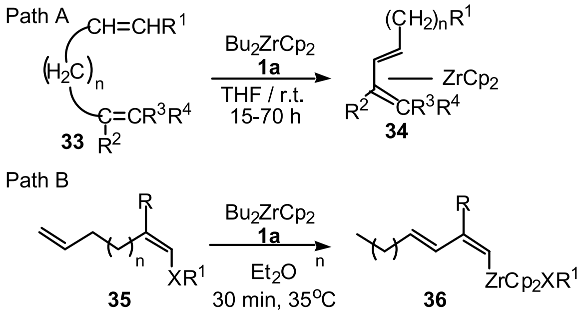
Table 3. Preparation of polysubstituted vinyl zirconocenes



Entry	R^1	R^3	R^2	E^+	Products	Yield (%)[a]
1	Oct	H	Bu	H_3O^+	**25**	70
2	Oct	H	Bu	MeOD	**26**	60
3	Oct	H	Me	H_3O^+	**27**	68
4	Oct	H	Me	I_2	**28**	67
5	Ph	H	Bu	H_3O^+	**29**	64
6	Ph	Me	H	H_3O^+	**30**	70
7	Me	Ph	H	H_3O^+	**30**	60
8	Ph	Et	H	H_3O^+	**31**	65
9	hept	Me	H	H_3O^+	/	/
10	$(CH_2)_4$	$(CH_2)_4$	H	I_2	**32**	40

[a] Yields after purification by column chromatography.

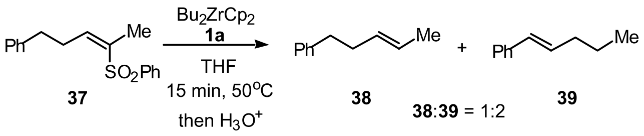
On the other hand, it is well known that transition metal catalyzed isomerization of terminal olefins into internal olefins and in general a mixture of 1-alkenes, (*E*)- and (*Z*)-2-alkenes, reflecting the thermodynamic equilibrium, is obtained.[35] Some low-valent titanocene derivatives are highly effective and stereoselective in favor of the (E)-2-isomer.[36] When non-conjugated dienes such as **33** containing one or two substituted vinyl groups are treated with zirconocene **1a**, a regioisomerization of the less-substituted double bond occurs and lead to the formation of the conjugated diene–zirconocene complexes **34** (Scheme 11, path A).[37]



Scheme 11.

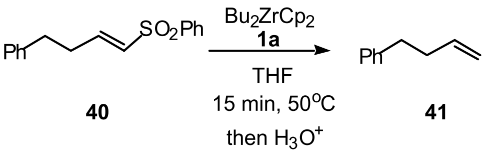
We have recently used this concept of isomerization for the stereoselective preparation of dienyl zirconocene **36** derivatives in a single-pot operation for substituted enol ether **35** (Scheme 11, Path B).[38]

Therefore, we have examined the case of 4-phenyl-sulfonyl-pent-3-enylbenzene **37**, as dialkyl substituted vinyl sulfone, but with also an aromatic group in a remote position of the alkyl chain to see if we have an isomerization reaction. The reaction of **37** with **1a** lead to the expected *trans* isomer **38** but also to the isomerized product **39** in a 1:2 ratio, respectively, in 60% combined yield as described in Scheme 12.



Scheme 12.

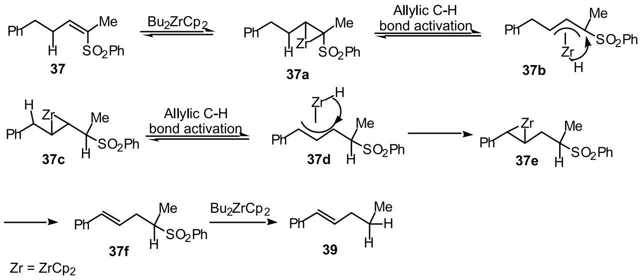
Here again, no traces of terminal olefin that could result from the isomerization to the opposite side of the molecule were detected. The isomerization occurs towards the most stable isomer in which the double bond is conjugated with the phenyl ring. More surprisingly, when iodine was added at the end of the reaction to potentially trap organometallic derivatives, no iodinated products were detected. On the other hand, when terminal vinyl sulfone **40** with the same remote aromatic ring was treated with **1a**, no isomerization reaction was found; only **41** was formed in 67% yield (Scheme 13).



Scheme 13.

From this experiment, we can conclude that alkyl substituents in α- and β-position of the olefin induce the isomerization process. As nothing is known on the exact nature of our intermediate, we must await further investigations to elucidate completely the mechanism of this reaction, but should arise most probably from the destabilization of the zirconacyclopropane intermediate (such as **13** in Scheme 4, compare Schemes 12 and 13).

Based on the reported data, we reasoned that α-substituted vinyl sulfones might undergo the isomerization towards the most stable alkene via a mechanism similar to the one described in Scheme 11. Indeed, **37** can react with **1a** to form the zirconacyclopropane **37a**, which undergo via a double allylic C–H bond activation (transformation of **37a** to **37e** by formation of two η^3-allyl intermediates **37b**,**d**). Once **37e** is formed, the zirconocene must be released (the sulfonyl moiety can eventually induce this release by intramolecular chelation) and induce the reduction of the sp^3 alkyl sulfone into **39** (see Scheme 14).



Scheme 14.

Although several pendant questions have to be solved to confirm this mechanistic hypothesis, we have already confirmed that zirconocene **1a** reduces efficiently primary sp^3 alkyl sulfone into the corresponding alkane. When iodine was added at the end of the reaction, minor amount of the alkyl iodide was formed confirming that primary alkyl sulfone undergo reductive desulfonylation most probably via single-electron transfer process.

In conclusion, by using zirconocene **1a**, we have been able for the first time to develop an easy and straightforward new method for the preparation of sp^2 zirconocene derivatives from a wide range of heterosubstituted alkenes such as vinyl sulfides, sulfoxides and sulfones. In all cases, a complete isomerization of the stereochemistry is observed and only the *E*-isomer is obtained. The reactivity of the resulting vinylic organometallic can be increased by a transmetalation reaction into organocopper, organozinc or organopalladium species and therefore, several carbon–carbon formation were easily realized. When more substituted vinyl sulfones such as β,β′-disubstituted- or α,β-disubstituted (with at least one substituent aromatic) were used, this method also leads to the corresponding organometallic derivatives. On the other hand, when α,β-disubstituted vinyl sulfones have only alkyl groups, an isomerization occurs to give a mixture of isomers. This isomerization can be used for the preparation of the most stable olefin if an aromatic group is present in the carbon skeleton.

3. Experimental

All our starting materials (vinyl sulfides,[39] vinyl sulfoxides[40] and vinyl sulfones[41]) were prepared by conventional methods described in the above references.

3.1. General procedure for the transformation of heterosubstituted alkenes into vinylic zirconocenes

A solution of *n*-butyllithium in hexane (1.6 M, 3.4 equiv., 3.4 mmol) was added slowly to a solution of bis(cyclopentadienyl)zirconium dichloride (1.7 equiv., 1.4 mmol) in dry THF (7 ml) at −78 °C. After the solution was stirred for 1 h at −78 °C, heterosubstituted alkene was added (1 equiv., 1 mmol) as solution in 3 ml of dry THF at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 3–5 h. The quantitative formation of the adduct was checked by gas chromatography. Then, the solution was cooled to −20 °C, and the electrophile was added. The reaction was warmed to room temperature and the mixture was diluted with ether and with an aqueous solution of HCl (1 M) [in case of transmetalation with CuCl, a mixture of saturated aqueous solution of NH_4Cl (2 equiv.) and aqueous solution of NH_4OH (25%, 1 equiv.) was used]. The aqueous phase was then extracted three times with ether. The combined organic phases were then washed successively with a solution of saturated aqueous sodium hydrogen carbonate, brine and water (in case of addition of iodine as electrophile, aqueous $Na_2S_2O_3$ was used), dried over $MgSO_4$, and evaporated under reduced pressure. The residue was finally purified by column chromatography on silica gel.

Note. Reaction of vinyl sulfoxides *E*-**21** and *Z*-**21** according to the above mentioned procedure produced the corresponding vinyl sulfide.**7a**,**c**. By using 2.5 equiv. of Cp_2ZrCl_2 and 5 equiv. of *n*-BuLi, the desired vinyl zirconium derivative is obtained.

The reaction of β,β′- and α,β-disubstituted vinyl sulfones was carried out by using an excess of Cp_2ZrCl_2 (2 equiv.) with 4 equiv. of *n*-BuLi.

1-Decene (**9**). Purification by column chromatography on silica gel (eluent: hexane) gave a colorless liquid in 85% yield, spectrally identical with an authentic sample commercially available. ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.86 (t, 3H, J=6.4 Hz), 1.42 (m, 12H), 2.00 (m, 2H), 4.93 (m, 2H), 5.78 (m,1H).

(*E*)-1-Deuterio-1-decene (**9d**).[42] Purification by column chromatography on silica gel (eluent: hexane) gave a colorless liquid in 83% yield: ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.87 (t, 3H, J=6.56 Hz), 1.25 (m, 12H), 1.97–2.07 (m, 2H), 4.87–5.00 (d, 1H, J=16.85 Hz), 5.72–5.87 (m, 1H). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 14.21, 22.84, 29.16–29.86 (4C), 32.07, 33.92, 113.47 (t), 139.27.

(*E*)-1-Iodo-1-decene (**10**).[43] Purification by column chromatography on silica gel (eluent: hexane) gave a yellow liquid in 55–78% yield, spectrally identical with an authentic sample. ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm)

0.86 (t, 3H, J=5.89 Hz), 1.09–1.34 (m, 12H), 1.96–2.15 (m, 2H), 5.98 (d, 1H, J=15.3 Hz), 6.41–6.56 (m, 1H). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 14.19, 22.79, 28.51–29.83 (4C), 32.03, 36.16, 74.29, 146.98.

(*E*)-1,4-Tridecadiene (**17**).[44] The general procedure was performed as described above. When the formation of the vinyl zirconium was complete (checked by GC), 0.12 ml of allyl chloride (1.5 mmol, 1.5 equiv.), copper chloride (0.1 mmol, 10 mg, 0.1 equiv.) and lithium chloride (2 mmol, 85 mg, 2 equiv.) were added at 0 °C. Then, the solution was stirred at 50 °C for 5 h. After usual treatment, the residue was purified by column chromatography on silica gel (eluent: hexane) to give a colorless liquid in 65%. ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.88 (t, 3H, J=6.56 Hz), 1.11–1.25 (m, 12H), 1.98 (m, 2H), 2.73 (m, 2H), 4.89–5.05 (m, 3H), 5.34–5.45 (m, 1H), 5.71–5.83 (m, 1H).

(*E*)-1-Cyclohexanone-1-decene (**18**). The general procedure was performed as described above. When the formation of the vinyl zirconium was complete (checked by GC), 2-cyclohexene-1-one (2.5 equiv., 1.35 mmol, 0.13 ml), TMSCl (2.6 equiv., 1.41 mmol, 0.18 ml), copper chloride (0.1 equiv., 0.054 mmol, 5 mg) and lithium chloride (2 equiv., 1.08 mmol, 46 mg) were added at room temperature. Then, the solution was stirred at 60 °C for 6 h. After usual treatment, the residue was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate (30:1) to give a colorless liquid in 50% yield: ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.85 (t, 3H, J=6.79 Hz), 1.23 (m, 12H), 1.68 (m, 4H), 1.83–2.14 (m, 3H), 2.15–2.41 (m, 4H), 5.33–5.40 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 14.048, 22.63, 23.87, 28.84–29.67 (4C), 31.34, 31.62, 31.86, 41.51, 41.54, 47.71, 130.02, 132.93, 211.27.

(*E*)-1-Phenyl-1-decene (**19**).[45] The general procedure was performed as described above. When the formation of the vinyl zirconium was complete (checked by GC), phenyl iodide (0.26 g, 1.3 mmol, 1.3 equiv.), copper chloride (0.15 g, 1.5 mmol, 1.5 equiv.) and 5% of $Pd(PPh_3)_4$ (60 mg, 0.05 mmol) were added at room temperature. The solution was heated for 3 hr at 50 °C. After usual treatment, the residue was purified by column chromatography on silica gel (eluent: hexane) to give a colorless liquid in 68% yield. ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.88 (t, 3H, J=7.1 Hz), 1.29–1.52 (m, 12H), 2.15–2.25 (m, 2H), 6.17–6.29 (m,1H), 6.34–6.42 (d, 1H, J=15.99 Hz), 7.17–7.37 (m, 5H). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 14.06, 22.67, 29.26, 29.28, 29.41, 29.50, 31.91, 33.05, 125.92 (2C), 126.72, 128.44 (2C), 129.75, 131.24, 138.04.

4-Methyl-1-dodecene (**20**).[46] The general procedure was used as described above. When the formation of the vinyl zirconium was complete (checked by GC), zinc dibromide (1.9 equiv., 1.9 mmol, 0.43 g) was added at room temperature followed by addition of allylmagnesium bromide (1.9 equiv., 1.9 mmol, 0.85 M in ether, 2.24 ml) at −30 °C. Then, the mixture was warmed to room temperature for 3 h. After usual treatment, the residue was purified by column chromatography on silica gel (eluent: hexane) to give a colorless liquid in 73% yield. ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.83 (t, 3H, J=3.39 Hz), 0.86 (t, 3H, J=6.69 Hz), 1.24 (m, 15H), 1.77–2.11 (m, 2H), 4.88–5.02 (m, 2H), 5.64–5.87 (m, 1H). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 14.07, 22.67, 29.34–31.92 (8C), 31.92, 117.5, 135.6.

1-(Propylthio)-2-ethyl-decane (**16**). The general procedure was performed using EtLi or EtMgBr instead of *n*-BuLi. The starting material was the vinyl propyl sulfide **7b**. The reaction mixture was quenched with aqueous solution of HCl (1 M) after 1 h stirring at room temperature. The major product, 3-(propylthio)-ethyl-decane **16**, was purified by column chromatography on silica gel (eluent: hexane) to give a yellow liquid. ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.81–1.00 (m, 9H), 1.25–1.64 (m, 19H), 2.41–2.48 (m, 4H). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 10.83, 13.51, 14.07, 22.67, 23.12, 25.66, 26.73, 29.36, 29.64, 29.99, 31.92, 32.82, 35.03, 36.83, 39.54.

2-(2′-Deuterioethyl)-1-(1′-deuteriodecyl) methyl sulfone (**24**). The general procedure was performed using EtLi or EtMgBr instead of *n*-BuLi. The starting material was the vinyl methyl sulfone *E*-**22c**. The reaction mixture was quenched with MeOD after stirring for 1 h at room temperature after adding the starting material at −78 °C. After usual work up, two products were obtained. The minor product was *E*-1-deuterio-1-decene **9d** and the major product was 2-(2′-deuterioethyl)-1-(1′-deuteriodecyl) methyl sulfone **24**, which was purified by column chromatography on silica gel (hexane/ethyl acetate, 4/1) to give a yellow liquid. ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.84 (t, 5H, J=6.54 Hz), 1.07–1.55 (m, 17H), 1.96–2.05 (m, 1H), 2.86 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 9.83 (t), 13.98–34.91 (9C), 41.71, 57.99 (t). HRMS (ESI, methanol) Calcd for $C_{13}H_{26}D_2O_2S$ (MH+) 273.432, Found 273.4453.

Butyl-1-decene (**25**).[47] Purification by column chromatography on silica gel (eluent: hexane) gave a yellow liquid in 70% yield: ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.86 (t, 6H, J=6.67 Hz), 1.14–1.51 (m, 16H), 1.93–1.97 (m, 4H), 4.67 (s, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 22.50–42.78 (12C), 108.34, 150.39.

2-Butyl-1-deuterio-1-decene (**26**). Purification by column chromatography on silica gel (eluent: hexane) gave a yellow liquid in 60% yield: ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.87 (t, 6H, J=5.06 Hz), 1.24 (m, 16H), 1.94–2.01 (m, 4H), 4.69 (s, 1H). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 14.08–42.72 (12C), 108.37 (t), 150.37.

2-Methyl-1-decene (**27**).[48] Purification by column chromatography on silica gel (eluent: hexane) gave a yellow liquid in 68% yield: ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.86 (t, 3H, J=6.93 Hz), 1.17–1.50 (m, 12H), 1.69 (s, 3H), 1.98 (t, 2H, J=7.59 Hz), 4.65 (s, 2H).

2-Methyl-1-iodo-1-decene (**28**).[49] Purification by column chromatography on silica gel (eluent: hexane) gave a yellow liquid in 67% yield as a mixture of two isomers in a 1 to 1 ratio. ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.86 (t, 3H, J=6.46 Hz), 1.17–1.38 (m, 12H), 1.79 (s, 3H, the second isomer was singlet at 1.85 ppm), 2.17 (t, 2H, J=7.82 Hz), 5.79 (s, 1H, the second isomer was singlet at 5.82 ppm).

α-Butylstyrene (**29**).[50] Purification by column chromatography on silica gel (eluent: hexane) gave a yellow liquid in 64% yield: ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.86 (m, 3H), 1.07–1.53 (m, 4H), 2.49 (t, 2H, J=6.98 Hz), 5.05 (s, 1H), 5.25 (s, 1H), 7.13–7.43 (m, 5H).

***E*-β-Methylstyrene** (**30**).[51] Purification by column chromatography on silica gel (eluent: hexane) gave a colorless liquid in 70% yield: ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 1.87–1.90 (d, 3H, J=5.92 Hz), 6.15–6.32 (m, 1H), 6.37–6.46 (d, 1H, J=16.03), 7.15–7.36 (m, 5H).

***E*-β-Ethyl styrene** (**31**).[52] Purification by column chromatography on silica gel (eluent: hexane) gave a colorless liquid. Isolated yield 65% (0.095 g).^{1}H NMR: δ 7.21 (d, J=7 Hz, 2H), 7.09 (d, J=7 Hz, 2H), 6.33 (d, J=16 Hz, 1H) 6.25–6.11 (m, 1H), 2.19 (q, J=6.8 Hz, 2H), 0.95 (t, 6.8 Hz, 3H).

1-Iodo-1-cyclohexene (**32**).[53] The general procedure was performed. With an excess of Cp_2ZrCl_2 (3 equiv.) and *n*-BuLi (6 equiv.). After usual work up the residue was purified by column chromatography on silica gel (eluent: hexane) to give yellow liquid in 40% yield. ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.79–0.90 (m, 2H), 1.58–1.73 (m, 2H), 2.06–2.11 (m, 2H), 2.47 (m, 2H), 6.29–6.32 (m, 1H).

Pentyl-3-enylbenzene (**38**).[54] Colorless liquid. ^{1}H NMR: δ 7.19–7.07 (m, 5H), 5.34–5.26 (m, 1H), 2.52–2.69 (m, 2H), 2.32 (q, J=6.5 Hz, 2H), 1.62 (d, J=4.8 Hz, 3H).

Propyl-1-enylbenzene (**39**).[55] Colorless liquid. ^{1}H NMR: δ 7.24–7.21 (m, 5H), 6.22 (d, J=15.9 Hz, 1H), 6.16–6.11 (m, 1H), 2.28–2.37 (m, 4H), 0.88 (t, J=6 Hz, 3H).

Butyl-3-enyl-benzene (**41**).[56] Slight yellow liquid. Isolated yield 67% (0.085 g).^{1}H NMR: δ 7.26–7.15 (m, 5H), 5.85–5.83 (m, 1H), 5.06–4.94 (m, 2H), 2.67 (t, J=7.2 Hz, 2H), 2.34 (q, J=7.2 Hz, 2H).

Reduction of sulfoxides into sulfides

Diphenyl sulfide (Table 2, entry 1). Purification by column chromatography on silica gel (eluent: hexane) gave a colorless liquid in 95% yield, spectrally identical with an authentic sample. ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 7.24–7.38 (m). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 127.07 (2C), 129.22 (4C), 131.18 (4C), 131.23 (2C).

3-Phenylthio-3-hexene (Table 2, entry 4). Purification by column chromatography on silica gel (eluent: hexane) gave colorless liquid in 85% yield. ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.97–1.06 (m, 6H), 2.06–2.30 (m, 4H), 5.81 (t, 1H, J=7.32 Hz), 7.13–7.31 (m, 5H).

Dodecyl tolyl sulfide (Table 2, entry 5).[57] Purification by column chromatography on silica gel (eluent: hexane) gave a colorless liquid in 73% yield. ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.87 (t, 3H, J=6.74 Hz), 1.20–1.63 (m, 20H), 2.30 (s, 3H), 2.77–2.89 (m, 2H), 7.05–7.25 (m, 4H).

2-Phenylthio-3-ethyl-4-hydroxyl-4-phenyl-1-butene (Table 2, entry 6). The general procedure was used as described above, 2.5 equiv. of Cp_2ZrCl_2 and 5 equiv. of *n*-BuLi were used. After usual work up the residue was purified by column chromatography on silica gel (eluent: hexane/ ethyl acetate, 3/1) to give yellow liquid in 92% yield. ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 0.87 (t, 3H, J=7.25 Hz), 1.60–1.80 (m, 2H), 2.13 (s, 1H), 2.39–2.49 (m, 1H), 4.64 (s, 1H), 4.89–4.92 (d, 1H, J=5.92 Hz), 4.99 (s, 1H), 7.24–7.36 (m, 10H).

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