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Development of Highly Chemoselective Bulky Zincate Complex, $t\mathrm{Bu}_4\mathrm{ZnLi}_2$: Design, Structure, and Practical Applications in Small-/Macromolecular Synthesis

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Abstract: We present full details of the unique reactivities of the newly developed dianion-type bulky zincate, dilithium tetra-*tert*-butylzincate ($t\mathrm{Bu}_4\mathrm{ZnLi}_2$). With this reagent, halogen–zinc exchange reaction of variously functionalized haloaromatics and anionic polymerization of *N*-isopropylacrylamide (NIPAm)/styrene with excellent chemoselectivity were realized. Halogen–zinc exchange reaction followed by electrophilic trapping with propargyl bromide provided a convenient route to functionalized phenylallenes, particularly those with electrophilic functional groups (such as cyano, amide and halogens). Spectral and computational studies of the structure in the gas and liquid phases indicated extraordinary stabilization of this dianion-type zincate by its bulky ligands.

Keywords: chemoselective metalation · halogen–metal exchange · nucleophilic substitution · polymerization · zinc

Introduction

The use of organozinc compounds has opened up new avenues in organic and organometallic chemistry. Diorganozinc reagents such as Reformatsky-type (RZnX) and dialkylzinc (RZnR′) compounds have widely been used for various chemoselective reactions in organic synthesis, but these reagents are often plagued by poor reactivity in the absence of transition-metal catalysts or activating ligands, such as aminoalcohols.[1] Organozinc ate complexes ($\mathrm{R}_3\mathrm{Zn}^-\mathrm{M}^+$) are another important class of organozinc reagents, showing higher reactivities than the diorganozinc reagents, for instance, in 1,4-conjugated additions,[2] iodine–zinc exchange reactions of organic halides,[3] and directed *ortho*-zincation reactions.[4] In 1996, we reported dianion-type zincates ($\mathrm{R}_4\mathrm{Zn}^{2-}\cdot 2\,\mathrm{Li}^+$) as a new type of zinc–ate complexes, which added a new dimension to organozincate reagents: they can promote bromine (or tellurium)–zinc exchange, and carbo- (or silyl-)zincation reactions.[5] Various dianion-type zincates have subsequently been developed, focusing mainly on high aptitude for the transfer of ligands.

In this article, we present a new type of dianion-type zincate, dilithium tetra-*tert*-butylzincate[6] ($t\mathrm{Bu}_4\mathrm{ZnLi}_2$), which we designed as a highly crowded, bulky zincate by utilizing the feature that dianion-type zincates have four ligands. $t\mathrm{Bu}_4\mathrm{ZnLi}_2$ turned out to have a range of attractive features, such as remarkable low basicity, excellent chemoselectivity, high halogen–zinc exchange ability, and wide anionic polymerization ability. Furthermore, it showed excellent $\mathrm{S_N}2'$ selectivity in the reaction with propargyl bromide due to its steric bulkiness, which led to a simple one-pot synthesis of various kinds of phenylallene derivatives from functionalized halobenzenes via successive chemoselective metalation/regioselective $\mathrm{S_N}2'$ reaction with propargyl bromide. In order to understand the origin of the unique reactivity/selectivity of $t\mathrm{Bu}_4\mathrm{ZnLi}_2$, we also examined the structural features of the bulky ligand–zincates by means of multidimensional NMR, ESI-MS, and DFT studies.

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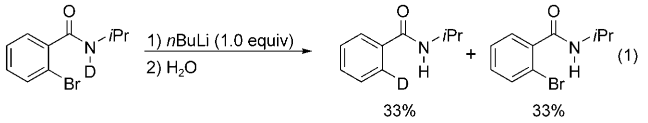
Results and Discussion

Unique reactivities of tBu$_4$ZnLi$_2$ (I): Application as a highly chemoselective halogen-zinc exchange reagent: Traditional organometallic reagents, including alkyllithiums or Grignard reagents, are useful in procedures for C–C, C–X, and C–metal bond formation in organic synthesis.[7] However, the application of these organometallic reagents for metalation of highly functionalized substrates is generally limited by low functional group tolerance, significant formation of by-products, and severe restrictions regarding reaction conditions, particularly the need for extremely low temperature, strict exclusion of acidic protons, and hence tedious protection/deprotection processes typically required for such reactions. These limitations arise because general organometallic reagents have not only halogen–metal exchange ability, but also high nucleophilicity and basicity, and these features have been regarded as difficult or impossible to separate. Therefore, the development of highly chemoselective metalating reagents/reactions in which the nucleophilicity and basicity are masked is still highly desirable.

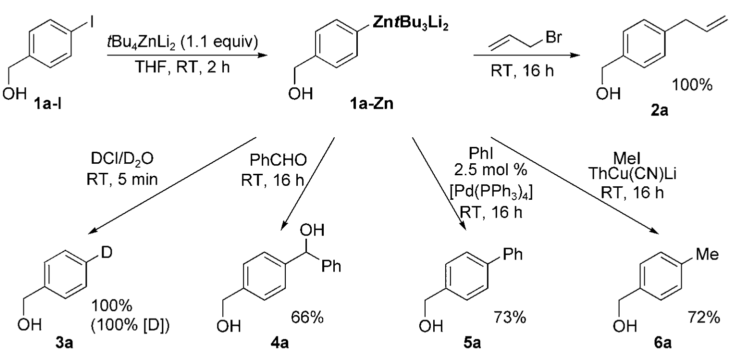
Development of chemoselective halogen–zinc exchange reaction compatible with acidic proton: Beak et al. have reported that in the lithiation reaction of o-bromo-(N-deuterio)benzamide using nBuLi, o-deuterated benzamide was obtained as the main product [Eq. (1)], which clearly shows that the halogen–metal exchange reaction occurred faster than the deprotonation reaction of the amide N-H proton with nBuLi, but due to the strong basicity of an intermediary C-lithiated species, the intermediate was quenched smoothly with inter-/intramolecular acidic amide N-H proton to give the thermodynamically more stable N-lithiated product.[8]



Therefore, our approach capitalizes on the stability of intermediary aromatic zincates (relative to their lithium analogues), which is well-known to minimize subsequent rearrangement or side reactions.[9] We hypothesized that a bulky zincate might improve the stability (or isolability) of the aromatic C-metal intermediate and prevent successive side reactions.

In the initial screening of suitable zincates, p-iodobenzyl alcohol (**1a-I**) was selected as a model substrate having an alcoholic proton on the iodobenzene ring. When alkyllithiums, dialkylzinc, or monoanion-type zincates were used as metalating reagents, the desired C-allylated product was not obtained at all. On the other hand, when dianion-type zincates were used, the C-allylated product was obtained preferentially. Among them, tBu$_4$ZnLi$_2$ metalated **1a-I** smoothly, affording **2a** in quantitative yield. Stepwise treatments of **1a-I** with alkyllithiums, followed by addition of zinc reagents, were examined, but all were ineffective for the formation of the arylzincates. These observations suggest that the precomplexation of tBu$_4$ZnLi$_2$ is essential for successful metalation. (See Supporting Information, Table S1, for details.)

The arylzincate intermediate (**1a-Zn**) can be utilized as an aryl anion equivalent. We next tested whether the arylzincate intermediate (**1a-Zn**) can be utilized as an aryl anion equivalent for the C–C bond-forming reaction with various electrophiles without any protection of the OH moiety. The intermediate **1a-Zn**, generated by the exchange reaction of **1a-I** with tBu$_4$ZnLi$_2$ could be trapped with various electrophiles, such as DCl/D$_2$O, allyl bromide and benzaldehyde, to give the desired adducts without any O-functionalized side-products (Scheme 1). The intermediate **1a-Zn** also undergoes copper- and palladium-catalyzed C–C bond-forming reactions, such as phenylation (**5a**) and alkylation (**6a**) in modest to good yields and with high chemoselectivity. Importantly, neither extremely low temperature nor protection/deprotection processes for the OH moiety are required in any of these transformations.



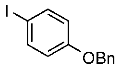
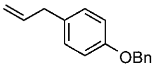
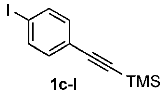
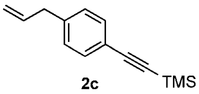
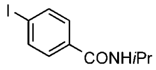
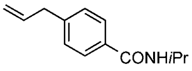
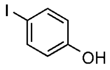
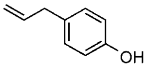
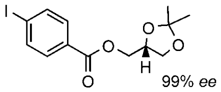
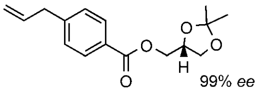
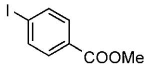
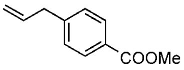
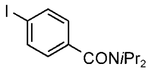
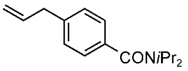
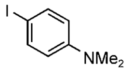
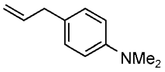
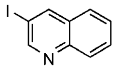
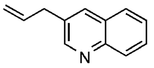
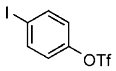
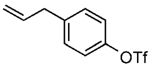
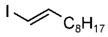
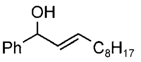
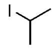
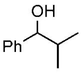
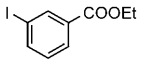
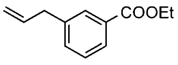
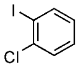
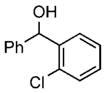
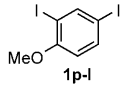
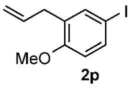
Scheme 1. Trapping of the intermediate with various electrophiles.

Scope and limitations of the halogen–zinc exchange reaction using tBu$_4$ZnLi$_2$: With optimized conditions in hand, we studied the scope of this unique metalation reaction for various functionalized organic iodides (Table 1). Not only suitably protected alcohols and terminal alkyne (entries 1–2), but also unprotected acidic protons (amide N-H, phenolic O-H, glycerol C2 proton) were compatible with the reaction (entries 3–5). No epimerization at all was observed with **1f-I**, although epimerization to give racemic mixtures often occurs in base-catalyzed reactions of glycerol derivatives. Substrates containing electrophilic functional groups, such as ester and amide groups, can be utilized for the zincation (entries 5–7). Although a methyl ester is generally inconsistent with the halogen–metal exchange reaction, essentially no side reaction was observed under our reaction conditions, due to the high chemoselectivity and mild conditions of this interconversion reaction[5c] (entry 6). Nitrogen-containing substrates such as aniline derivatives and π-deficient heteroaromatic moieties also caused no problem (entries 8–9). Aryl triflate was inert to metalation with $t\mathrm{Bu}_4\mathrm{ZnLi}_2$ (not shown), and the metalation reaction turned out to proceed with complete selectivity in triflate mixed substrates (entry 10).

Besides *p*-iodobenzene derivatives, aliphatic iodides including C(sp^2)- and C(sp^3)-I derivatives can be utilized as substrates in this exchange reaction (entries 11–12). *meta*- and *ortho*-Substituted compounds were also good substrates (entries 13–14). *ortho*-Halo (including pseudo-halogens) metallobenzenes, which are well-known as good precursors for benzynes,[10] also worked smoothly when a low equivalent amount of $t\mathrm{Bu}_4\mathrm{ZnLi}_2$ was used (entry 14). In the reaction of a multi-iodo substrate, the *ortho* position of iodide to the methoxy group was metalated with high regioselectivity, mainly due to the coordination of DMG to the cation moiety of zincate[11] (entry 15).

Generally, the halogen-metal exchange ability of aryl bromides is lower than that of iodides.[12] We next turned our attention to the bromine-zinc exchange reaction of aryl bromides with $t\mathrm{Bu}_4\mathrm{ZnLi}_2$ (Table 2). Although a higher reaction temperature was required, the exchange reactions proceeded smoothly (entry 1) and were compatible with various functional groups, such as TMS-protected acetylene, amides, π-deficient heteroaromatic moiety, and triflates (entries 2–5). However, in the case of using *p*-bromobenzyl alcohol (**1a-Br**) as a substrate, the deprotonation reaction took place prior to bromine-zinc exchange, and the desired C−C bond formation was not observed at all (entry 6).

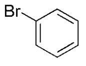
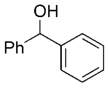
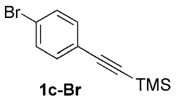
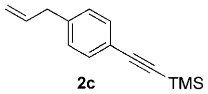
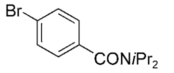
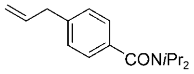
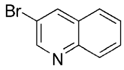
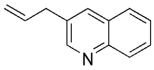
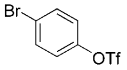
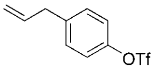
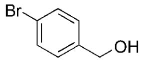
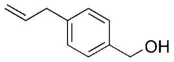
Table 1. Metalation of various functionalized organic iodides.[a]

Entry	Substate	Product	Yield[b] [%]	Electrophile
1	 **1b-I**	 **2b**	86	allyl bromide
2	 **1c-I**	 **2c**	94	allyl bromide
3[c]	 **1d-I**	 **2d**	62	allyl bromide
4[c,d]	 **1e-I**	 **2e**	79	allyl bromide
5	 **1f-I**	 **2f**	74	allyl bromide
6	 **1g-I**	 **2g**	90	allyl bromide
7	 **1h-I**	 **2h**	79	allyl bromide
8	 **1i-I**	 **2i**	78	allyl bromide
9	 **1j-I**	 **2j**	77	allyl bromide
10	 **1k-I**	 **2k**	87	allyl bromide
11	 **1l-I**	 **4l**	74	PhCHO
12	 **1m-I**	 **4m**	62	PhCHO
13	 **1n-I**	 **2n**	87	allyl bromide
14[e,f]	 **1o-I**	 **4o**	60	PhCHO
15[f]	 **1p-I**	 **2p**	69	allyl bromide

[a] Unless otherwise noted, the metalation was carried out using $t\mathrm{Bu}_4\mathrm{ZnLi}_2$ (1.1 equiv) and substrate (1.0 equiv) in THF at 0 °C for 2 h, and the resultant metalated intermediate was treated with an electrophile (allyl bromide or benzaldehyde). [b] Isolated yield. [c] Zincate (2.2 equiv) was used. [d] Metalated at 40 °C. [e] Zincate (0.55 equiv) was used. [f] Metalated at −40 °C.

Unique reactivities of $t\mathrm{Bu}_4\mathrm{ZnLi}_2$ (II): Application for highly regioselective $\mathrm{S_N2'}$ reaction: Allenic compounds have come to occupy a very important position in recent organic synthesis as building blocks and pharmaceuticals.[13] Several methods have been reported to date for the preparation of

Table 2. Metalation of various functionalized aromatic bromides.[a]

Entry	Substate	Product	Yield[b] [%]	Electrophile
1	 **1q-Br**	 **4q**	74	PhCHO
2	 **1c-Br**	 **2c**	98	allyl bromide
3	 **1h-Br**	 **2h**	87	allyl bromide
4[c]	 **1j-Br**	 **2j**	77	allyl bromide
5	 **1k-Br**	 **2k**	87	allyl bromide
6[d]	 **1a-Br**	 **2a**	0	allyl bromide

[a] Unless otherwise noted, the metalation was carried out using $t\mathrm{Bu_4ZnLi_2}$ (1.1 equiv) and substrate (1.0 equiv) in THF at 60 °C for 2 h, and the resultant metalated intermediate was treated with an electrophile (allyl bromide or benzaldehyde). [b] Isolated yield. [c] Metalated at refluxing temperature. [d] Benzyl alcohol was obtained as a major product.

allenic compounds,[14] such as the Doering–Moore–Skatteböl reaction,[15] the homologation of 1-alkynes,[16] the stereoselective reduction of alkynes,[17] and cross-coupling reactions with allenyl–metal species.[18] Among them, one of the simplest and widely used methods is the S_N2'-type reaction of organocuprate reagents with propargyl halides. However, its application to the preparation of aryl allenes has generally been limited by low availability of various functionalized aryl copper compounds and unsatisfactory S_N2' selectivity. A highly chemoselective halogen–copper exchange reaction developed by Kondo et al.[19] and the introduction of transmetalation via an aryl Grignard intermediate prepared by Knochel's method[20] were major advances in the preparation of functionalized arylcuprates, but the S_N2' selectivity remains an issue. We hypothesized that the steric bulkiness of multiple *t*Bu ligands on the Zn atom might favor S_N2'-selective ligand transfer.

In order to compare the reactivities and chemo- and S_N2' selectivities of intermediary arylcuprate and arylzincate, we carried out comparative reactions using *p*-iodo ethylbenzoate as a functionalized aryl halide and propargyl bromide as an allenyl precursor (Table 3). With organocuprate, the yields and selectivities were unsatisfactory regardless of the procedure or the amount of the cuprate (entries 1–2). In contrast, the use of $t\mathrm{Bu_4ZnLi_2}$ turned out to improve drastically the S_N2' selectivity, and the desired 4-ethoxycarbonyl phenyl allene was obtained in a quantitative yield (entry 3). Addition of a catalytic amount of a cuprate in this zincate reaction resulted in a decrease of the S_N2' selectivity, resulting in a lower yield of the allenic product (entry 4).

Representative results from the exchange reactions of various functionalized aromatic iodides with $t\mathrm{Bu_4ZnLi_2}$, followed by S_N2/S_N2' reaction with propargyl bromide are summarized in Table 4. Aryl tri(*tert*-butyl)zincate intermediates prepared from the exchange reaction of various iodobenzene derivatives with $t\mathrm{Bu_4ZnLi_2}$ reacted smoothly with propargyl bromide at room temperature in a S_N2' fashion to give corresponding allenic compounds in good to excellent yields (entries 1–9). Substrates bearing an OH group and a variety of polar functional groups, including TMS-acetylene, amide, triflate, halogens, cyano, and ester, caused no problems in terms of yields and chemo- and regioselectivities. A naphthalene derivative (entry 10) could also be utilized in this transformation.

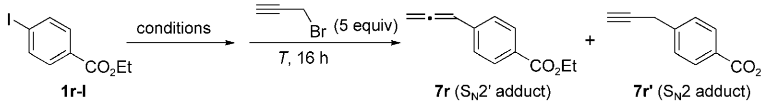
In summary, this is an exceedingly practical method for chemoselective arylallene preparation and offers an attractive alternative to more traditional procedures.

Unique reactivities of $t\mathrm{Bu_4ZnLi_2}$ (III): Application for chemoselective anionic polymerization

Polymerization of* N*-isopropylacrylamide (NIPAm) in aqueous media: We have described the high chemoselectivity of the newly developed bulky zincate, $t\mathrm{Bu_4ZnLi_2}$ in previous sections. On the basis of its soft nucleophilicity and weak basicity, we next focussed on the development of a new organozincate-mediated anionic polymerization using $t\mathrm{Bu_4ZnLi_2}$ as an initiator. Acrylic acid derivatives, which behave as activated olefins owing to the conjugated carbonyl group, were chosen as the first target monomer.

Poly(*N*-isopropylacrylamide) (PNIPAm, **P8**) exhibits unique temperature-sensitive properties.[21] It has been applied in various ways in organic chemistry,[22] materials sciences,[23] and biotechnology.[24] However, since NIPAm (**8**) is a multifunctionalized monomer, especially possessing an acidic amide-NH proton, the polymerization of unprotected

Table 3. Comparison of S_N2' selectivities.

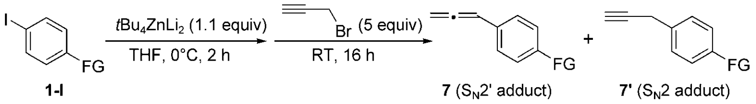


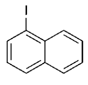
1r-I **7r** (S_N2' adduct) **7r'** (S_N2 adduct)

Entry	Condition	T [°C]	Yield[a] [%]	Ratio[b] (**7r**/**7r'**)
1	*i*PrMgBr (1.1 equiv), THF, −40 °C, 1 h; then CuCN (10 mol %)	−40	76	79:21
2	$\mathrm{Me_2CuCNLi_2}$ (1.1 equiv), THF, 0 °C, 2 h	RT	54[c]	63:37
3	$t\mathrm{Bu_4ZnLi_2}$ (1.1 equiv), THF, 0 °C, 2 h	RT	100	98:2
4	$t\mathrm{Bu_4ZnLi_2}$ (1.1 equiv), THF, 0 °C, 2 h; then CuCN (10 mol %)	RT	89	93:7

[a] Isolated yield of a mixture of S_N2' adduct **7r** and S_N2 adduct **7r'**. [b] The ratio was determined by ^{1}H NMR. [c] Biphenyl-4,4'-dicarboxylic acid diethyl ester (17 %) was also formed.

Table 4. One-pot synthesis of phenylallene derivatives by using tBu_4ZnLi_2.



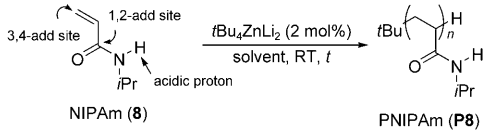
Entry	Substrate	Yield[a] [%]	Ratio[b] (**7**/**7′**)
1	$-CH_2OH$ **1a-I**	77[c]	99<:1
2	$\equiv$–TMS **1c-I**	98	99<:1
3	–CON*i*Pr$_2$ **1h-I**	78	99<:1
4	–OTf **1k-I**	79	99<:1
5	–Cl **1s-I**	70	99<:1
6	–Br **1t-I**	71	99<:1
7	–I **1u-I**	90	99<:1
8	–CN **1v-I**	83	99<:6
9	$-CO_2Et$ **1r-I**	100	98:2
10	 **1w-I**	95	99<:1

[a] Isolated yield of a mixture of S_N2' and S_N2 adducts. [b] The ratio was determined by ^1H NMR. [c] Recovered 5% of **1a-I**.

8 has been reported only by a radical process, and anionic polymerization of unprotected **8** presents a challenge.

We first evaluated the ability of tBu_4ZnLi_2 to promote chemoselective anionic polymerization using **8** as a monomer (Table 5). When a mixture of tBu_4ZnLi_2, and **8** (1:50 molar ratio) in THF was stirred at room temperature for 24 h, **P8** was obtained, though in only 8% yield; this is the first successful anionic polymerization of unprotected **8** (entries 1–2). On the other hand, the polymerization reactions with the use of Me ligand zincates, Me_3ZnLi, or Me_4ZnLi_2, as initiators did not proceed at all, but instead undesired reactions occurred. This confirms the unique character of *t*Bu ligand(s) in zincates.

Table 5. Solvent effects in anionic polymerization of NIPAm by using tBu_4ZnLi_2.



Entry	Solvent	*t* [h]	Yield[a] [%]	M_n[b]	M_w/M_n[b]
1	THF	24	8	7000	1.50
2	THF	7 d	33	7000	2.17
3	MeOH	3	76	18000	1.65
4	H_2O	3	92	27000	2.72

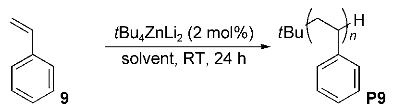
[a] Hot water-insoluble part. [b] Determined by GPC based on polystyrene standards with DMF/LiBr as a solvent.

After extensive experimentation, we found an interesting solvent effect in this polymerization, and **P8** was obtained in good yield in a protic solvent (MeOH or H_2O) in only 3 h (entries 3–4). To evaluate the solvent effects in more detail, we monitored the time/yield profiles. In H_2O, the yield reached the maximum (92%) within 15 min (see Supporting Information, Figure S1 for details). On the other hand, no polymerization reaction took place with *t*BuLi, $ZnCl_2$, LiCl, or LiOH. This rules out the promotion of this polymerization by these species.

This polymerization in water proved to be applicable for the polymerization of acryl acid derivatives, such as *N*,*N*-dimethylacrylamide (DMA, 74%), acrylamide (AM, 84%), and 2-hydroxyethylmethacrylate (HEMA, 92%).

Polymerization of styrene: Styrene derivatives are not activated by a conjugate carbonyl group, in contrast to acryl acid derivatives, and therefore it is of interest to know whether the present anionic polymerization method is applicable to polystyrene synthesis[25] (Table 6). Polystyrene (**P9**) is among the most important synthetic polymers, being encountered ubiquitously in daily life. The control of its polymerization is of great commercial significance. Whereas controlled thermal polymerization produces the highest molecular weight product in radical initiated synthesis of polystyrene, undesirable spontaneous polymerizations can clog styrene production facilities.

Table 6. Anionic polymerization of styrene by using tBu_4ZnLi_2.



Entry	Solvent	Yield [%]	M_n[a]	M_w/M_n[a]
1	H_2O	3.9	5500	1.58
2	MeOH	0.2	–	–
3	Et_2O	76	3500	1.02
4	Bulk (no solvent)	92	4200	1.13

[a] Determined by GPC based on polystyrene standards using DMF/LiBr as a solvent. –: Not determined.

In the polymerization of styrene with tBu_4ZnLi_2, when protic solvents were used, deprotonation reaction of solvents took place prior to carbozincation (polymerization) reaction between styrene (**9**) and tBu_4ZnLi_2, and very small amounts of polystyrenes were obtained (entries 1–2). On the other hand, in an aprotic solvent, such as Et_2O, or under bulk polymerization conditions,[26] polymerization proceeded smoothly at room temperature to give polystyrene with low polydispersity in quantitative yield (entries 3–4). The ^1H NMR data of the obtained polystyrene were consistent with linear structures, strongly supporting an anionic mode of polymerization.

To understand this polymerization process, and to obtain spectroscopic evidence of the "active terminus", we monitored the polymerization of styrene using in situ FT-Raman spectrometry[27] (Figure 1). The polymerization process was found to be very efficient, and Raman bands at ν 1425, 1620, and 1645 $\mathrm{cm^{-1}}$ in the spectrum of styrene diminished in intensity as the reaction proceeded. The bands at ν 1590 and 1615 $\mathrm{cm^{-1}}$, assigned to the vibrations of polystyrene, increased in intensity. At 1 and 3 h after the first addition of styrene monomer, further monomer was added twice, and the monomer peaks again disappeared rapidly in both cases. The bands assigned to the vibrations of polystyrene increased in intensity, and the finally obtained polystyrene showed low molecular dispersion ($M_n = 45\,000$, $M_w/M_n = 1.05$). These observations strongly suggest that the polymer terminal in this polymerization is the "active" zincate complex.

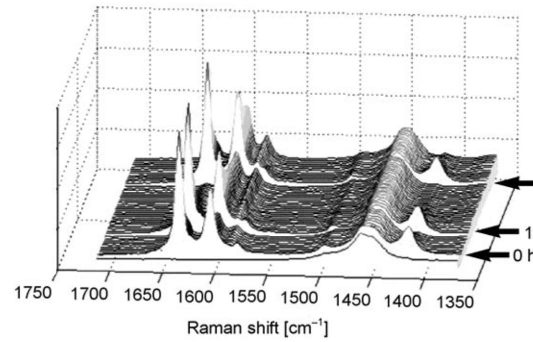


Figure 1. Raman monitoring of polymerization of styrene. Further styrene was added after 1 and 3 h.

Moreover, we carried out postpolymerization experiments (Figure 2). A mixture of **9** and 2 mol % of initiator (*t*BuLi or *t*$\mathrm{Bu_4ZnLi_2}$) was stirred for 12 h at room temperature, then the same amount of **9** was added to the mixture and polymerized. The resulting polymers were analyzed with GPC. When *t*BuLi was used as an initiator, the GPC curve of the obtained polystyrene was rather broad, with two peaks ($M_n = 21\,000$ and 13 000). This means the polymer terminal was unstable at room temperature and gradual quenching occurred before the 2nd addition of **9** to give a low-molecular-weight polystyrene. In contrast, the use of *t*$\mathrm{Bu_4ZnLi_2}$ as an initiator gave a single sharp peak ($M_n = 5100$, $M_w/M_n = 1.15$) on GPC, which strongly suggests that the polymer terminal zincate is sufficiently stable at room temperature, resulting in a narrow molecular dispersion. This is in good agreement with the above Raman analysis.

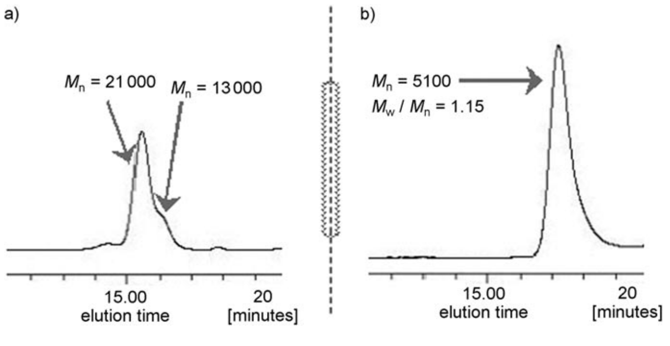


Figure 2. GPC curves of postpolymerized polystyrene using a) *t*BuLi as the initiator. b) *t*$\mathrm{Bu_4ZnLi_2}$ as the initiator.

Structural study of *t*$\mathbf{Bu_4ZnLi_2}$: Direct effect of steric bulkiness of *t*Bu ligand on the zincate structure: Finally, NMR, ESI-MS, and density functional theory (DFT) studies were performed in order to examine the origin of the unique selectivity and reactivity of the *t*$\mathrm{Bu_4ZnLi_2}$-mediated reactions. Structural information on *t*$\mathrm{Bu_4ZnLi_2}$ would aid rational design and development of even more efficient metalating reagents. The aims of our structural study were as follows: 1) characterization of the structure of *t*$\mathrm{Bu_4ZnLi_2}$ in the liquid/gas phases, 2) analysis and comparison of the stability of mono- and dianion type zincates with bulky ligands.[28]

The ^{13}C NMR spectra of a $\approx$1 M THF solution of *t*$\mathrm{Bu_2Zn}$ or *t*$\mathrm{Bu_4ZnLi_2}$ showed only singlet peaks for α-carbon of the *t*Bu groups (22.7 (*t*$\mathrm{Bu_2Zn}$) or 24.4 ppm (*t*$\mathrm{Bu_4ZnLi_2}$)) and for β-carbon of the *t*Bu groups (34.5 (*t*$\mathrm{Bu_2Zn}$) or 36.8 ppm (*t*$\mathrm{Bu_4ZnLi_2}$)) (Figure 4 and Supporting Information). When one equivalent of *t*BuLi was added to a THF solution of *t*$\mathrm{Bu_4ZnLi_2}$, only one set of new peaks (17.0 (αC) and 40.6 ppm (βC)), corresponding to *t*BuLi, was clearly observed. The ESI-MS of a $\approx$1 M THF solution of *t*$\mathrm{Bu_4ZnLi_2}$ was then measured, and a peak ($[M]^- = 299.2$) attributed to $[t\mathrm{Bu_4ZnLi}]^-$ (calcd for $\mathrm{C_{16}H_{27}ZnLi}$: 299.2) was observed (Figure 3). Based on these observations, *t*$\mathrm{Bu_4ZnLi_2}$ exists in THF solution as a single, highly symmetrical species (dianion-type zincate), not as a mixture of *t*$\mathrm{Bu_3ZnLi}$ and *t*BuLi.

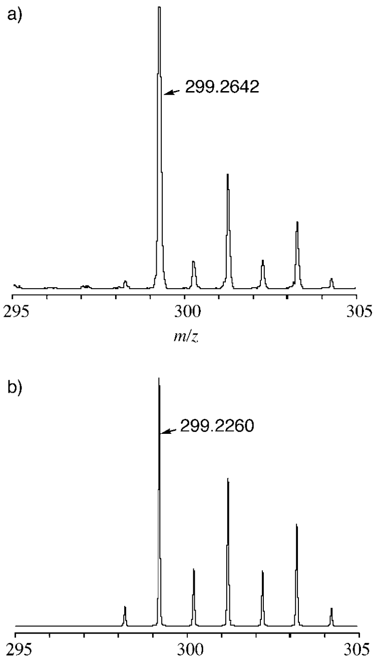


Figure 3. a) Observed ESI-MS Spectra of *t*$\mathrm{Bu_4ZnLi_2}$ in THF. b) Calculated isotropic pattern of $[t\mathrm{Bu_4ZnLi}]^-$.

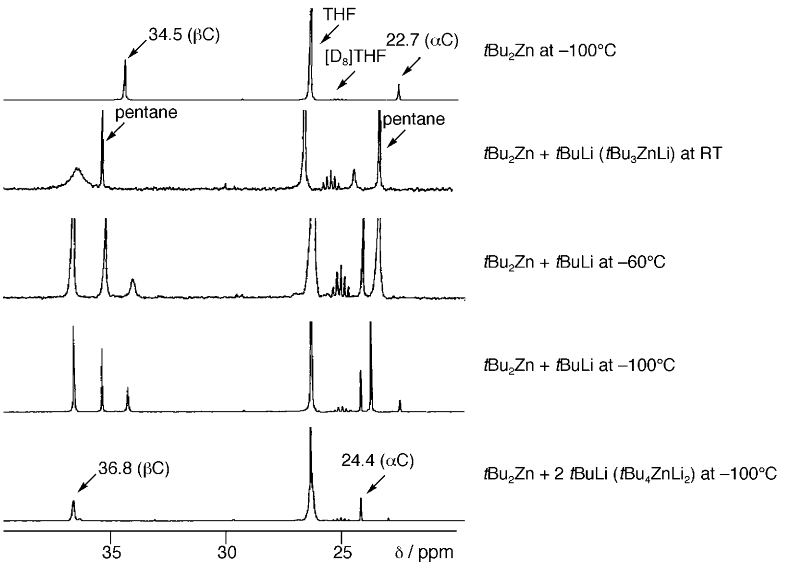


Figure 4. ^{13}C NMR spectra of *t*Bu ligand organozinc reagent: A capillary tube containing [D$_8$]THF was used as the ^{13}C chemical shift reference and lock solvent. ^{1}H and ^{13}C NMR spectra were referenced to a solvent signal.

Next, the monoanion-type *t*Bu zincate (*t*Bu$_3$ZnLi), prepared by mixing *t*Bu$_2$Zn and *t*BuLi (1 equiv) in THF,[3c] was investigated. Unexpectedly, the ^{13}C NMR spectrum of *t*Bu$_3$ZnLi at room temperature gave two broad singlets at δ 36.2 and 24.3 ppm, and ^{1}H NMR spectrum also showed two singlet peaks (0.82 and 0.78 ppm). Interestingly, these singlet peaks were split and became sharper with decreasing temperature,[29] and were completely separated into two sharp signals at −100 °C. These signals were assigned to a mixture of *t*Bu$_2$Zn and *t*Bu$_4$ZnLi$_2$ on the basis of DEPT, HMQC, and HMBC experiments. These results strongly suggest that *t*Bu$_3$ZnLi does not exist in THF solution as a single species, but disproportionates to *t*Bu$_2$Zn and *t*Bu$_4$ZnLi$_2$. These observations are in sharp contrast to the Me-coordinated zincates, and are in agreement with the experimental results (see Scheme S1 in the Supporting Information for details).

On the basis of NMR and ESI-MS results, we compared the thermodynamic stability of *t*Bu-ligand zincate complexes by means of a DFT study, employing Me$_2$O as a model for THF (Figure 5). *t*BuLi and *t*Bu$_2$Zn react to form a trigonal planar complex [*t*Bu$_3$Zn]$^-$Li$^+$ with small exothermicity (−4.8 kcal mol^{-1}; B3LYP/631SVPs[30]), and dissociation of *t*Bu$_3$ZnLi into an ion pair, [*t*Bu$_3$Zn]$^-$ and Li$^+$, occurs with 143.4 kcal mol^{-1} endothermicity. This structure, [*t*Bu$_3$Zn]$^-$Li$^+$, is essentially similar to the crystallographic structure of Me$_3$ZnK, and the average of the calculated Zn–C bond lengths of [*t*Bu$_3$Zn]$^-$Li$^+$ (2.160 Å) is in good agreement with the experimental data for [Me$_3$Zn]$^-$K$^+$.[31] We could not find other energetically plausible structures, and confirmed that the planar geometry is the global minimum. Upon further addition of *t*BuLi to *t*Bu$_3$ZnLi, the tetrahedral dianion-type zincate *t*Bu$_4$ZnLi$_2$ forms with 11.7 kcal mol^{-1} stabilization. Among other possible structures of *t*Bu$_4$ZnLi$_2$, we found one more stable structure (**10**), which consists of a complex of *t*Bu$_2$Zn–*t*BuLi dimer. However, solvation of the lithium atom of **10** with one molecule of Me$_2$O led to the collapse of **10**. The feasibility of the disproportionation of *t*Bu$_3$ZnLi to *t*Bu$_2$Zn and *t*Bu$_4$ZnLi$_2$ was then examined. The gas-phase calculations indicated that this reaction was thermodynamically favored ($\Delta E_{\mathrm{rel}} = -6.9$ kcal mol^{-1}; B3LYP/631SVPs). These results imply that *t*Bu$_4$ZnLi$_2$ is highly stable, and *t*Bu$_3$ZnLi does *not* exist in THF. Although *t*Bu$_3$ZnLi has been reported to be a good metalating reagent for organic halides, this observation implies that the real active species is *t*Bu$_4$ZnLi$_2$, not *t*Bu$_3$ZnLi.

Conclusion

A new type of dianion-type zincate, *t*Bu$_4$ZnLi$_2$, a highly crowded, bulky zincate, has been developed. This reagent turned out to be effective for a protecting-group-free halo-

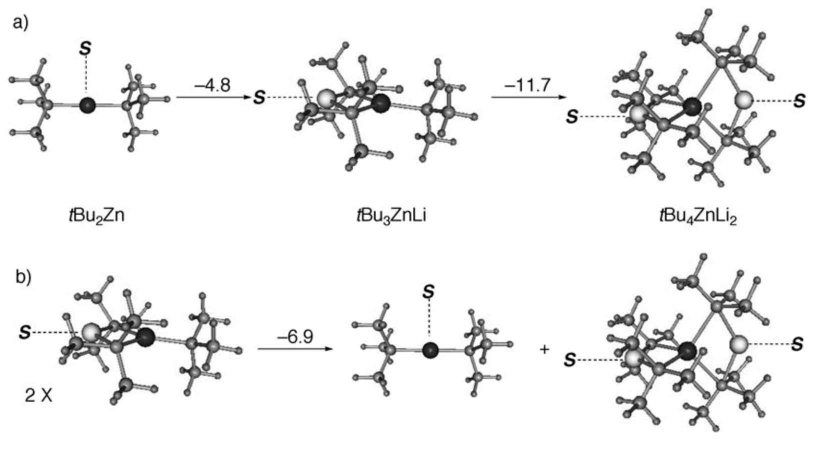


Figure 5. a) Optimized structures at B3LYP/631SVPs for *t*Bu ligand zincate compounds. Solvent (Me$_2$O) is abbreviated as *S*. The number of imaginary frequencies is 0 for all structures. Relative energies E_{rel} are given in kcal mol^{-1}. b) Energy diagram of *t*Bu$_3$ZnLi disproportionation reaction.

gen–metal exchange reaction. It is consistent with a wide variety of functional groups, including esters, amides, and acidic protons (C-H, N-H or O-H) (i.e., protection/deprotection processes for these electrophilic moieties are not required). We also highlighted the effectiveness of the steric bulkiness of this reagent in promoting regioselective S_N2' reaction with propargyl bromide. The method provides a simple and direct route for the synthesis of various functionalized phenylallene derivatives. We have also developed a new organozincate-mediated anionic polymerization using $t\mathrm{Bu_4ZnLi_2}$ as an initiator. This method possesses great versatility and high chemoselectivity, and various monomers, such as styrene, NIPAm, DMA, AM, and HEMA, could be polymerized in high yields. A combined spectral/theoretical investigation on the structure of $t\mathrm{Bu_4ZnLi_2}$ strongly supports the idea that $t\mathrm{Bu_4ZnLi_2}$ exists as a remarkably stable single species with tetrahedral dianion-type structure both in THF solution and in the gas phase. Surprisingly, in contrast to this, $t\mathrm{Bu_3ZnLi}$ is less stable and turned out to disproportionate to $t\mathrm{Bu_2Zn}$ and $t\mathrm{Bu_4ZnLi_2}$ in THF solution. The stoichiometry of ligands at the central atom in an ate complex has generally been considered as the most important factor determining the coordination number of the ate complex. However, the present work underlines the steric factor of ligands as another tuneable functionality in the development of highly coordinated (dianion-type) ate complexes. Further studies to expand the scope and synthetic utility of highly coordinated bulky zincates, including $t\mathrm{Bu_4ZnLi_2}$, are under way, together with mechanistic and structural investigations to find the reason for the unique selectivity and reactivity of $t\mathrm{Bu_4ZnLi_2}$-mediated reactions.

Experimental Section

Preparation of $t\mathrm{Bu_4ZnLi_2}$·THF solution (1.1 mmol): $ZnCl_2$ (2.2 mL, 0.5 M THF solution, 1.1 mmol) was added to THF (5 mL). Then, tBuLi (3.17 mL, 1.39 M n-pentane solution, 4.4 mmol) was added dropwise to the solution at −78 °C and it was stirred for 30 min at 0 °C to give a pale yellow $t\mathrm{Bu_4ZnLi_2}$·THF solution (1.1 mmol).

4-Allylbenzylalcohol (2a): A solution of the 4-iodobenzylalcohol (242.5 mg, 1.01 mmol) in dry THF (5 mL) was added dropwise to a solution of $t\mathrm{Bu_4ZnLi_2}$ (1.1 mmol) in THF at −78 °C, warmed to RT and stirred for 2 h. Then, allyl bromide (0.43 mL, 5 mmol) added to the solution and it was warmed to RT and stirred for 12 h. The reaction mixture was quenched with sat. NH_4Cl aq (2 mL), diluted 2 N HCl (10 mL) and extracted with Et_2O (3×10 mL). The organic layer was washed with brine and dried over Na_2SO_4, filtered and concentrated in vacuo. Purification by silica gel open column chromatography (n-hexane/ethyl acetate 2:1) yielded title compound as a colorless oil (149.5 mg, 100 %). ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ = 7.29 (d, 2 H, J = 8.0 Hz), 7.18 (d, 2 H, J = 8.0 Hz), 6.01–5.91 (m, 1 H), 5.11–5.05 (m, 2 H), 4.65 (s, 2 H), 3.39 ppm (d, 2 H, J = 6.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.4, 138.5, 137.2, 128.7, 127.1, 115.7, 65.2, 40.0 ppm; HRMS (FAB$^+$): m/z: calcd for $C_{10}H_{12}O$: 148.0888; found 148.0838 $[M]^+$.

4-Allenyl ethylbenzoate (7r): 4-Iodoethylbenzoate (276 mg, 1.0 mmol) was added dropwise at 0 °C by a syringe to a stirred solution of $t\mathrm{Bu_4ZnLi_2}$ (1.1 mmol) in THF, and the solution was stirred for 2 h. Then, propargyl bromide (0.38 mL, 5.0 mmol) was added at −78 °C. The solution was slightly warmed to room temperature and stirred for 16 h. The reaction mixture was quenched with sat. NH_4Cl aq (2.0 mL) and a few drops of diluted 2 N HCl and extracted with Et_2O (2×30 mL). The organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography (n-hexane/AcOEt 19:1) and the mixture of the titled compound and 4-propargyl ethylbenzoate was given as a yellow oil (188 mg, 100 %). The ratio of the products was determined by ^{1}H NMR. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 7.98 (d, 2 H, J = 8.1 Hz), 7.34 (d, 2 H, J = 8.1 Hz), 6.20 (t, 1 H, J = 6.9 Hz), 5.21 (d, 2 H, J = 6.9 Hz), 4.37 (q, 2 H, J = 7.2 Hz), 1.39 ppm (t, 3 H, J = 7.2 Hz); HRMS (EI$^+$): m/z: calcd for $C_{12}H_{12}O$: 188.0837; found: 188.0821 $[M]^+$.

Anionic polymerization of NIPAm (8) by using $t\mathrm{Bu_4ZnLi_2}$: A solution of $t\mathrm{Bu_4ZnLi_2}$ (0.10 mmol) in THF was added to an aqueous solution of N-isopropylacrylamide (0.57 g, 5.0 mmol; 25 mL), and the reaction mixture was stirred at room temperature. After 3 h, the polymerization was quenched with HCl (1 mL, 2.0 M Et_2O solution). For the isolation of the polymer, the reaction mixture was heated over 80 °C, and the precipitate was collected by filtration and centrifugation. The product was dissolved in THF and poured into an excess amount of Et_2O. The white precipitate formed was collected and dried in vacuo at 100 °C and yielded poly-N-isopropylacrylamide as a white powder (0.53 g, 92 %). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 6.51 (s, 1 H), 3.86 (m, 1 H), 2.05 (s, 1 H), 1.8–1.2 (m, 2 H), 1.11 ppm (s, 6 H).

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