parallel defect lines running across the long axes of the tubules (Figure 3a and c). Lines of this nature are usually associated with chirality, and in particular helicity which results from the way the chiral molecules pack together. These results suggest that the tubules either have a helical multilayer structure composed of several hundred molecular layers, or else they have a periodic defect structure that is based on some form of helicity. Periodic defect structures are well known for thermotropic liquid crystals, and are often manifested when the need for the molecules to form a twisted macrostructure is confronted with some structural or spatial limitation (e.g., Blue Phases, TGB Phases). This competition results in a frustration which is relieved by the creation of defects.

In the case of **1** and **3**, the lines running across the tubules could be related to defects produced by a localization of the twist, in a similar way to how twist is localized in the structure of the twist grain boundary phase.[28] Conversely, **2** does not exhibit tubules. This may be because it has a different stereochemical structure to **1** and **3**, and as a result may not experience the same competition in the packing of the asymmetric moieties of its molecules. Detailed studies and explanations of these self-assembled structures are, however, complex, and a more comprehensive explanation of their properties will be given elsewhere.

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A Facile Generation of a Cyclopropylzinc Compound from an Alkenylzinc Derivative and Its Reaction with Electrophiles[**]

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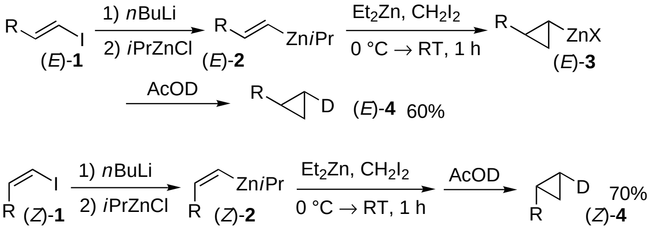
Cyclopropylmetal compounds are useful reagents for the construction of cyclopropane derivatives. The most common method for the preparation of these reagents is metalation of halocyclopropane derivatives with metals or organometallic compounds such as lithium, magnesium, or butyllithium.[1, 2] However, present synthetic approaches to the halocyclopropanes[3] are very lengthy and rather inefficient. Thus, development of a more convenient and direct access to cyclopropylmetal derivatives should expand their synthetic utility. Although the direct cyclopropanation of some 1-alkenylmetal compounds[4] (B, Al, Si, Sn) by the Simmons–Smith reaction[5] has been reported, the resulting cyclopropylmetal compounds have low reactivities with respect to electrophiles; there are no examples of their direct reaction with carbon electrophiles. Here we report the first example of the preparation of a cyclopropylzinc derivative from a 1-alkenylzinc compound and its synthetic use for further reaction with electrophiles in a one-pot procedure.

The 1-alkenylzinc compound was prepared from isopropylzinc chloride[6] and a 1-alkenyllithium reagent, which was generated from a 1-iodo-1-alkene upon treatment with butyllithium in hexane (Scheme 1).[7] Diethylzinc and CH_2I_2 were



Scheme 1. Stereospecific cyclopropanation of alkenylzinc compounds. R = n-$C_{10}H_{21}$; X = I, iPr.

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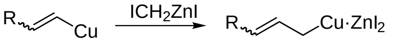
added to the resulting zinc reagent, and the mixture was stirred for 1 h at ambient temperature. The mixture was quenched with AcOD to give *trans*-1-deuteriocyclopropane (*E*)-**4** stereoselectively in 67 % yield. Cyclopropanation of the alkenylzinc compounds proceeded in a stereospecific manner. Thus, starting from a *cis*-1-alkenylzinc compound, the corresponding *cis*-1-deuteriocyclopropane (*Z*)-**4** was obtained exclusively.

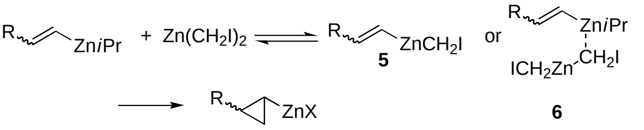
Knochel and co-workers reported that the reaction of a 1-alkenylcopper reagent with iodomethylzinc afforded the homologated allylcopper species [Eq. (1)].[8] In contrast,



(1)

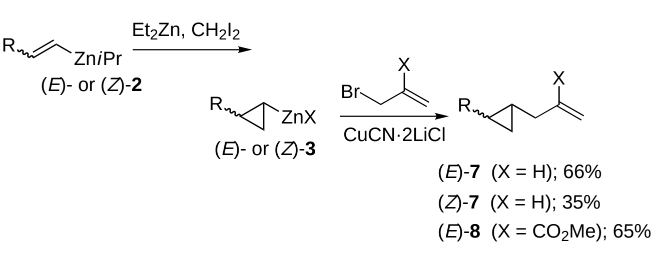
there was no evidence for the formation of the corresponding allylzinc reagents in our experiments.

Cyclopropanation of alkenylzinc compounds proceeded very quickly under milder conditions than that of other alkenylmetal derivatives. Even at −15 °C, the reaction was complete within 1 h to afford the corresponding cyclopropane in 65 % yield upon quenching with aqueous HCl. Selective cyclopropanation of 1-dodecenylzinc occurred in the presence of 5-triisopropylsiloxy-1-pentene, and the pentene was recovered completely. From these results, we are tempted to assume that this rapid cyclopropanation is intramolecular in nature. The ligand exchange reaction between alkenylisopropylzinc compounds and bis(iodomethyl)zinc afforded **5**, which was intramolecularly converted into the corresponding cyclopropylzinc compound (Scheme 2). Alternatively, a mixed aggregate of the alkenylzinc compound and iodomethylzinc such as **6** might be involved.



Scheme 2. Ligand exchange reaction between the alkenylisopropylzinc compound and bis(iodomethyl)zinc. X = I, *i*Pr.

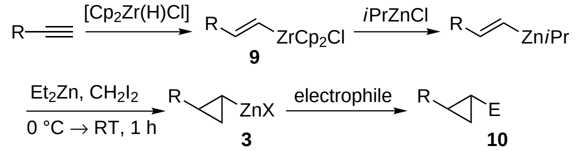
Treatment of the cyclopropylzinc intermediate with allyl bromides in the presence of CuCN · 2 LiCl[9] afforded the allylated cyclopropane derivatives **7** and **8** (Scheme 3).[10] As a consequence of the steric hindrance, the *cis* isomer (*Z*)-**3** was less reactive than the *trans* isomer (*E*)-**3**.



Scheme 3. The trapping of the intermediate cyclopropylzinc compound with allyl bromide in the presence of CuCN · 2 LiCl. R = *n*-$C_{10}H_{21}$.

We then turned our attention to the one-pot synthesis of cyclopropylzinc compounds from 1-alkynes. The 1-alkenylzinc compounds could be prepared by transmetalation between the alkylzinc and 1-alkenylzirconium compounds; the latter was obtained from the reaction of the corresponding 1-alkyne with [$Cp_2Zr(H)Cl$].[11] Cyclopropanation of these zinc species also proceeded smoothly to give *trans*-cyclopropylzinc species **3** with high stereoselectivities. These intermediates **3** were trapped with electrophiles (Table 1). The zinc species containing a heteroatom were stabilized by coordination of oxygen and reacted poorly with allyl bromide (20–28 %).[12]

Table 1. Reaction of cyclopropylzinc compounds **3**, obtained from 1-alkynes, with electrophiles.



R	Electrophile	Yield of **10** [%]
n-$C_{10}H_{21}$	AcOD	65
n-$C_{10}H_{21}$	$CH_2{=}CHCH_2Br$[a]	69
$BnOCH_2CH_2$	AcOD	63
$BnOCH_2CH_2$	$CH_2{=}CHCH_2Br$[a]	20
$EtO_2C(CH_2)_8$	AcOD	65
$EtO_2C(CH_2)_8$	$CH_2{=}CHCH_2Br$[a]	28

[a] In the presence of CuCN · 2 LiCl.

Experimental Section

To a suspension of [$Cp_2Zr(H)Cl$][13] (387 mg, 1.5 mmol) in CH_2Cl_2 (5 mL) was added 1-dodecyne (166 mg, 1.0 mmol) at 25 °C. After 20 min the mixture was cooled to 0 °C, and a solution of *i*PrZnCl (1.1 mmol) in hexane was added. After 30 min at 0 °C Et_2Zn (2.0 mmol, 1.0 M solution in hexane, 2.0 mL) and CH_2I_2 (0.32 mL, 4.0 mmol) in ether (4 mL) were added to the mixture, and the solution was allowed to warm to 25 °C over 1 h. The solvent and Et_2Zn were removed under reduced pressure. After cooling of the residue to −10 °C, THF (5 mL) and a solution of CuCN · 2 LiCl (1.1 mmol) were added. Then, allyl bromide (0.26 mL, 3.0 mmol) was added at −78 °C. After 12 h with gradual warming to 25 °C, the reaction mixture was poured into a mixture of saturated aqueous NH_4Cl and aqueous ammonia and was extracted with hexane (3 × 10 mL). Concentration and purification by chromatography on silica gel afforded *trans*-1-allyl-2-decylcyclopropane (153 mg, 0.69 mmol) in 69 % yield.

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[10] Compound (*E*)-**3** was also coupled with acetyl chloride under Pd^0 catalysis (30% yield).[14]

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Magnesium Complexes Bearing η^2-Pyrazolato Ligands[**]

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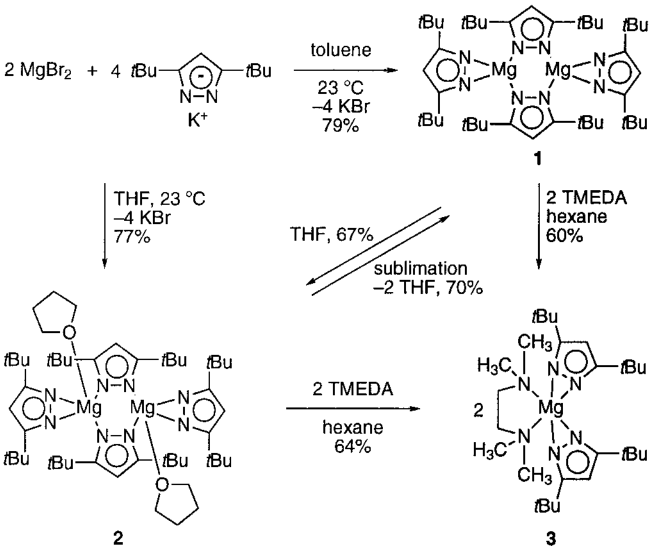
Pyrazolato ligands are commonly employed in complexes of the middle to late d-block metals, and either exhibit η^1 bonding to a single metal ion or bridge two metal centers.[1] η^2-Pyrazolato bonding is generally observed in lanthanide(III) complexes as a consequence of the more ionic bonding and larger size of the metal centers, relative to the d-block metals.[2] We have described several titanium(IV) and tantalum(V) complexes that contain η^2-pyrazolato ligands, and demonstrated that this binding mode is significantly favored over η^1 binding unless the coordination sphere is sterically congested.[3–5] Very recently, we reported the crystal structure of a hexameric potassium pyrazolato complex that contains bridging η^2-pyrazolato ligands.[6] Since the η^2 coordination mode was observed in the potassium complex it seemed very likely that this coordination mode would be observed in other main group metal complexes.

Our motivation for exploring pyrazolato complexes concerns the development of improved source compounds for chemical vapor deposition (CVD) applications. Volatile metal complexes composed of Group 2 or lanthanide metals with 1,3-diketonate ligands are widely used in CVD processes.[7] However, the presence of oxygen makes diketonate-based precursors inappropriate for the deposition of non-oxide materials, such as magnesium-doped gallium nitride.[8] With these considerations in mind, we report the synthesis, structure, and reactivity of several magnesium pyrazolato complexes. Surprisingly, η^2-pyrazolato coordination is observed in these complexes, despite the small size of the magnesium ion. This study gives the first structural documentation of terminal η^2-pyrazolato ligands with the main group metals and offers new insight into the design of volatile Group 2 compounds for use in film depositions through CVD methods.

Treatment of magnesium bromide with potassium 3,5-di-*tert*-butylpyrazolate[6] (2 equiv) in toluene led to the formation of bis[bis(3,5-di-*tert*-butylpyrazolato)magnesium] (**1**, 79%; Scheme 1) as colorless crystals after workup. If the reaction of magnesium bromide with potassium 3,5-di-*tert*-butylpyrazolate was carried out in tetrahydrofuran (THF), workup afforded bis[bis(3,5-di-*tert*-butylpyrazolato)(tetrahydrofuran)magnesium] (**2**, 77%) as colorless crystals. Treatment of **1** or **2** with *N*,*N*,*N*′*N*′-tetramethylethylene diamine (TMEDA, 1 equiv per magnesium) led to the formation of bis(3,5-di-*tert*-butylpyrazolato)(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)magnesium (**3**, 60–64%). Dissolution of **1** in THF followed by workup, afforded **2** (67%), while sublimation of **2** at 150 °C (0.1 torr) afforded **1** (70%) with loss of the



Scheme 1. Synthesis and reactions of the pyrazolatomagnesium complexes **1**–**3**.

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