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[19] Currently, we do not have an explanation as to why the selectivity factor is not higher ($s > 200$) in this resolution as could be expected from Figure 2. A possible explanation is that the kinetics are more complicated with $Me_2Zn$ than with the other zinc reagents in which case the formula given in reference [9] is no longer valid.

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# Highly Enantioselective Regiodivergent and Catalytic Parallel Kinetic Resolution[**]

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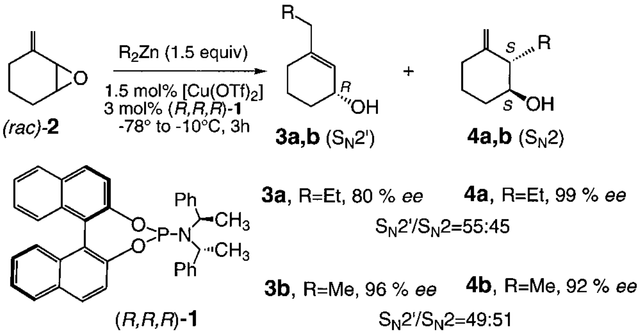
Mauro Pineschi,[*] and Ben L. Feringa[*]

The development of new methodologies for the preparation of chiral compounds of high optical purity by means of asymmetric catalysis is presently an area of great importance in organic chemistry. Kinetic resolution of a racemic mixture with a chiral reagent is a well-documented strategy in which a maximum of only one half of the racemic starting material is converted into non-racemic products.[1] Parallel kinetic resolution (PKR) is an interesting strategy recently introduced, in which both enantiomers of a racemate can be converted into useful products.[2] This conceptual variation often requires the use of two different stoichiometric chiral reagents in parallel.[3] Parallel reactions under non-stoichiometric conditions have previously been described in the asymmetric Bayer–Villiger oxidation of racemic ketones, by means of enzymatic methods[4] or chiral catalysts,[5] and in the intramolecular cyclopropanation of racemic allylic diazoacetates catalyzed by chiral rhodium complexes.[6] The latter is the only example of a PKR reaction involving the formation of a C–C bond. In this special case, there are distinct reactivities for both enantiomers: one enantiomer gave intramolecular cyclopropanation, whereas the other enantiomer was transformed by means of a hydride abstraction/elimination into achiral compounds. Herein we report the first highly stereocontrolled transformation of a racemic mixture by an organometallic reagent and a chiral catalyst to give separable regioisomeric products.

Recently, we described a new catalytic kinetic resolution of racemic vinyloxiranes with dialkylzinc reagents (0.50 equiv) by using copper complexes of non-racemic phosphoramidite as chiral catalysts.[7a] When racemic vinyl epoxide **2** was treated with excess $Et_2Zn$ (1.5 equiv) in the presence of the catalyst prepared in situ from $[Cu(OTf)_2]$ (1.5 mol %) (Tf = triflate = $OSO_2CF_3$) and (*R*,*R*,*R*)-**1** (3 mol %), complete conversion of **2** took place in 3 h to give, after usual work-up and chromatographic purification (see Experimental Section), the corresponding $S_N2'$-addition product (*R*)-**3a** (46 % yield, 80 % *ee*; Scheme 1) together with the regioisomeric alcohol (1*S*,2*S*)-**4a** (37 % yield) having a surprising 99 % *ee*! The progress of the reaction in terms of the the conversion and enantioselectivities (Figure 1a and 1b, respectively) was therefore closely monitored.[8] The peculiarity of this reaction stems from the fact that regioisomeric products were derived from opposite enantiomers of **2** in two clearly distinct phases: The first one was very fast, proceeding with $S_N2'$-regioselectivity to yield (*R*)-**3a** (15 min at −78 °C), whereas the second slower one which provided (1*S*,2*S*)-**4a** (−10 °C and 3 h to go to completion) exhibited a complementary $S_N2$ regioselectivity. In fact, after 15 min at −78 °C, the remaining vinyloxirane (1*S*,2*R*)-**2** (62 % conversion) was enantiomerically pure, (> 98 % *ee*)[9] and it reacted with nearly complete regioselectivity, and with complete *anti* stereoselectivity, at the 2-position. The catalyzed addition of $Me_2Zn$ followed an even more pronounced regiodivergent behavior, affording, after complete conversion of **2**, (*R*)-**3b** (49 % GC yield, 96 % *ee*) and (1*S*,2*S*)-**4b** (51 % GC yield, 92 % *ee*) (Scheme 1).



Scheme 1. Enantioselective and regiodivergent addition of $R_2Zn$ to racemic **2** catalyzed by $[Cu(OTf)_2]$/(*R*,*R*,*R*)-**1**.

The complementary enantiomer-dependent regioselectivity was also demonstrated by a reaction carried out with the racemic catalyst (*R*,*R*,*R*)(*S*,*S*,*S*)-**1**. In this case, the conjugate-addition product **3** was obtained with almost complete regioselectivity ($S_N2'/S_N2 = 98{:}2$), clearly indicating that chiral recognition leads to enantio- and regiodivergent reactivity when the reaction is performed with the chiral catalyst.

The mechanism for the copper-catalyzed organometallic addition reactions has been discussed in a number of reports.[10] Probably the initially formed π complex **2A**[11][12] undergoes an oxidative addition resulting in the formation of

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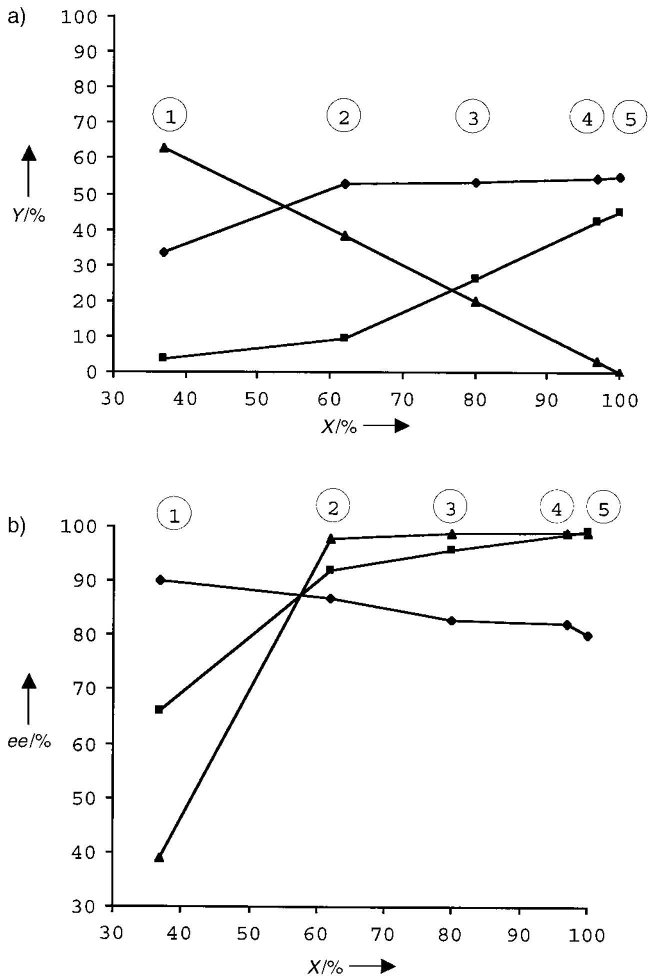
[**] This work was supported by the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST, Roma) and by the University of Pisa. We gratefully acknowledge Merck for the generous financial support derived from the 2000 ADP Chemistry Award.

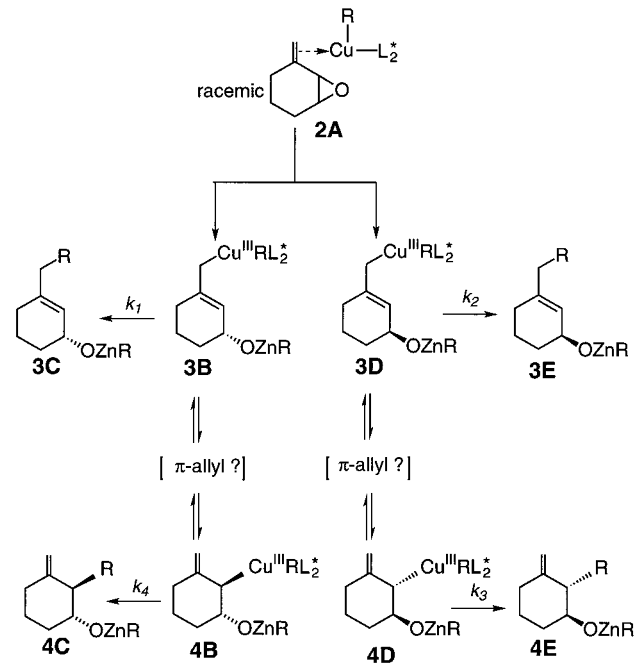
Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.



| | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| *t* [min] | 3 | 15 | 120 | 150 | 180 |
| *T* [°C] | −78 | −78 | −55 | −35 | −10 |

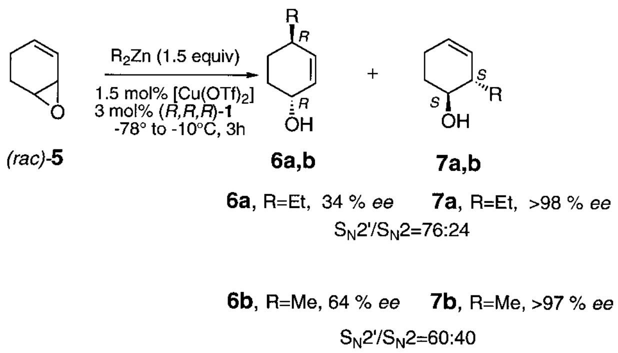
Figure 1. GC yield *Y* [%] (a) and enantiomeric excesses [%] (b) of compounds **2** (-▲-), **3a** (-◆-), **4a** (-■-) present in the reaction mixture at different conversions *X* of **2**. Values determined by GC using a β-cyclodextrin column (see Supporting Information).

(σ-allyl)copper(III) species **3B** and **3D** (Scheme 2). It is proposed that the regioselectivity of the reaction depends on the relative rates of reductive elimination from diastereoisomeric complexes **3B** and **3D**, and isomerization to (σ-allyl)copper(III) complexes **4B** and **4D**, respectively, (through a π-allyl complex or a 1,3-sigmatropic rearrangement) with subsequent reductive elimination.[13] The fast reductive elimination ($k_1$) of **3B** without concomitant isomerization could account for the nearly complete conversion of (1*R*,2*S*)-**2** into $S_N2'$-adduct **3C**. Probably, the slower corresponding reductive elimination ($k_2$) from **3D** allows an isomerization to the regioisomeric complex **4D** which undergoes a faster ($k_3$) reductive elimination to afford a large amount of $S_N2$-adduct **4E** with a high *ee*. Evidently, the acceleration of the C–C bond formation by the chiral ligand is unequal for complexes **3B**,**D** and **4B**,**D**, thus affording the observed stereo- and regioselectivity.[14]



Scheme 2. Postulated mechanism of the regiodivergent PKR.

The efficient catalytic conversion of a racemic compound to two different and separable chiral products of high isomeric purity has been accomplished also by the use of a vinyloxirane having a blocked s-*cis* conformation such as 1,3-cyclohexadiene monoepoxide **5** (Scheme 3). The addition of $Me_2Zn$ (1.5 equiv) to (±)-**5** catalyzed by $[Cu(OTf)_2]$/(*R*,*R*,*R*)-**1** afforded a 60:40 mixture of (+)-(1*R*,4*R*)-**6b** ($S_N2'$-adduct, 64% *ee*) and (1*S*,2*S*)-**7b** ($S_N2$-adduct, >97% *ee*).[15] The catalyzed addition of $Et_2Zn$ (1.5 equiv) to the same racemate afforded a 76:24 mixture of regioisomer (+)-(1*R*,4*R*)-**6a** (34% *ee*) and (+)-(1*S*,2*S*)-**7a** (>98% *ee*). Evidently with this substrate, while keeping the corresponding $k_1 \gg k_4$ for one enantiomer of the substrate, the rates of reductive elimination versus isomerization for the other one ($k_2$ vs. $k_3$ of Scheme 2) are not very different, thus allowing the formation of regioisomeric $S_N2$ adducts **7a**, **b** with very high *ee*, together with large amounts of $S_N2'$ substitution products **6a**, **b** with a reduced enantioselectivity.



Scheme 3. Enantioselective and regiodivergent addition of $R_2Zn$ to racemic **5** catalyzed by $[Cu(OTf)_2]$/(*R*,*R*,*R*)-**1**.

The mechanism of this reaction and the exact nature of the copper species involved in this highly efficient catalytic process still need to be established. Nevertheless, this unprecedented regiodivergent catalytic parallel kinetic resolution with an organometallic reagent supports the notion that the oxidative addition might be a very fast process and reductive elimination is instead a regio- and stereodetermining step.

### *Experimental Section*

General procedure: A solution of $[Cu(OTf)_2]$ (10.83 mg, 0.030 mmol) and **1** (32.3 mg, 0.06 mmol) in anhydrous toluene (4.0 mL) was stirred at room temperature for 40 min. The colorless solution was cooled to $-78\,^{\circ}C$, and subsequently solutions of racemic vinylepoxide (2.0 mmol) in toluene (1.0 mL) and $R_2Zn$ (3.0 mmol) in toluene were added. The resulting light yellow solution was quenched with saturated aqueous $NH_4Cl$ (5.0 mL) once the reaction reached completion (GC analysis). Extraction with $Et_2O$ and evaporation of the dried ($MgSO_4$) organic phase gave the crude product, which was subjected to flash chromatography (see Supporting Information). Enantioselectivities were determined by chiral GC (CP-cyclodex-$\beta$-column).

Received: October 30, 2000 [Z16011]

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[9] The reaction was also carried out in $CH_2Cl_2$ instead of toluene to obtain vinyloxirane (1*S*,2*R*)-**2** in an enantiomerically pure form (>98% *ee*) by distillation, stopping the reaction after the first faster-phase.

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[13] E. S. M. Persson, M. van Klaveren, D. M. Grove, J. E. Bäckvall, G. van Koten, *Chem. Eur. J.* **1995**, *1*, 351. Even if not indicated for the sake of simplicity in Scheme 2, the copper(III) complexes **3B**, **D** and **4B**, **D** are probably cationic species with $TfO^-$ as a possible counterion.

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# From Oligomers to Conducting Polymers of the Metal–Dinitrogen Functionality[**]

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This report opens, in the use of dinitrogen, a completely new avenue, which is derived neither from any of the bioinspired processes[1] nor from the objectives pursued so far in the metal-assisted dinitrogen chemistry.[2, 3]

Although $:N{\equiv}N:$ and $[:C{\equiv}C:]^{2-}$, the deprotonated form of acetylene, are isoelectronic, this similarity has not helped in establishing a practical parallelism between the two species, namely in the triple bond cleavage[2h–j] or in their use in material science. In the latter context, the polymeric forms of acetylene, such as polyacetylene and related cumulenes, have a relevant importance.[4, 5] This report deals with the oligomerization of the metalla–dinitrogen functionality and with a perspective to polymerize this moiety. This entry into material science using dinitrogen opens a new avenue in this domain. We report herein how we were able to achieve the unprecedented oligomerization of the metalla–dinitrogen functionality and thereby anticipating and planning the formation of the corresponding polymers.

The alkylation of $[WCl_4(dme)]$ (DME = dimethoxyethane) using MesMgBr (Mes = 2,4,6-$(CH_3)_3C_6H_2$) under a nitrogen atmosphere occurs with a fast absorption of dinitrogen

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[**] This work was supported by the "Fonds National Suisse de la Recherche Scientifique" (Grant No. 20-53336.98), Action COST D9 (European Program for Scientific Research, OFES No. C98.008), and Fondation Herbette (University of Lausanne).

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