1,1-Dimetallic Reagents for the Elaboration of Stereoselectively Di- or Trisubstituted Linear Substrates

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ABSTRACT

Although *gem*-dimetallic species have been known for a long time, and reacted once or twice with electrophiles, the allyl zincation of substituted vinyl metals has emerged as a particularly efficient access to such species. This is due to a high face selectivity, in the addition to the C=C bond, which can be governed by vicinal or more remote heteroatoms. This strategy has some aspects in common with the well-known allylations or aldol condensations to carbonyl derivatives. But in the present case, the C=C bond has a low polarity. We present here some examples which lead to di- or polysubstituted linear substrates, of given geometry, where the organodimetallic obtained has been doubly protonated by water. Further elaborations (to alkenes, ketones, etc.) are possible.

I. Introduction

gem-Dimetallic substrates[1] have been known since the pioneering studies of Wittig,[2] Ziegler,[3] and West and Rochow,[4] but their use in synthesis has been particularly developed with the parent, simplest derivatives CH_2M_2 or $CH_2(M^1)M^2$, to create C=C bonds from carbonyl derivatives: $M^1 = Ti$, $M^2 = Al$ (Tebbe,[5] Petasis[6]), $M^1 = Ti$, $M^2 = Zn$ (Nozaki,[7] Lombardo[8]), $M = Zn$ or Cr (Takai, Utimoto,[9] Nysted[10]), $M^1 = Li$, $M^2 = SiMe_3$ (Peterson[11]). More elaborate substrates, particularly α,α-dilithionitriles[12] and sulfones,[13] have been shown to react twice with mono- or bis-electrophilic species, while *gem*-borolithio-[14] (borozincio-,[15] borozirconio-[16]) alkanes and 1,1-dialuminoalkanes[17] have led to interesting "one-pot" synthesis. However, the elaboration of polysubstituted chains, with a given geometry, was not considered in these studies.

In 1971, Gaudemar[18] found that allyl zinc bromide, prepared in THF, was able to add to various vinyl Grignard reagents at 35 °C with fair to good yields (35–60%). This reaction has been developed substantially since then,[19] and various substituents on the vinylic or the allylic substrate were shown to promote high diastereoselection during the addition process. In this Account, we shall focus on several such strategies which lead to 1,2-, 1,3-,

or 1,4-disubstituted structures, and to 1,2,3-, 1,2,4-tri- and 1,2,3,4-tetrasubstituted systems, where one single (or highly predominant) diastereomer is formed.

## II. 1,2- and 1,2,3-Diastereoselection

II.1. Hydrocarbon Substrates. A high diastereoselection is obtained during the addition of a crotyl zinc reagent to a *Z* (eq 1) or an *E* (eq 2) vinyl lithium reagent.[19] The key
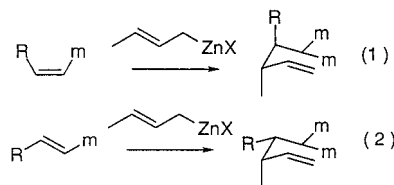
point is the use of ether as a solvent. Ether is less basic than THF and allows coordination of zinc with the electron-rich C=C bond. The reaction is faster and now occurs at around −50 °C. However, zinc metal insertion in the allyl−Br bond is not efficient in ether. The problem is solved by using allyl Grignards (made in ether) via a transmetalation with zinc bromide. In this case, $MgBr_2$ is formed. It may have a role in accelerating the addition step as well as further reactions of the *gem*-dimetallics (vide infra). Preformed vinyl zinc bromide reacts directly with an allyl Grignard, as do other vinyl metals (Li, B, MgX, Al, Cu), but only if zinc (or cadmium) salts are added in the latter case: the requirement of zinc is crucial.

Theoretical calculations, performed independently by two groups,[20] have led to very similar conclusions: the allyl zinc bromide and the vinyl lithium reagent first form a very stable complex due to a square planar arrangement of the Li−C−Zn−Br atoms. The transition state leads to an energetic lithio-zinca adduct, which gives the trimer or tetramer form of a dizinca compound[20b] (Figure 1). These calculations clearly show that whatever the initial reagents are, the initial stable complex is formed exothermally[20a] (Figure 2). We had initially postulated a "metalla-Claisen rearrangement" in which a zinc atom, in a preformed vinylallyl zinc, would play a role similar to that of oxygen in the Claisen sigmatropy. This assumption is not inferred but is not necessary.

Also of interest is the fact that the crotyl zinc reagent, which is prone to metallotropy (eq 3), reacts preferentially in a cisoid form (Figure 3). This accounts for the observed
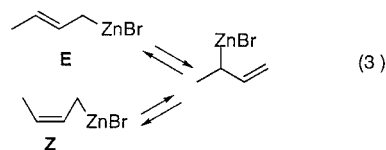

syn or anti products, depending on the geometry (*E* or *Z*) of the starting vinyl lithium used.[20]

II.2. Heterosubstituted Vinyl Metals. When the vinylic partner is heterosubstituted (O, N, S) on the allylic site,

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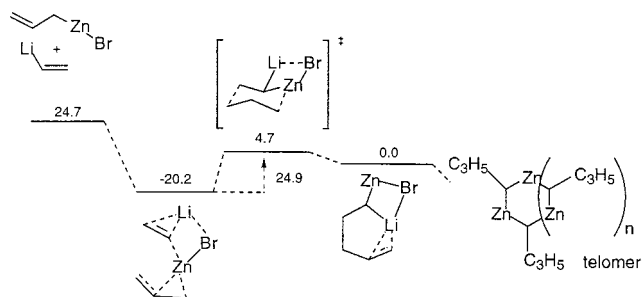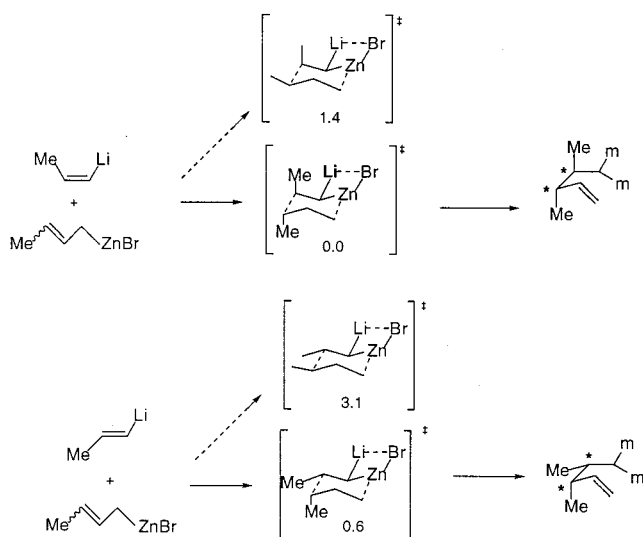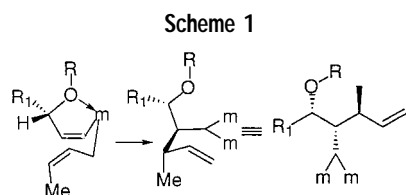
FIGURE 1. Energetic process (computational) of the carbometalation (values in kcal/mol).
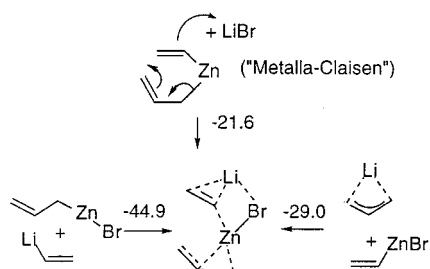
FIGURE 2. Different exothermal approaches (computational) to the initial complex (values in kcal/mol).
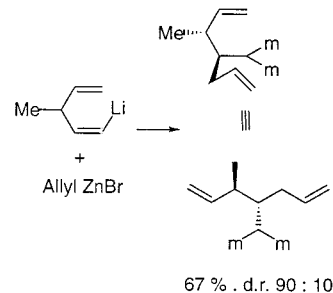

FIGURE 3. Computational evaluation of TS for the crotyl zincation of (E)- or (Z)-propenyllithium (in kcal/mol).
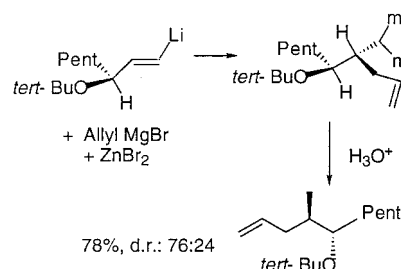
Scheme 1

good facial selectivity can be explained by internal coordination during the addition process (Scheme 1), which takes place on the face anti to the R^1 group.[19]

Instead of chelation by a heteroatom, it is even possible to take advantage of π-stacking of an ethylenic bond (Scheme 2). In this example, replacement of the vinyl group by an ethyl group leads to a 1:1 ratio of diastereomers.
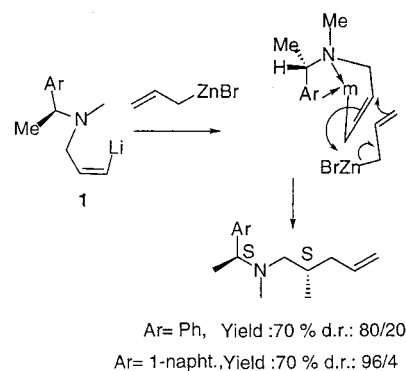
Scheme 2

67 % . d.r. 90 : 10

Scheme 3

78%, d.r.: 76:24

Scheme 4

Ar= Ph,   Yield :70 % d.r.: 80/20
Ar= 1-napht.,Yield :70 % d.r.: 96/4

When the γ-alkoxy vinyl lithium is of E geometry, no chelation takes place, and the allylic 1,3-strain is then responsible for the observed diastereoselection[21] (76:24) (Scheme 3).
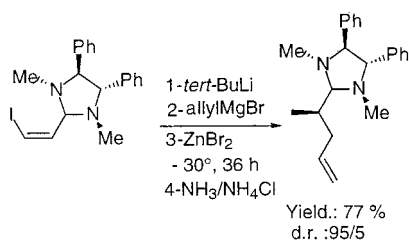
When the allylic carbon of the Z vinyl metal partner is primary, it is possible to induce face selection via the introduction of a chiral appendage (Scheme 4).Thus, a 1-phenylethyl substituent on nitrogen in **1** promotes a facial choice, which is also attributed to π-stacking between the phenyl group and the vinyl metal, so that an 80:20 d.r. is obtained. If the phenyl moiety is replaced by a 1-naphthyl group, the d.r. jumps[22] to 96:4.

In the same way, (Z)-β-iodo acrolein can be derivatized to a C_2-symmetric aminal[23] and submitted to an I/Li exchange followed by crotyl zincation. A single isomer is then formed, easily hydrolyzed to the parent aldehyde[22b] (Scheme 5).
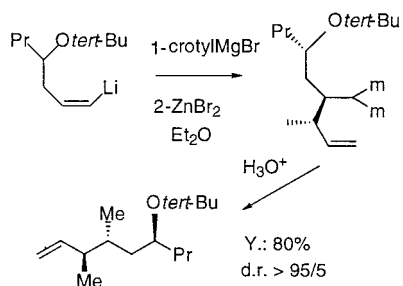
In vinyl lithiums derived from homoallylic ethers, the chiral center is now more remote (γ to the metal). Nevertheless, excellent induction occurs, delivering a 3,4,6-trisubstituted 1-alkene as a single isomer[24] (Scheme 6).

Of course, if the preceding starting ether already contains a substituent in the allylic position, either syn
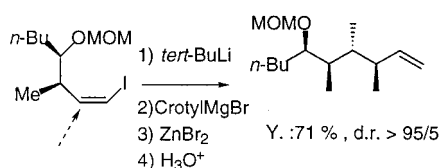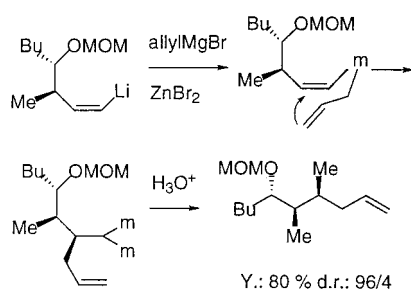
Scheme 5

1-*tert*-BuLi
2-allylMgBr
3-ZnBr$_2$
- 30°, 36 h
4-NH$_3$/NH$_4$Cl

Yield.: 77 %
d.r. :95/5

Scheme 6

1-crotylMgBr
2-ZnBr$_2$
Et$_2$O

H$_3$O$^+$

Y.: 80%
d.r. > 95/5

Scheme 7

1) *tert*-BuLi
2)CrotylMgBr
3) ZnBr$_2$
4) H$_3$O$^+$

Y. :71 % , d.r. > 95/5

Scheme 8

allylMgBr
ZnBr$_2$

H$_3$O$^+$

Y.: 80 % d.r.: 96/4

Scheme 9

Allyl *anti*
to Butyl

Scheme 10

1- allylMgBr
2- ZnBr$_2$
3-H$_3$O$^+$

Y.: 51 % d.r.: 95/5

Scheme 11

1) MeO⌐⌐ZnBr
TMEDA
ether, 24 h
2) H$_3$O$^+$

Y.: 80 % d.r. 95/5

1) EtO⌐⌐ZnBr
TMEDA (cat.)
ether, 72 h.
2) H$_3$O$^+$

Y.: 52% d.r. 65/35

or anti to the butyl group, a matched or mismatched diastereomer is created in the carbometalation process. In the following examples, a methoxy methyl (MOM) ether is used for securing better chelation. The matched isomer undergoes the crotyl addition on the face anti to both Bu and Me groups (Scheme 7).

The mismatched isomer, unexpectedly, reacts with the allyl zinc bromide extremely diastereoselectively, and the allyl group adds syn to the methyl group (although in the allylic position) and anti to the homoallylic *n*-Bu group[24,25] (Scheme 8). This curious outcome is better accounted for by considering an analogy with addition to substituted cyclohexenes, as described by Toromanoff,[26] which follows a trans diaxial preference. Insofar as the six membered heterocycle derived from chelation of the MOM group would behave as an analogous six-carbon ring, the allyl zinc will add axially, anti to the pseudoequatorial *n*-Bu group (Scheme 9).

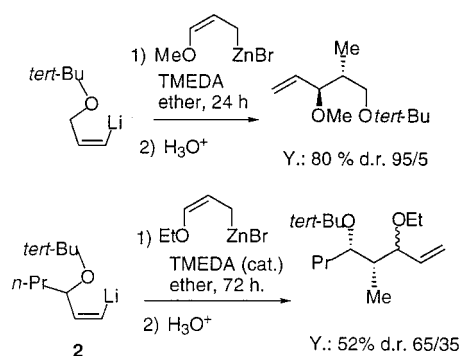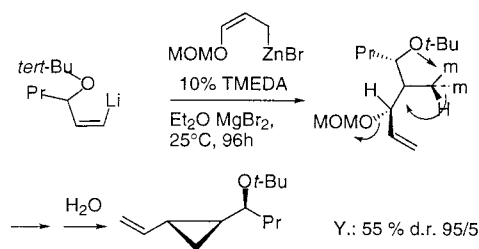These schemes apply to cases where the allylic and homoallylic substituents belong to a cyclohexane[25] (Scheme 10).
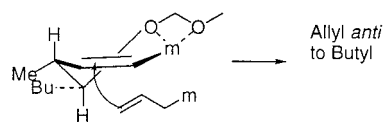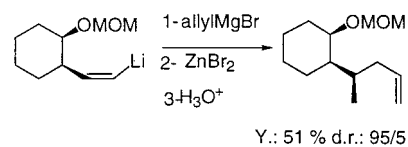
II.3. Heterosubstituted Allyl Zinc Reagents. The crotyl reagents discussed so far ultimately delivered a methyl group diastereoselectively set up on the final linear chain. We decided to check whether an alkoxyallyl zinc reagent would also add with good regioselectivity to introduce an oxygenated substituent. If such is the case, what about the diastereoselectivity of the addition process? Allyl ethyl ether is easily deprotonated by *sec*-BuLi in THF at −60 °C, and the derived allyl lithium is transmetalated to zinc uneventfully.[27] Although the use of *sec*-BuLi and TMEDA in ether avoids the use of THF, the resulting allyloxy−zinc−TMEDA complex reacts very slowly, particularly when a secondary allylic ether (**2**) is used. However, deprotonation of the allylic ether by *sec*-BuLi in the presence of a *catalytic* amount of TMEDA (10%) in ether is possible and increases the yield to 52%, but nevertheless in this latter case, two diastereomers are formed in a 2:1 ratio (Scheme 11).

However, if chelation is better secured (with an OMOM group), and if magnesium bromide is added to accelerate the addition process, then a single addition product arises, which immediately undergoes γ-elimination of the OMOM moiety. (It behaves as a leaving group in the presence of MgBr$_2$). Thus, we have direct access to 2-vinyl-substituted *trans*-cyclopropyl syn secondary carbinols with three defined stereocenters[28] (Scheme 12).

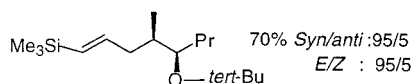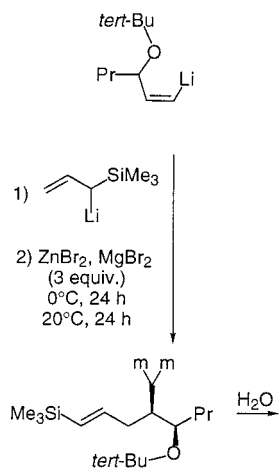Metalated allyl silanes are also interesting precursors, allowing further elaborations via silicon chemistry. Preliminary experiments showed that silicon ends up in the vinylic position, and that the stereoselectivity is only fair (73:27) in the presence of 1 equiv of ZnBr$_2$ at 0 °C for 92 h (Scheme 13).

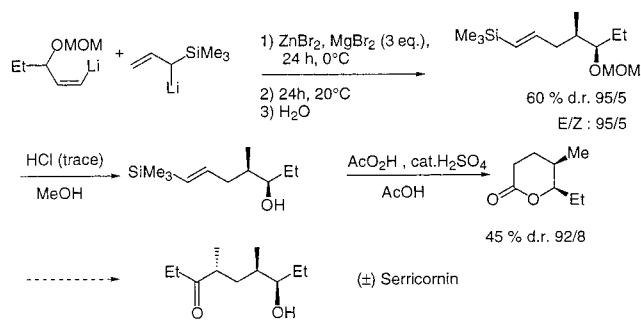However, use of excess ZnBr$_2$ and MgBr$_2$ (3 equiv each) speeds up the reaction, which is then over within 24 h at

Scheme 12

Scheme 13

Scheme 14

Scheme 15

Scheme 16

by a peracid. This lactone has already been methylated stereoselectively via its lithium enolate and ring opened by an ethyl Grignard to form the corresponding serricornin.

1,1-Dizinca reagents of the *vinylidene* type[30] can also lead to interesting 1,3- or 1,4-diastereoselections. For example, crotyl zincation of a propargylic ether, metalated on the acetylenic position, can be highly diastereoselective (Scheme 15).

In **3**, the intramolecular chelation of one metal (m_1) lowers its nucleophilicity and allows the selective replacement of m_2 by chlorine (using PhSO$_2$Cl). The vinylidene zinc carbenoid thus formed is prone to undergo a Fritsch–Buttenberg–Wiechell (FBW) rearrangement[31] (the analogous lithio carbenoid would not do so), whereby the alkoxyalkyl moiety migrates exclusively[32] (as checked by ^{13}C labeling), and with retention of configuration of the migrating carbon atom (Scheme 16). So far, the FBW rearrangement was known to be operative only when H, alkoxy, or aryl moieties were involved in the migration step. This new elaboration of 1,4-stereoselection in **4** from the initial 1,3-relationship in **3** relies on the use of a *zinc* carbenoid.

III. Conclusion

In this Account, it is demonstrated not only that the addition of substituted allyl metals to substituted vinyl metals requires the presence of zinc salts, but also that good regio- and diastereoselectivities are then obtained if a low polar solvent is used. At the outcome, this strategy allowed the introduction of two vicinal methyl groups, either syn or anti, on a nonfunctionalized linear chain, starting from (*E*)- or (*Z*)-1-metalla-1-alkenes and crotyl zinc bromide. The presence of heteroatoms on the two reagents was then considered. The vinyl metal partner can bear heteroatoms (O, N, S) on allylic or homoallylic positions, and the crotyl zinc reagent can be replaced by a silylallyl or an alkoxyallyl zinc reagent. In all cases, the di-, tri-, or tetrasubstituted linear skeletons are formed
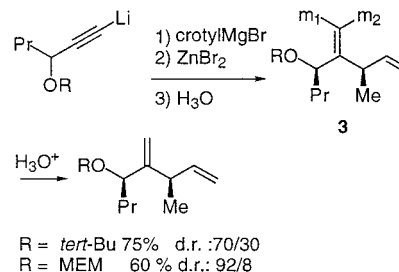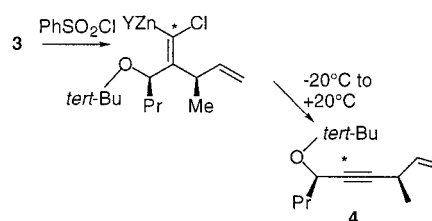
0 °C. An analogous yield (73%) of the single syn isomer is now obtained, but at the cost of a diminished *E/Z* ratio (87:13). This latter drawback can be overcome if, after the addition process, the reaction mixture is warmed to +20 °C for another 24 h. *Z*-to-*E* isomerization takes place, and a single syn-*E* isomer is formed (70%). Protection of the alcohol by a MOM group is equally efficient and allows for easier deprotection. Thus, taking advantage of the silicon moiety, a new approach of serricornin has been developed[29] according to Scheme 14. Allyltrimethylsilane is deprotonated and mixed with the lithiated MOM ether derived from (*Z*)-1-iodopent-1-en-3-ol. ZnBr$_2$ and MgBr$_2$ are added at 0 °C to promote the addition reaction, and warming to +20 °C allows for *Z*-to-*E* isomerization. The resulting δ-hydroxyvinylsilane, obtained with a good d.r., is converted to the corresponding lactone by oxidation

diastereoselectively. Alkoxyallyl zinc reagents are also a good source of metalated disubstituted cyclopropanes. More work is required to get direct access to the starting vinyl metals, for instance, by hydrometalation of alkynes, and to the starting allyl metals, which are difficult to prepare in low-polarity solvents. The influence of Lewis acid additives, i.e., $MgBr_2$, has been briefly alluded to, but the fundamental point is that, among the clusters involved in the various transition states, the C–Zn bond has a tremendous importance in promoting the observed high stereoselectivities.[33]

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