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[19] The bulk amount of catalysts **1** remained undissolved during RCM as observed through the windows of the high-pressure reactor. Complex **2**, however, was at least partly soluble, giving rise to an intensively colored reaction mixture.

Unusual Regioselectivity in the Reductive Coupling of Alkynes and Allenes by Hydrozirconation and Zinca-Claisen Rearrangement

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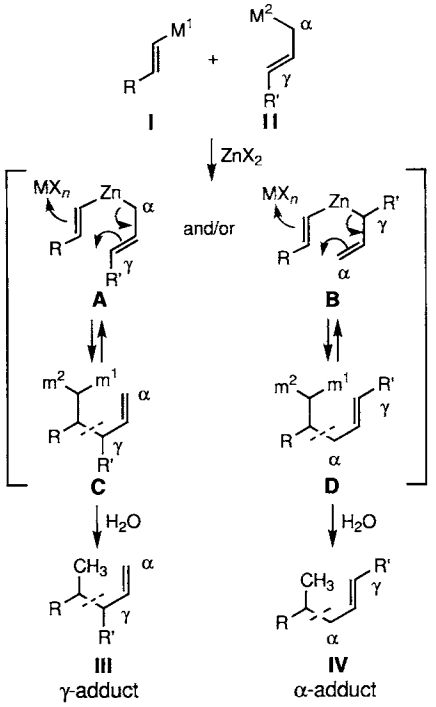
Dedicated to Prof. Dr. Dieter Seebach on the occasion of his 60th birthday

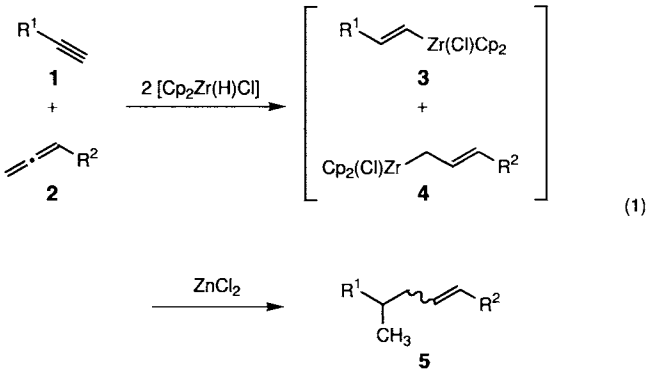
The allylmetalation of vinylmetal compounds is a new approach to C–C bond formation.[1, 2] Although the precise mechanism must still be elucidated, various features of the reaction are nicely summarized by the zinca-Claisen mechanism of Knochel and Normant and their co-workers[1d–h, 3a, 4] (Scheme 1): Coupling of vinylmetal compound **I** and allylmetal derivative **II** (M^1, M^2 = Li, MgX, ZnX, etc.) occurs by transmetalation with zinc to form **A** and/or **B**, which then undergoes bond reorganization.[4, 5] Substituted allyl–metal compounds (**II**: R′ ≠ H) tend to couple through **A** to form *gem*-bismetallic compounds **C** as the kinetically controlled products that give, upon hydrolysis, the γ-adducts **III**. Prolonged reaction results in equilibration of the organometallic species, leading to an increase in the fraction of isomeric *gem*-bismetallic compounds **D** that in turn produce the α-adducts **IV**. Unfortunately,



Scheme 1. Zinca-Claisen mechanism for the allylmetalation of vinylmetal compounds.

IV cannot be obtained selectively, because equilibration is slow and the α/γ ratio remains low even after extended reaction.[3] From an experimental standpoint, preparation of the starting organometallics **I** and **II** is sometimes troublesome as well.[6]

We report here an in situ approach to such precursors as **I** and **II** involving hydrozirconation[7, 8] [Eq. (1)], which facilitates the



(1)

reductive coupling of a series of alkynes and allenes. A noteworthy feature of this method is that the α-adduct is obtained with high selectivity. We also discuss possible explanation for the unusual regioselectivity that is observed and examine the synthetic utility of the reaction in remote asymmetric induction for synthesis of the vitamin E side chain.

Treatment of alkyne **1a** (R^1 = TrOCH$_2$) and allene **2a** (R^2 = CH_2CH_2OMOM) with the Schwartz reagent[9] in CH_2Cl_2 (−78 → 25 °C) led to a red solution that was subsequently treated with $ZnCl_2$ at 0 °C. Stirring at 25 °C for 2 h gave the α-adduct **5a** (see Table 1) as the sole product; none of the γ-adduct was detected (α:γ > 98:2).[10, 11] Under the same conditions this unusual regioselectivity proved applicable to a wide range of starting allene/alkyne combinations (Tables 1 and 2).[11] The sole exception was reaction of methyl-

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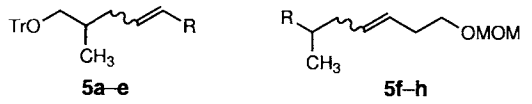


5a–e **5f–h**

Table 1. α-Adducts **5a–e** obtained by reaction of alkyne **1a** with various allenes (25 °C, 2 h)[a]. In no case could the presence of γ-product be verified[11].

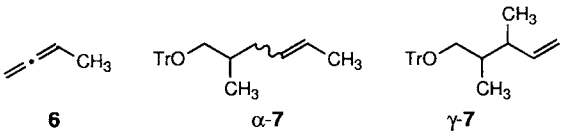
	R	Yield[%]	*E*:*Z*
5a	CH_2CH_2OMOM	83	1:2.7
5b	$CH_2CH_2OTBDPS$	85	1.3:1
5c	*cyclo*-C_6H_{11}	76	ca. 1:1
5d	C_6H_5	60	49:1
5e	$CH_2CH(OC_2H_5)_2$	76	1:2.6

[a] Tr = triphenylmethyl, MOM = methoxymethyl, TBDPS = *tert*-butyldiphenylsilyl.

Table 2. Summary of α-adducts **5f–h** obtained by reaction of allene **2a** with various alkynes (25 °C, 2 h). In no case could the presence of γ-product be verified[11].

	R	Yield[%]	*E*:*Z*
5f	*n*-C_4H_9	82	1:4.9
5g	$C_6H_5(CH_3)_2Si$	83	1:2.7
5h	*cyclo*-C_6H_{11}	82	1:1.8

allene **6** with alkyne **1a**, which gave adduct **7** as an α/γ-mixture. This in turn provided a clue to the source of the unusual regioselectivity.



6 α-**7** γ-**7**

Figure 1 shows the time course for α-adduct content in the overall adduct mixture, which shows the existence here also of a $\gamma \rightarrow \alpha$ isomerization pathway (**C** → **D** in Scheme 1); however, in this case the isomerization is exceptionally rapid. Curve B describes the reaction of alkyne **1a** with **6**. After an initial γ-selective reaction,[12] the α/γ ratio steadily increases, reaching 83/17 after 9 h and 94/6 after 36 h (not shown). Such a rapid and complete $\gamma \rightarrow \alpha$ isomerization has not been observed previously

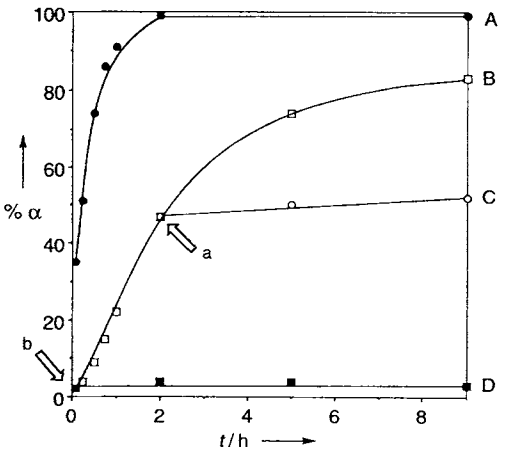
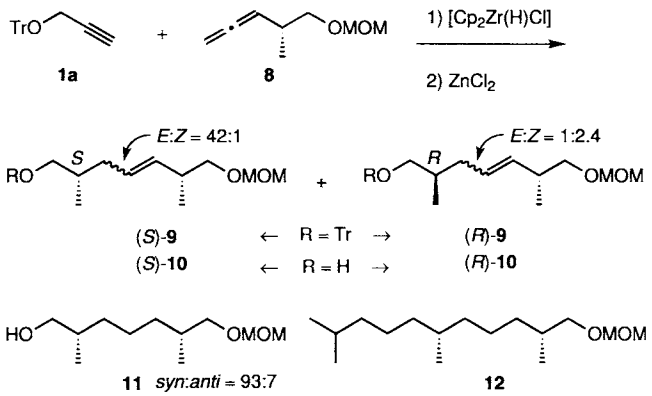


Figure 1. Time dependence of the fraction of α-adduct in the overall amount of adduct [$\alpha/(\alpha+\gamma) \times 100\%$]. A: Reaction of **1a** with **2a**. B: Reaction of **1a** with **6**. C: $MgBr_2$ addition 2 h after $ZnCl_2$ introduction (arrow a). D: $MgBr_2$ addition 5 min after $ZnCl_2$ introduction (arrow b).

in related reactions that involve organolithium and/or -magnesium reagents (vide supra).[3] The isomerization proceeds even more rapidly in reactions of other allenes, as exemplified by the reaction of allene **2a** (curve A): the $\gamma \rightarrow \alpha$ shift is so fast here that after 2 h at 25 °C only the α-adduct **5a** is observable.[12]

Why, then, does the present isomerization rate differ so markedly from that associated with the conventional protocol? A Mg^{II} salt plays a key role.[13] Thus, in the reaction of **1a** and **6**, the $\gamma \rightarrow \alpha$ isomerization virtually ceases upon addition of $MgBr_2$, as shown by curves C and D.[12, 14] Thus, the observed γ-selectivity in the previous examples[3] can be explained through inhibition of $\gamma \rightarrow \alpha$ isomerization by a Mg^{II} salt. In contrast, the present case is "magnesium-free," so the α-adduct is obtained selectively. Nevertheless, the precise nature of the inhibitory effect remains unknown.[14]

The process described here presented an opportunity for a new vitamin E synthesis involving remote stereocontrol.[15] Reaction of homochiral allene **8**[16] and alkyne **1a** as above gave the α-adduct **9** (Scheme 2). GC-Analysis of alcohol **10**, derived



Scheme 2. Synthesis of an intermediate along the pathway to vitamin E (**12**) through the coupling of an alkyne with an allene. **9**: R = Tr; **10**: R = H.

from **9** [TsOH (cat.)/MeOH, quantitative], showed the ratio of the four isomers, (*S*,*Z*):(*S*,*E*):(*R*,*Z*):(*R*,*E*) to be 91:2:2:5, indicating a remarkable degree of selectivity *S*:*R* of 93:7 with respect to the newly formed chiral center.[17] Indeed, hydrogenation of **9** gave a 93:7 mixture of *syn*- and *anti*-**11**,[18] which could be converted (TsCl; $Me_2CH(CH_2)_2MgBr$, Cu^{2+}; H_3O^+) into **12**, a known intermediate in vitamin E synthesis.[15a] The origin of this high level of 1,5-asymmetric induction is currently under investigation.[19]

Experimental Section

In a typical experiment, a suspension of Schwartz reagent [9] was prepared by adding CH_2Cl_2 (1.0 mL) to $Cp_2Zr(H)Cl$ (603 mg, 2.34 mmol) at −78 °C [8c]. Then a mixture of alkyne **1a** (193 mg, 0.648 mmol) and allene **2a** (116 mg, 0.906 mmol) in CH_2Cl_2 (2.5 mL) was added. After gradual warming to 25 °C, the resulting red solution was chilled to 0 °C, and to this was added $ZnCl_2$ (0.69 M in ether, 1.3 mL). After 2 h at 25 °C the mixture was diluted with ether and poured into cooled, saturated aqueous $NaHCO_3$. The ether solution was extracted three times with EtOAc and the combined organic extracts were washed with saturated aqueous Na_2SO_4, dried over Na_2SO_4, and filtered through a Celite pad. Evaporation of volatile components and purification by preparative TLC (hexane/EtOAc = 9/1) gave **5a** (231 mg, 83%).

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[5] No additional zinc salt is required if at least one of the starting materials is an organozinc derivative.
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[10] Quenching the reaction with D_2O led to doubly deuterated **5a** (CHD_2 instead of CH_3).
[11] Absence of the γ-adduct was established by ^1H NMR, HPLC, and/or capillary GC. In each case, a comparison sample containing the γ-adduct was prepared by early quenching. Upon hydrogenation, each α-adduct gave a single saturated compound.
[12] The coupling reaction itself is complete within a few minutes after addition of $ZnCl_2$.
[13] Lithium salts (LiI, LiBr) also have a retarding effect, but much smaller. We originally thought that $[Cp_2ZrCl_2]$ present in the reaction mixture was responsible for the unusual regioselectivity, but this turned out not to be the case.
[14] Simple quenching by protic impurities that may have contained $MgBr_2$ was ruled out: Quenching with D_2O after addition of $MgBr_2$ produced a doubly deuterated product [10].
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[16] >98% *ee*. The synthesis of **8** will be described elsewhere.
[17] Analysis is based on a comparison with the authentic stereoisomers.
[18] Based on an MTPA(= α-methoxy-α-trifluoromethylphenylacetic acid) analysis of **11** by ^{19}F NMR spectroscopy.
[19] A chelating group in the allene is essential: Stereoselectivity fell to about 1:1:1:1 if the MOM substituent in **8** was replaced by a TBDPS group. On the other hand, the protective group of the alkyne is less influential, and *S*/*R* selectivity remains 9:1 irrespective of protection. The high (*Z*)-selectivity with (*S*)-**9** is noteworthy because of the contrast with lower selectivities with (*R*)-**9** or simpler, nonstereogenic substrates.

Copper Pnictogenides as Selective Reagents: A New Access to Functionalized Phosphanes and Arsanes**

Christian Meyer, Hansjörg Grützmacher,* and Hans Pritzkow

Dedicated to Professor Gottfried Huttner on occasion of his 60th birthday

Many catalytically effective transition metal complexes contain phosphane ligands, and increasing demands concerning the reactivity and selectivity of these catalysts require the synthesis of special ligands. Phosphanes are usually prepared by allowing either a halophosphane $R_{3-n}P(Hal)_n$ to react with carbanion equivalents M^+R^- or an alkali metal phosphide $(R_{3-n}P)^-M_n^+$ (M = Li, Na, K) to react with a carbocation equivalent R^1-Z (Z = leaving group).[1] Copper reagents proved to be versatile for the selective formation of C–X bonds (X = C, Si, Sn, S, Se, Te).[2] Recently we synthesized tris(telluro)carbenium ions $[(RTe)_3C]^+[CuBr_2]^-$ by treating the copper complex [(bpy)CuTeR] (bpy = 2,2′-bipyridyl) with CBr_4.[3] We now extended these investigations to the reaction of copper phosphides and arsanides with organohalides R–Hal, which, to our knowledge, has not been reported to date.

According to the method of Caulton et al.,[4] tetrameric copper(I) *tert*-butoxide (**1**) was allowed to react with diphenyl(element) hydrides **2**–**4** to provide the partially new copper pnictogenides **5**[5]–**7** as insoluble, red-brown coordination polymers of unknown structures (Scheme 1). In the presence of the nitrogen heterocycles bpy (**8**), phenanthroline (**9**, phen), or neocuproine (**10**, neocup), deeply colored complexes such as **11**–**14**, which are relatively soluble in aromatic hydrocarbons, are formed. In the copper phosphides, the R_2P group can take either a μ_2- (three-center four-electron bond) or a μ_3-bridging position (four-center four-electron bond) between the copper centers,[6a–e] as evidenced by ^{31}P NMR spectroscopy (significant shift towards low-resonance frequencies in the case of μ_3-PR_2 units: $\delta < -50$ versus 85% H_3PO_4). Accordingly, species with μ_2-bridging Ph_2P groups dominate in solutions of **12** and **13** (^{31}P NMR: $\delta = -25$; Table 1).

The X-ray structure analysis shows that in the solid state **12** consists of a six-membered Cu_3P_3 ring in a twist conformation with alternating Cu–P distances (2.24 and 2.30 Å, Scheme 1). The Cu–Cu distances (3.9–4.1 Å) preclude significant metal–metal bonding interactions.[7] The structure of the species

Table 1. Selected physical data for copper pnictogenide complexes **11**–**14**.

Compd	m.p. [°C]	$\delta(^{31}P\{^1H\}$ NMR) (121.5 MHz, C_6D_6)	$\lambda_{max}/\varepsilon$ [nm]/[L mol^{-1} cm^{-1}]
11	83–90	−15.3; −84.0	646.9/661
12	92 (decomp)	−24.0	651.7/3520
13	135 (decomp)	−25.2	556.1/3192
14	127 (decomp)	–	572.2/23980

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