From Vinyl Sulfides, Sulfoxides, and Sulfones to Vinyl Transition Metal Complexes**

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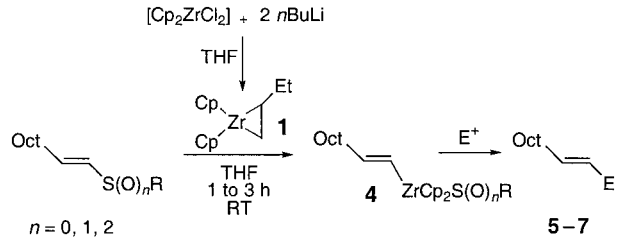
Numerous methods for the preparation of vinyl transition metal complexes are known and have been used frequently in organic synthesis.[1] However, despite these widespread methods, there are still some impossible synthetic transformations. For example, the direct transformation of vinyl sulfones into vinylic organometallic derivatives is still unknown.[2] The importance of the sulfone moiety stems from its application in carbon–carbon bond formation, and this in turn derives from key aspects of its properties and reactivity. In these applications the sulfone unit is simply a synthetic tool, which must almost always be disposed of at the end of the sequence.[3] To date, the available methods fall roughly into three groups: those resulting in replacement of the sulfone by hydrogen (reductive desulfonylation),[4] those in which sulfone removal is accompanied by C–C bond formation (alkylative desulfonylation),[5] and finally those in which the sulfone is a good leaving group in β-elimination with formation of the sulfinate moiety (RSO_2^-).[6]

Also unknown is the transformation of vinyl sulfoxides into vinylic organometallic derivatives, although sulfoxides are used in many settings, including asymmetric synthesis.[3b] Only phenyl vinyl sulfide has been transformed into vinyllithium derivatives through reductive metalation.[7] This method involves the reductive lithiation of alkenyl phenyl sulfides by either a stoichiometric amount of the radical anion *p,p'*-di-*tert*-butylbiphenyl lithium (LDBB)[7] or an excess of lithium metal in the presence of a catalytic amount of *p,p'*-di-*tert*-butylbiphenyl (DBB; 5 mol%).[8] Such transformations failed with alkyl vinyl sulfides.[7, 8] To fill these gaps new methods must still be found. In this communication, we report a new and general approach to these proposed transformations.

Recently we have been interested in the chemistry of low-valent zirconium and titanium species in organic synthesis,[9] and we have found that bis(cyclopentadienyl)zirconacyclopropane **1** (easily prepared in situ by treatment of $[Cp_2ZrCl_2]$ with two equivalents of *n*-butyllithium, and known as the Negishi reagent)[10, 11] is the reagent of choice for the stereoselective transformation of various enol ethers into vinyl zirconium derivatives.[12] Based on this finding, we thought to apply this new concept to the previously described unknown transformation (sulfur-substituted alkenes into vinyl transition metal derivatives).

We were indeed very pleased to find that **1** reacts smoothly with (*E*)-decenyl phenyl sulfide **2**[13] at room temperature in THF to give the vinyl zirconium complex **4** quantitatively ($n = 0$, R = Ph, Scheme 1), as determined by analysis of a hydrolyzed aliquot containing an internal standard by gas chromatography. Hydrolysis of the reaction mixture gives the corresponding alkene **5** in 85% yield after purification (Table 1, entry 1).



Scheme 1. Stereoselective transformation of sulfur-substituted alkenes into vinyl zirconium derivatives. Oct = octyl. RT = room temperature. For the substituents see Table 1.

Table 1. Preparation of vinyl zirconium derivatives **4** from sulfur-substituted alkenes and subsequent reactions according to Scheme 1.

Entry	Starting compound	Electrophile	Product	Yield [%][a]
1	Oct, **2**(*E*), SPh	H_3O^+ (D_3O^+)	Oct, **5** E = H, **6** E = D, E	85 (80)
2		I_2	Oct, **7**, I	78
3	Oct, **3**, SPr	H_3O^+	**5**	81
4		I_2	**7**	75
5	Oct, (*Z*)-**2**, SPh	I_2	**7**	70
6	Oct, (*E*)-**12**, SPh, O	I_2	**7**	75
7	Oct, (*Z*)-**12**, O, SPh	I_2	**7**	63
8	Oct, (*E*)-**13a**, SO_2Ph	H_3O^+	**5**	90
9		I_2	**7**	70
10	Oct, **13b**, SO_2Tol	H_3O^+	**5**	80
11	Oct, **13c**, SO_2Me	H_3O^+	**5**	86
12	Oct, (*Z*)-**13a**, SO_2Ph	H_3O^+	**5**	89
13		I_2	**7**	75

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

The formation of a discrete organometallic species was checked by deuterolysis and iodinolysis of the reaction mixture (**6** and **7** in 80 and 78% yield, respectively, entries 1 and 2). The reaction also proceeds efficiently from the *alkyl* vinyl sulfide **3**, to give **5** and **7** in 81 and 75% yield, respectively, after hydrolysis and iodinolysis (entries 3 and 4). When the reaction was performed on the (*Z*) isomer of aryl vinyl sulfide **2**, followed by addition of iodine, only the (*E*) vinyl iodide **7** was obtained (entry 5). Thus, the reaction is stereoselective and leads only to the (*E*) vinyl zirconium derivative.

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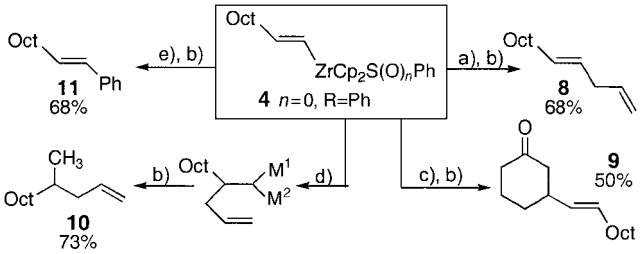
To further increase the scope of the reaction, transmetalation of the vinyl zirconium derivative **4** ($n = 0$, R = Ph) to give different vinylic organometallic derivatives was studied (Scheme 2).[14] For example, the addition of a catalytic amount



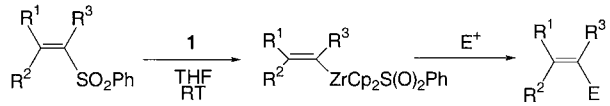
Scheme 2. Transmetalation reactions of vinyl zirconium derivative **4** ($n = 0$, R = Ph) and further reactions. Reagents and conditions: a) 10% CuCl/2 LiCl, allyl chloride; b) 1N HCl; c) 10% CuCl/2 LiCl, cyclohexenone, Me_3SiCl; d) allylmagnesium bromide, $ZnBr_2$; e) 10% CuCl/2 LiCl, 10% $[Pd(PPh_3)_4]$, PhI. M^1, M^2 = MgBr, ZnBr.

of CuCl in the presence of LiCl leads to the corresponding (*E*) vinyl copper derivative.[15] This intermediate can react either by an S_N2' process with allyl chloride to give **8** (68% yield) or in a 1,4-addition with cyclohexenone in the presence of Me_3SiCl to give **9** (unoptimized yield 50%).[15] The vinyl zirconium derivative can also be easily transformed in situ into the corresponding organobismetallic derivative by the successive addition of allylmagnesium bromide and zinc dibromide.[16] After hydrolysis **10** is obtained in 73% yield. Finally, the palladium-catalyzed cross-coupling reaction with phenyl iodide opens a new route for further functionalization as shown by the formation of **11**.[17]

Vinyl transition metal derivatives are also easily obtained upon reaction of vinyl sulfoxides[18] with two equivalents of **1**. Indeed, we found that the first equivalent of zirconacyclopropane **1** reduces the sulfoxides (*E*)-**12** and (*Z*)-**12** into the vinyl sulfides (*E*)-**2** and (*Z*)-**2**, respectively, in one hour at room temperature with concomitant formation of solid $[Cp_2Zr{=}O]_n$.[19] This unexpected, mild reduction[20] occurs without isomerization of the double bond.[21] When the newly formed phenyl vinyl sulfides **2** are treated in situ with a second equivalent of **1**, the organometallic derivative **4** ($n = 0$, R = Ph; and (*E*)-**7** after iodinolysis) forms with complete isomerization of the double bond (see Table 1, entries 6 and 7) in analogy to the previous reactions (entries 1 and 5).

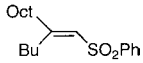
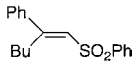
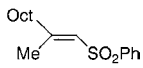
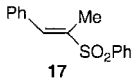
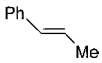
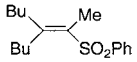
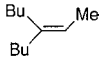
Finally, we turned our attention to vinyl sulfones.[4, 5] We first tested the effect of the R group on the elimination of the sulfinate moiety in our sequence (Table 1, entries 8, 10, 11).[22] Regardless of the R group of the sulfone—phenyl (**13a**), tolyl (**13b**), or methyl (**13c**)—we observed a very fast transformation of the (*E*) vinyl sulfone into the corresponding vinylic organometallic derivatives **4** and then **5** after hydrolysis in excellent yields. By reaction with iodine (*E*)-**13a** gives the pure *trans* vinyl iodide **7** in 70% yield (entry 9). Again, the (*Z*) isomer of vinyl sulfone **13a** undergoes complete isomerization in this process and gives only the (*E*) isomer, **7**, in good yield (entry 13).

The scope of this reaction is even broader since the transformation of vinyl sulfones into vinyl transition metal complexes can be generalized to polysubstituted olefins, as described in Scheme 3 and Table 2. Although the yield decreases slightly, as expected, with the degree of substitution



Scheme 3. Synthesis of polysubstituted vinyl zirconium derivatives and further reactions. For the substituents see Table 2.

Table 2. Preparation of vinyl zirconium derivatives from polysubstituted vinyl sulfones and subsequent reactions according to Scheme 3.

Entry	Starting compound	Electrophile	Product	Yield [%][a]
1	 **14**	H_3O^+	**19**	70
2		MeOD	**20**	60
3	 **15**	H_3O^+	**21**	64
4	 **16**	H_3O^+	**22**	68
5		I_2	**23**[b]	67
6	 **17**	H_3O^+	 **24**	70
7	 **18**	H_3O^+	 **25**	48

[a] Yield of isolated product after purification by column chromatography. [b] As a 1:1 mixture of geometrical isomers.

of the starting vinyl sulfone (cf. entries 1–6 to entry 7 of Table 2), the reaction proceeds smoothly in all cases. When the reaction is performed on β,β-disubstituted vinyl sulfones **14**–**16**, good overall yields are obtained (see entries 1–5). However, the quenching of the resulting vinyl zirconium derivatives with I_2 leads to two isomers in a 1:1 ratio (entry 5). On the other hand, when the α,β-disubstituted vinyl sulfone **17** is treated with **1**, a single (*E*) isomer, **24**, is obtained after hydrolysis (entry 6). Even a tetrasubstituted alkene such as **18** is easily transformed into the corresponding vinylic organometallic derivative and then into **25** after acidic treatment (entry 7).

Although further investigations are needed to elucidate completely the mechanism of this reaction, it possibly involves the carbozirconation of the heterosubstituted double bond by zirconocene **1** to lead to the unstable functionalized zirconacycles **28** and **29** (Scheme 4). Although we were not able to trap **28** and **29** as intermediates (only complex **4**, R = Ph, could be isolated), **30** and **31**[23] were isolated in moderate yields when the same reaction was repeated with **26** Li and **27**

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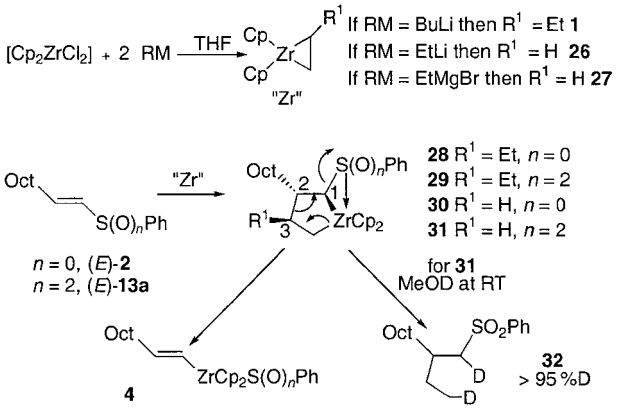
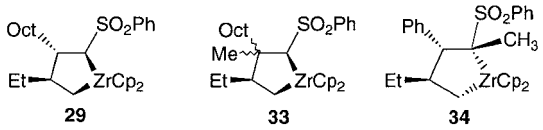


Scheme 4. Mechanistic rationalization of the isomerization and elimination in the reactions shown in Scheme 3.

MgBr, respectively (Scheme 4). Deuterolysis and hydrolysis of **31** yielded **32** and its hydrogen analogue, respectively. Decarbozirconation of **30** and **31** occurs with elimination of the leaving group to give the corresponding vinylic organometallic derivative **4**, R = Ph. This reaction seems to proceed through skeletal rearrangement,[24] since the zirconacycle intermediate disappears in favor of the vinyl transition metal complex, which is obtained in very good yield. In this case, whatever the stereochemistry of the starting olefin (as described in Tables 1 and 2), the carbon–heteroatom bond of the metalated center C^1 shifts to produce the most stable intermediate (see **28**–**31** in Scheme 4). Such an isomerization could be caused by an interaction between the sulfur moiety and the zirconium atom,[25] which would weaken the C^1–Zr bond and facilitate the isomerization. Then, whatever the stereochemistry of the starting material, a conformation is always possible in which the C^1–S bond is antiperiplanar to the C^2–C^3 bond (see **28**–**31**, Scheme 4). The elimination reaction (or decarbozirconation) occurs in a concerted way to give the vinyl zirconium compound.

The stereochemistry of the vinyl zirconium complex can then be rationalized by the zirconacyclopentane intermediates **29**, **33**, and **34**. Indeed, in **29** the most stable isomer is



expected to have an *anti* relationship between the octyl substituent and the zirconium atom. When one more substituent is added in the β-position, as in **16**, intermediate **33** leads to two isomeric vinyl zirconium derivatives in a 1:1 ratio (see Table 2, entry 5). However, when **17** is treated with **1**, **34** is expected to be the more stable zirconacycle as a result of the steric interaction between the phenyl and the alkyl groups.[26]

In summary, we have developed an easy and general new method for the conversion of vinyl sulfides, sulfoxides, and sulfones into vinylic organozirconium derivatives with good yields of isolated products. Our investigations of several different systems as well as of a catalytic process in zirconium are currently in progress.

Experimental Section

A solution of *n*-butyllithium in hexanes (1.6 M, 3.3 equiv) was added slowly to a solution of bis(cyclopentadienyl)zirconium dichloride (1.5 equiv) in dry THF at −78 °C. After the solution had been stirred for 1 h at −78 °C, vinyl sulfide, sulfoxide, or sulfone was added (1 equiv) at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 2.5–5 h. The quantitative formation of the adduct **4** was checked by gas chromatography. Then, the solution was cooled to −20 °C and the electrophile was added. The reaction mixture was warmed to room temperature and diluted with ether and 1 N HCl. The aqueous phase was then extracted three times with ether. The combined organic phases were washed successively with a solution of saturated aqueous sodium hydrogen carbonate, brine, and water (in case of addition of iodine, aqueous $Na_2S_2O_3$ was also used), dried over $MgSO_4$, and concentrated to dryness under reduced pressure. The residue obtained was finally purified by column chromatography on silica gel.

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Polymeric Surfactants for the New Millennium: A pH-Responsive, Zwitterionic, Schizophrenic Diblock Copolymer**

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Recently, we have demonstrated that certain hydrophilic AB diblock copolymers can self-assemble in aqueous media to form both conventional micelles (with the A block forming the micelle core) and reverse micelles (with the B block forming the micelle core),[1–3] and we have described these diblock copolymers as having "schizophrenic" character.[3] To date, only two well-documented examples of schizophrenic diblock copolymers have been reported. The first "proof-of-concept" example was reported by Bütün et al. who polymerized 2-(*N*-morpholino)ethyl methacrylate (MEMA), followed by 2-(diethylamino)ethyl methacrylate (DEA) using group-transfer polymerization (GTP).[1, 2] The two micellar transitions of this polymer were induced by changes in solution pH and ionic strength, respectively. In both cases micellization occurred at around 20 °C, but the addition of large quantities of electrolyte (1.0 M Na_2SO_4) to produce MEMA-core micelles was somewhat artificial. The second example involved using a poly(propylene oxide)-based (PPO) macro-initiator for the polymerization of DEA by atom-transfer radical polymerization (ATRP) in alcoholic media at 55 °C. The resulting PPO–DEA diblock copolymer dissolved in cold water at pH 6.5. DEA-core micelles were formed at 5 °C in mildly alkaline solution (pH 8.5) and PPO-core micelles were obtained at pH 6.5 at elevated temperatures (40–70 °C). Thus, neither micellar state was stable at ambient temperature; this is rather inconvenient for characterization purposes and, more importantly, for industrial applications of this particular polymeric surfactant.

Herein we describe a new zwitterionic AB diblock copolymer that undergoes spontaneous self-assembly in aqueous solution at ambient temperature to form both micelles and reverse micelles, simply by switching the solution pH (Figure 1). This remarkable diblock copolymer is poly(4-vinyl benzoic acid-*block*-2-(diethylamino)ethyl methacrylate) (VBA-*b*-DEA), which was synthesized by ATRP using protecting group chemistry, followed by hydrolysis; the degrees of polymerization of the VBA and DEA blocks are 60 and 66, respectively (for experimental details, see Supporting Information).

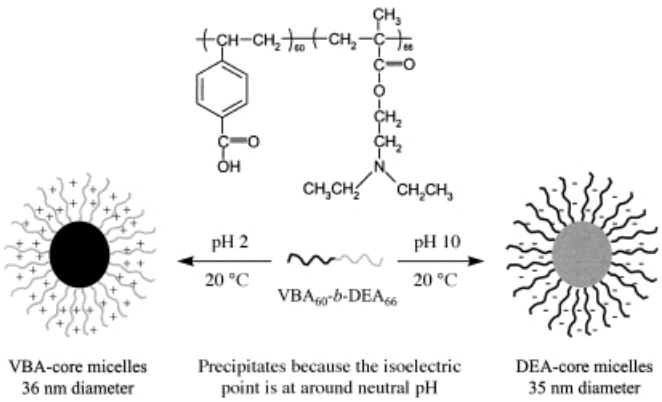

Figure 1. Chemical structure of VBA_{60}-*b*-DEA_{66} diblock copolymer and its pH-induced "schizophrenic" micellization behavior in aqueous solution.

It is known that DEA homopolymer is a weak polybase with a pK_a of approximately 7.3.[4] DEA homopoplymer dissolves in acid as a cationic polyelectrolyte, by protonation of its amine groups, but becomes insoluble above pH 7.1. VBA homopolymer has a pK_a of around 7.1 (determined by hydrogen ion titration); it is insoluble at low pH but becomes soluble as an anionic polyelectrolyte above pH 6.2, by ionization of its carboxylic acid groups. Hence, the VBA-*b*-DEA diblock copolymer is a more hydrophobic analogue of

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