4934 *J. Am. Chem. Soc.* **1998,** *120,* 4934−4946

New Formulas for Organozincate Chemistry

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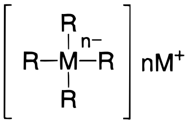
Received November 10, 1997

Abstract: As a new type of zincate, we designed various new organozinc derivatives, $Me_3Zn(R)Li_2$ (R = Me, CN, SCN), which could be prepared in situ from lithium trimethylzincate and anion species such as methyllithium, lithium cyanide, and lithium thiocyanate. We investigated the reactivities of these zincates toward the halogen (or tellurium)−zinc exchange, Michael addition, carbozincation, and epoxide ring opening reactions. On the basis of their excellent chemical yields and chemoselectivities, these species were considered to be differentiated from ordinary triorganozincates, R_3ZnLi. We also discuss the structure of the newly designed zincates using ^{1}H NMR/Raman/in situ FTIR/extended X-ray absorption fine structure (EXAFS) spectroscopic and the density-functional theory (DFT) theoretical studies. All results strongly support the fact that these newly designed zincates are *a new category of zincate species*. This observation is also identical with the fact that newly designed zincates have a higher and unique reactivity compared to the conventional triorganozincates.

Introduction

Organometallic reagents having Lewis acidity (vacant orbital) often form complexes with anion species, such as carboanions, alkoxy anions, and the like, to generate metallic anion complexes defined as ate complexes (Chart 1).[1] There have been many experimental and theoretical studies on the structure and reactivities of various ate complexes. Ate complexes, being bimetallic compounds, are known to show unique reactivities that metallic reagents themselves do not possess. For example, while the most important classes of organozinc derivatives are the organozinc halides (Reformatsky-type, symbolized as RZnX) and diorganozincs (R_2Zn), these organozinc reagents often have poor reactivity without catalysts such as amino alcohols, transition metals, etc. toward alkylation reaction of the carbonyl compounds and the halogen−metal exchange reaction of alkyl halides. However, triorganozincates (R_3Zn^- $Metal^+$) are known to proceed 1,4-conjugated addition reaction with α,*β*-unsaturated carbonyl compounds,[2] the metalation reaction of aromatic halides[3] or vinyl halides,[4] and the reduction of the various carbonyl compounds[5] (Figure 1).

Chart 1. Ate Complexes



$$\left[\begin{array}{c} R \\ | \\ R{-}M{-}R \\ | \\ R \end{array}\right]^{n-} nM^+$$

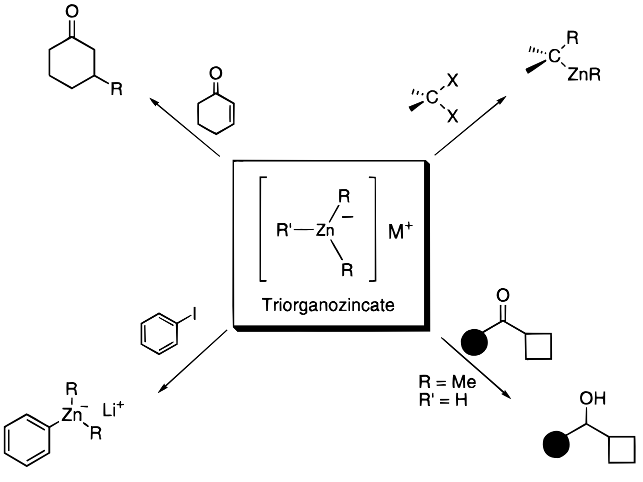


Figure 1. Reactivities of triorganozincates.

Lithium trimethylzincate, one of the triorganozincates, is a complex arising from Me_2Zn having Lewis acidity and MeLi possessing Lewis basicity. The outer shell of the zinc atom in a lithium trimethylzincate is filled with 16 electrons, and there is a vacant orbital for an additional ligand to coordinate, which could form a favorable 18 electron state (Figure 2). Therefore, lithium trimethylzincate possibly forms further complexes with anion species, such as MeLi, LiCN, LiSCN, and the like, to generate tetracoordinated organozinc derivatives. However, the reactivity of the tetraalkylzincates have never been well studied.

In this paper, we report the control of the reactivity of zincates by the change in the coordination environment on the Zn, that is, unique reactivities of "newly designed ate complexes" of organozinc derivatives, symbolized as $Me_3Zn(R)Li_2$ (R = Me, CN, SCN), toward halogen (or tellurium)−zinc exchange, inter-

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(1) (a) Wittig, G. *Q. Rev.* **1966**, 191−210. (b) Tochtermann, W. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 351−375.

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S0002-7863(97)03855-9 CCC: $15.00

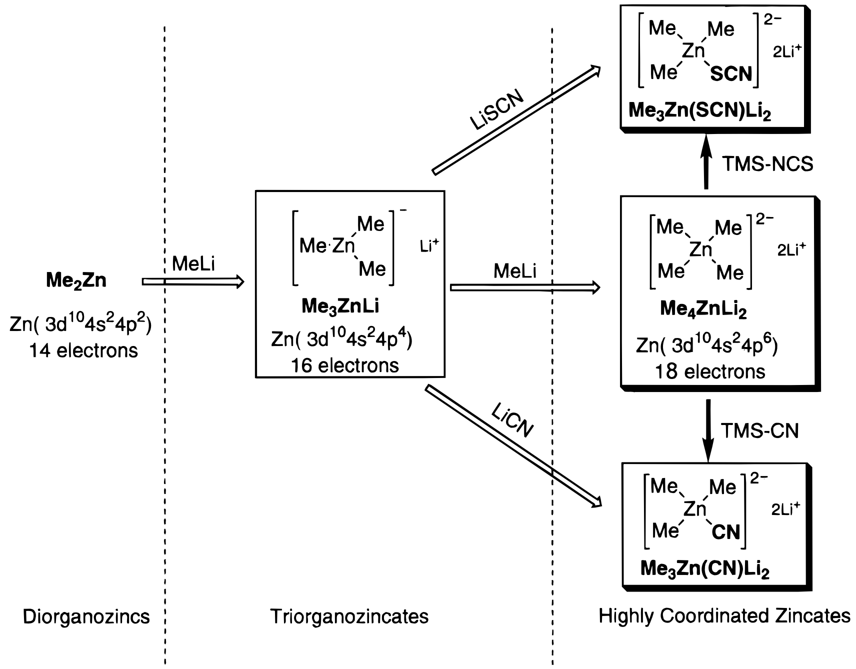
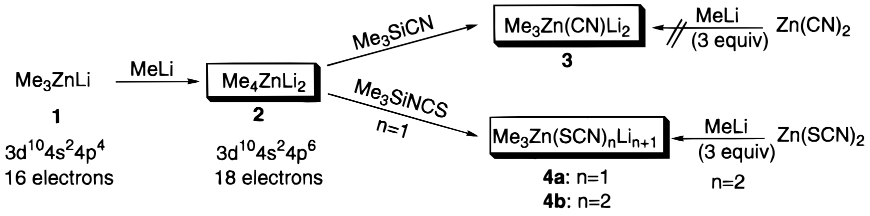


Figure 2. Design of new ate complexes of organozinc derivatives.

Scheme 1. Preparations of New Ate Complexes of Organozinc Derivatives



and intramolecular epoxide ring opening, Michael addition, and carbozincation reactions.[6] We also discuss the structure and the active species of the newly designed zincates using ^{1}H NMR/Raman/in situ FTIR/extended X-ray absorption fine structure (EXAFS) spectroscopic and the density-functional theory (DFT) theoretical studies.

Results and Discussion

Design and Preparation of Newly Designed Ate Complexes of Organozinc Derivatives. The preparation of newly designed zincates was investigated (Scheme 1) and the ^{1}H NMR spectra of the zincates were obtained for the preliminary estimation of the component of the zincate solution. First, the ^{1}H NMR spectra of the metal reagents were measured (Table 1). The methyl signals of MeLi, MeMgBr, Me_3Al, and Me_2Zn in THF (−20 °C) were observed as a sharp singlet at −1.96, −1.62, −0.82, and −0.84 ppm, respectively. A high field shift from the value of Me_4Si (0.00 ppm) was considered to show the anionic character of each metal reagent. Indeed, the order of the high field shift value is nearly consistent with the order of the reactivities of the metal reagents.

Table 1. ^{1}H NMR of Metal Reagents in THF (−20 °C)

entry	metal reagent	δ_{Me} (ppm)[a]
1	MeLi	−1.96
2	MeMgBr	−1.62
3	Me_3Al	−0.82
4	Me_2Zn	−0.84
5	Me_3SiNCS	+0.40
6	Me_3SiCN	+0.38

[a] The δ values are relative to β methylene proton (1.85 ppm) of THF.

With this information, we estimated the possibility of the formation and the reactivity of newly designed zincates using ^{1}H NMR spectroscopy (Figure 3). Dilithium tetramethylzincate was prepared by the reaction of zinc chloride with 4 equiv of MeLi in THF using the previously reported modified procedure.[7] The methyl signal of Me_4ZnLi_2 in THF (−1.44 ppm) was observed as a sharp singlet in the middle between the signals of Me_3ZnLi (−1.08 ppm) and MeLi (−1.96 ppm). Measurement at −78 °C gave very similar results but with a slight high field shift of each signal. The addition of one more equivalent of MeLi to the Me_4ZnLi_2 solution showed a broad singlet signal at −1.49 ppm at −20 °C which separated at −78 °C into two signals corresponding to the signal of MeLi and that of Me_4ZnLi_2. The high field shift from the value of Me_3ZnLi is considered to indicate the more anionic character of the zincates. Indeed, there are some reports of tetraalkylzincates,[8] and X-ray studies of the zincates which have disclosed that the crystal

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(6) (a) A part of the work was communicated in: Uchiyama, M.; Koike, M.; Kameda, M.; Kondo, Y.; Sakamoto, T. *J. Am. Chem. Soc.* **1996**, *118*, 8733−8734. (b) More recently, "highly coordinated" zincates were used as a reactive intermediates for asymmetric 1,2-migration reaction: McWilliams, J. C.; Armstrong, J. D., III; Zheng, N.; Bhupathy, M.; Volante, R. P.; Reider, P. L. *J. Am. Chem. Soc.* **1996**, *118*, 11970−11971.

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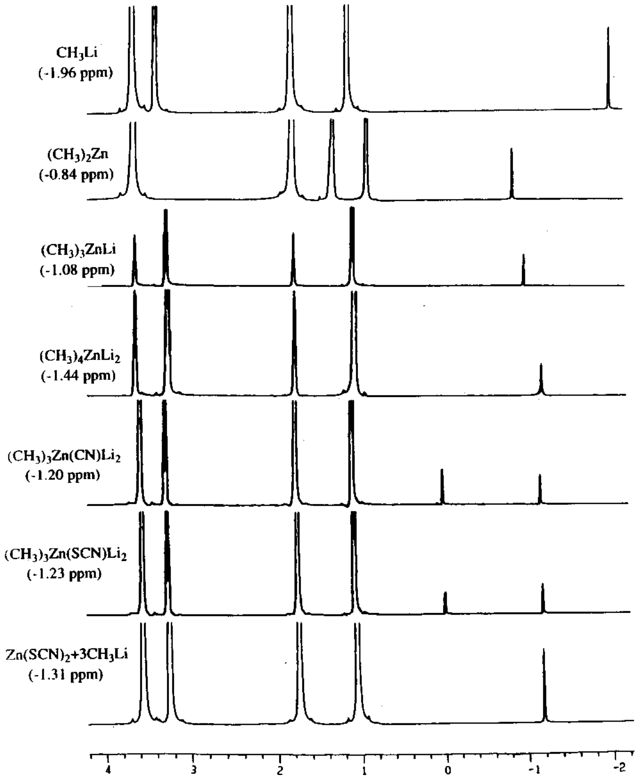


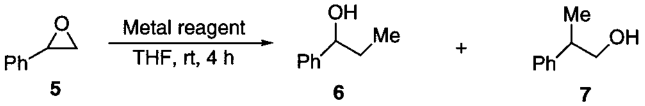
Figure 3. ^{1}H NMR spectra of organozincates in THF (−20 °C).

structures of the tetraalkylzincates are in a tetrahedral (sp^3 like) dianionic arrangement, while those of the trialkylzincates are in a trigonal (sp^2 like) monoanionic arrangement about the Zn atom.[9]

The addition of 1 equiv of Me_3SiCN or Me_3SiNCS to the Me_4ZnLi_2 solution should give the zincates with a methyl group replacement by the CN or SCN ligand. As we expected, the reaction of the tetramethylzincate with Me_3SiCN and Me_3SiNCS gave the new zincates, $Me_3Zn(CN)Li_2$ (**3**) and $Me_3Zn(SCN)Li_2$ (**4a**), and their methyl signals were observed as sharp singlets (−1.20 ppm for **3** and −1.23 ppm for **4a**). Also, the signal of the newly generated tetramethylsilane in the mixture was observed at 0.00 ppm together with the disappearance of the signal of Me_3SiCN (0.38 ppm) or Me_3SiNCS (0.40 ppm). As an alternative way to prepare CN or SCN ligated zincates, the reaction of $Zn(CN)_2$ or $Zn(SCN)_2$ with 3 equiv of MeLi was examined. From the preliminary ^{1}H NMR study, the reaction of $Zn(CN)_2$ with MeLi is sluggish and no formation of a zincate was observed,[10] while the reaction of $Zn(SCN)_2$ with MeLi gave a zincate (−1.31 ppm) similar to **4a**. These results indicate that the different zincate species are formed except for the reaction of $Zn(CN)_2$ with MeLi, and we are intrigued by the enhanced anionic character of these newly designed zincates compared to Me_3ZnLi to investigate the following reactions.

Intermolecular Ring Opening Reaction of Epoxides Using Various Zincates. The regioselectivity of intermolecular ring opening reaction of epoxides was investigated by focusing on the nature of the organometallic reagent, such as the Lewis acidity or basicity.[11] Styrene oxide was reacted with various organometallic derivatives, and the ratio of the two isomeric compounds, 1-phenyl-1-propanol (**6**) and 2-phenyl-1-propanol (**7**), was estimated. The results are listed in Table 2. The reaction with Me_3ZnLi gave almost equal amounts of **6** and **7**. Me_4ZnLi_2 also showed similar selectivity, although the yield (**6** + **7**) was increased. Furthermore, the reaction with $Me_3Zn(CN)Li_2$ and $Me_3Zn(SCN)Li_2$ gave **7** as a major product, while the reaction with MeLi and $Me_2Cu(CN)Li_2$ gave **6** as a major product. Although the reasons for the divergent selectivity are not clear at present, the inverse selectivity between $Me_3Zn(CN)Li_2$ and $Me_2Cu(CN)Li_2$ is attractive from a synthetic viewpoint.

Table 2. Intermolecular Epoxide Opening Reaction



5 **6** **7**

Entry	Metal reagent	Yield (%) **6** + **7**	**6** : **7**
1	MeLi	trace	71:29
2	Me_3ZnLi	70	56:44
3	Me_4ZnLi_2	93	51:49
4	$Me_3Zn(CN)Li_2$	41	29:71
5	$Me_3Zn(SCN)Li_2$	trace	37:63
6	$Zn(SCN)_2$+3MeLi	trace	32:68
7	$Me_2Cu(CN)Li_2$	93	68:32
8	$Me_2Cu(SCN)Li_2$	100	61:39

Table 3. Bromine−Zinc Exchange (1)

$$\text{Ph-Br} \xrightarrow[\text{2) PhCHO}]{\text{1) Metalating reagent, THF, -20°C, 2 h}} \text{Ph}_2\text{CHOH}$$

8 **9**

Entry	Metalating reagent	Yield (%)
1	MeLi	0
2	Me_3ZnLi	0
3	Me_4ZnLi_2	47
4	$Me_3Zn(CN)Li_2$	22
5	$Me_3Zn(SCN)Li_2$	23

Bromine−Zinc Exchange Reaction of Bromobenzene Derivatives Using Newly Designed Zincates. We have reported that Me_3ZnLi is effective for the selective iodine−zinc exchange reaction of functionalized aromatic iodides; however, aromatic bromides were unreactive to this metalation process.[3a] Since newly designed zincates are considered to have more anionic character on the basis of our preliminary ^{1}H NMR study, the bromine−zinc exchange reaction of bromobenzene (**8**) was then investigated (Table 3). First, in order to investigate the difference in the reactivity toward the bromine−zinc exchange reaction of bromobenzene between newly designed zincates and Me_3ZnLi (normally coordinated zincates), the reaction was carried out at fixed conditions (−20 °C, 2 h) and the resulting metal species was trapped with benzaldehyde. The reaction using Me_4ZnLi_2 proceeded to give benzhydrol (**9**) in 47% yield (entry 3). Under the same reaction conditions, the reaction with Me_3ZnLi did not proceed at all and MeLi was also found inactive under the same conditions (entries 1 and 2). The modified zincates, $Me_3Zn(CN)Li_2$ and $Me_3Zn(SCN)Li_2$, showed moderate reactivity toward the bromine−zinc exchange reaction and **9** was obtained in 22% and 23% yields, respectively (entries 4 and 5).

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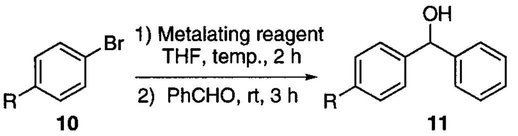
(9) For recent review, see: Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1501−1523.

(10) For recent discussion on the structure of $Zn(CN)_2$, see: Hoskis, B. F.; Robson, R. *J. Am. Chem. Soc.* **1990**, *112*, 1546−1554.

(11) Smith, J. G. *Synthesis* **1984**, 629−656.

Table 4. Bromine−Zinc Exchange (2)



Entry	R	Metalating reagent	Temp.(°C)	Yield (%)
1	H	Me_4ZnLi_2	0	90
2	H	$Me_3Zn(CN)Li_2$	rt	90
3	H	$Me_3Zn(SCN)Li_2$	rt	89
4	MeO	Me_4ZnLi_2	0	84
5	MeO	$Me_3Zn(CN)Li_2$	rt	90
6	MeO	$Me_3Zn(SCN)Li_2$	rt	92
7	COOMe	Me_4ZnLi_2	0	trace
8	COOMe	$Me_3Zn(CN)Li_2$	0	trace
9	COOMe	$Me_3Zn(SCN)Li_2$	0	trace

Next, we optimized the reaction conditions toward the bromine−zinc exchange reaction of bromobenzene using newly designed zincates, and applied for the reaction of a functionalized aromatic bromide (Table 4). Although the favorable reaction temperature depends to some degree on the newly designed zincates, the bromine−zinc exchange reaction proceeded smoothly to give benzhydrol (**11**; R = H) in excellent yields for all the bromobenzenes (entries 1−3). In connection with our recent studies on the chemoselective metalation reaction of functionalized aromatic compounds,[3] we then investigated the bromine−zinc exchange reaction of 4-substituted bromobenzenes. Newly designed zincates were also proved to be effective for the metalation reaction of 4-methoxybromobenzene (entries 4−6). However, during the reaction of methyl 4-bromobenzoate, complex mixtures were obtained in all cases, because the rate of the bromine−zinc exchange reaction was considered to be almost equal to that of the methylation reaction toward a methyl ester.

We then investigated the bromine−zinc exchange reaction of 4-cyanobromobenzene (**12**) using newly designed zincates (Table 5). In the reaction using $Me_3Zn(CN)Li_2$ and $Me_3Zn(SCN)Li_2$, 4-cyanobenzhydrol (**13**), the expected product, was obtained as the sole product in high yields (entries 1 and 2). However, when Me_4ZnLi_2 was used as a metalating reagent, the reaction proceeded further to give 4-acetylbenzhydrol (**14**) in 63% yield (entry 3). A possible mechanism for this unexpected reaction is shown in Figure 4. To begin with, the bromine−zinc exchange reaction of **14** with Me_4ZnLi_2 proceeded to give **16** and the subsequent reaction with benzaldehyde gave the expected lithium alkoxide (**17**). However, the cyano group of **17** more reacted with residual Me_3ZnLi to give **18**. Furthermore, **14** was considered to be obtained by hydrolysis (workup).

Indeed, the reaction of **12** using Me_3ZnLi as a metalating reagent proceeded only methylation reaction (not the bromine−zinc exchange reaction) to give 4-acetylbromobenzene (**15**) (Table 5, entry 4). The result strongly supports the proposed reaction mechanism. Also, these results of the halogen−zinc exchange reaction with various zincates indicate that the reactivities of zincates reflect the value of the high field shift of δ_{Me} of the reagents.

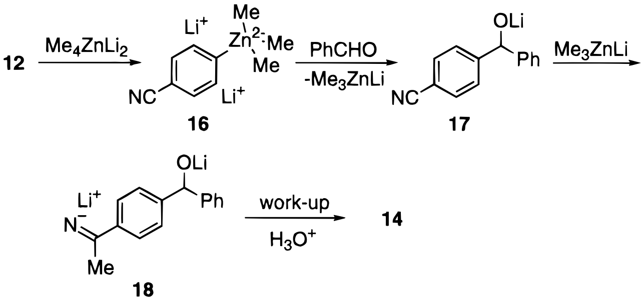
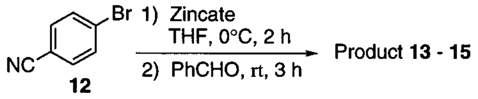
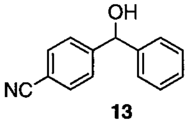


Figure 4. Possible mechanism for the formation of **14**.

Table 5. Bromine−Zinc Exchange (3)



Entry	Zincate	^{1}H-NMR δ_{Me}	Product	Yield (%)
1	$Me_3Zn(CN)Li_2$	-1.20 ppm	**13**	98
2	$Me_3Zn(SCN)Li_2$	-1.23 ppm	**13**	95
3	Me_4ZnLi_2	-1.44 ppm	**14**	63
4	Me_3ZnLi	-1.08 ppm	**15**	50



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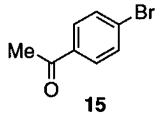

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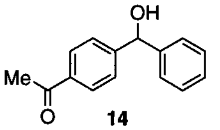

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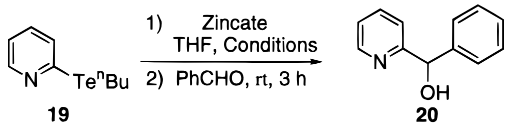
Table 6. Tellurium−Zinc Exchange Reaction



Entry	Zincate	^{1}H-NMR δ_{Me}	Conditions	Yield (%)
1	Me_3ZnLi	-1.08 ppm	rt, 18 h	0
2	$Me_3Zn(CN)Li_2$	-1.20 ppm	rt, 2h	63
3	$Me_3Zn(SCN)Li_2$	-1.23 ppm	rt, 2h	58
4	Me_4ZnLi_2	-1.44 ppm	0°C, 2h	81

Tellurium−Zinc Exchange Reaction of 2-Pyridinyltellurium Compounds. Synthetic applications of organotellurium compounds have increased in recent years.[12] Among their many synthetic uses, transmetalation reaction with organolithium or organocuprate reagents are considered to be important for carbon−carbon bond formation.[13] In connection with our recent studies on pyridinylmetal derivatives,[14] we investigated the tellurium−zinc exchange reaction of 2-pyridinyltellurium compounds using various zincates (Table 6). Butyl 2-pyridyltelluride (**19**) was prepared by the nucleophilic substitution of 2-bromopyridine and 2-chloropyridine with lithium butanetelluroate to give the telluride (**19**) in 70% and 61% yields, respectively.[13c] Compound **19** was treated with Me_4ZnLi_2 in THF at 0 °C in 2 h and then with benzaldehyde to give phenyl(2-pyridinyl)methanol (**20**) in 81% yield (entry 2), while the reaction with Me_3ZnLi did not proceed at all even under a

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(12) For recent review, see: Petragnani, N. *Tellurium in Organic Synthesis*; Academic Press: London, 1994.

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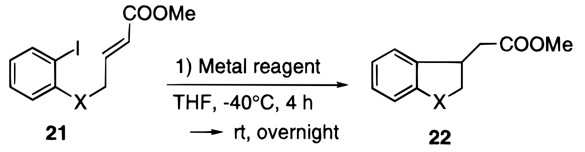
(14) (a) Sakamoto, T.; Kondo, Y.; Murata, N.; Yamanaka, H. *Tetrahedron Lett.* **1992**, *33*, 5373−5374. (b) Sakamoto, T.; Kondo, Y.; Murata, N.; Yamanaka, H. *Tetrahedron* **1993**, *49*, 9713−9720.

Table 7. Intramolecular Michael Addition



Entry	X	Metal reagent	Yield (%)
1	O	Me_3ZnLi	0
2	NSO_2Ph	Me_3ZnLi	0
3	O	$Me_3Zn(CN)Li_2$	5
4	NSO_2Ph	$Me_3Zn(CN)Li_2$	13
5	O	$Me_3Zn(SCN)Li_2$	8
6	NSO_2Ph	$Me_3Zn(SCN)Li_2$	22
7	O	Me_4ZnLi_2	39
8	NSO_2Ph	Me_4ZnLi_2	66

harsher conditions (room temperature, 18 h) (entry 1). The modified zincates, $Me_3Zn(CN)Li_2$ and $Me_3Zn(SCN)Li_2$, also showed high reactivity toward the tellurium−zinc exchange reaction although it required the higher temperature and **20** was obtained in 63% and 58% yields, respectively (entries 4 and 5). From these results, the tellurium−zinc exchange reaction using newly designed zincates is considered to proceed smoothly to form the newly designed 2-pyridinyl zincates.

All these results make it clear that the newly designed zincates have higher reactivity toward the halogen (or tellurium)−zinc exchange reaction than the "normally tricoordinated" zincate, Me_3ZnLi. These results also support the structural difference between the newly designed zincates and Me_3ZnLi.

Intramolecular Michael Addition Reaction. Our next interest was focused on the reactivities of *arylzinc ate complexes*, generated in situ from the halogen−zinc exchange reaction of zincates, toward various electrophiles. Intramolecular Michael addition was then examined using the iodine−zinc exchange reaction of **21** (Table 7). The reaction of **21** (X = O, NSO_2Ph) with ordinary Me_3ZnLi did not proceed at all, although the iodine−zinc exchange reaction occurred (entries 1 and 2).[15] However, when $Me_3Zn(CN)Li_2$ and $Me_3Zn(SCN)Li_2$ in place of Me_3ZnLi were used, the reaction proceeded to give the expected product (**22**) in moderate yields (entries 3−6). Furthermore, Me_4ZnLi_2 showed high reactivity toward the intramolecular Michael addition reaction, and **22** was obtained (entries 7 and 8). These results indicate that trialkylmonoarylzincates, generated from aryl iodide and newly designed zincates, are a more reactive species toward α,β-unsaturated compounds than the ordinary ("normally tricoordinated") aryldimethylzincates. These results indicate that newly designed zincates are useful reagents not only for the Michael addition reaction, but also for the selective iodine−zinc exchange reaction of iodobenzene derivatives possessing an ester moiety. Namely, the rate of the iodine−zinc exchange reaction using newly designed zincates (in contrast to the bromine−zinc exchange reaction) proved to be faster than that of the methylation of the ester.

Intramolecular Carbozincation Reaction. These high reactivities of newly designed arylzincates prompted us to further survey whether the zincates could be used for intramolecular carbometalation reaction toward the alkene possessing no activation group (COOR, CN, etc.).[16] First, intramolecular carbozincation reaction was examined using the iodine−zinc exchange reaction of the allyl 2-iodophenyl ether (**23**). When **23** was treated with Me_3ZnLi, the halogen−metal exchange reaction proceeded smoothly but no intramolecular carbometalation reaction was observed (Scheme 2, top). On the other hand, the reaction of **23** with Me_4ZnLi_2 followed by hydrolysis gave 3-methyl-2,3-dihydrobenzo[*b*]furan (**28**) in 42% yield, which probably results from the intramolecular carbozincation reaction of arylzincate (**26**) (Scheme 2, bottom). However, during the reaction of **23** with $Me_3Zn(CN)Li_2$, $Me_3Zn(SCN)Li_2$, and $Me_2Cu(CN)Li_2$, the intramolecular carbozincation reaction did not proceed at all. This method was also applicable to a synthesis of substituted indoline derivatives (Scheme 3).

Intramolecular Epoxide Opening Reaction. Our next interest was focused on the intramolecular ring opening reaction of epoxide **33** using the zincates as metalating agents (Table 8).[17] Interestingly, all newly designed zincates showed almost the completely opposite regioselectivity from Me_3ZnLi for the ring opening reaction. Especially, the reaction with Me_3ZnLi and the reaction with $Me_3Zn(SCN)Li_2$ showed almost perfect reverse regioselectivity (entries 1 and 4). The reaction with Me_3ZnLi gave an *anti*-Baldwin's rule product,[18] *endo*-cyclized 1,2,3,4-tetrahydroquinoline derivative (**35**), as the major product, while the reaction with $Me_3Zn(SCN)Li_2$ gave the *exo*-cyclized indoline derivative (**34**). This method was considered to be applicable for the chiral synthesis of 3-indolinemethanol derivatives and 3-hydroxytetrahydroquinoline derivatives, key precursors for the synthesis of CC-1065/duocarmycin pharmacophore known as potent antitumor antibiotics (Figure 5).[19−21]

Interestingly, the cyano-modified reagents, $Me_3Zn(CN)Li_2$ and $Me_2Cu(CN)Li_2$, showed the completely opposite regioselectivity in this system. $R_2Cu(CN)Li_2$ has been called a "higher order cuprate" [22] implying dianionic Cu(I) species containing three covalently bonded ligands on Cu and the structure of these cuprates has been a controversial issue.[23] However recent studies on the structure revealed that the CN ligand is not on

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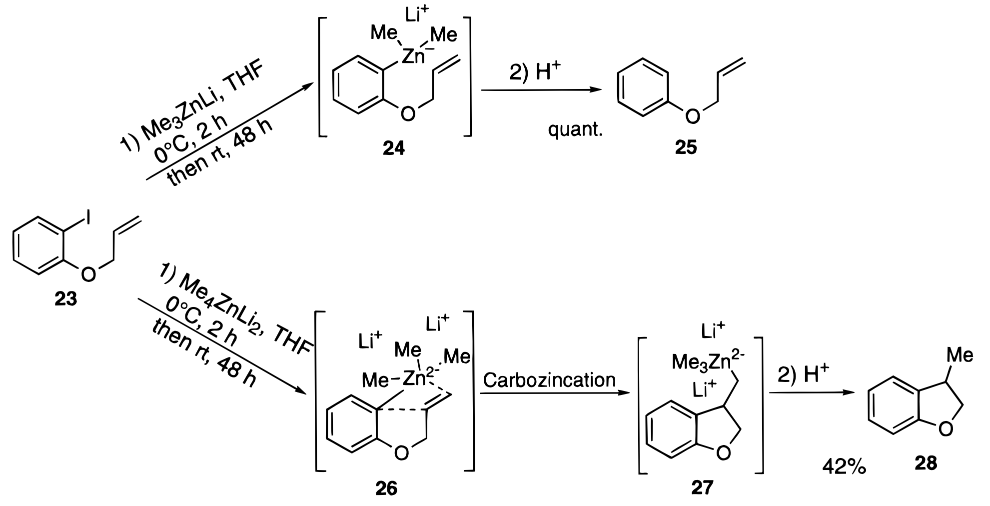
Scheme 2. Intramolecular Carbozincation (1)



Scheme 3. Intramolecular Carbozincation (2)

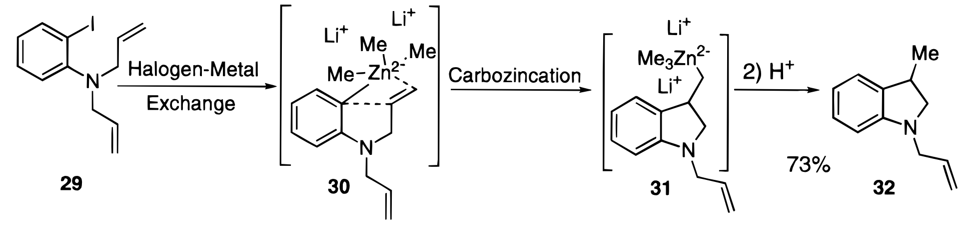
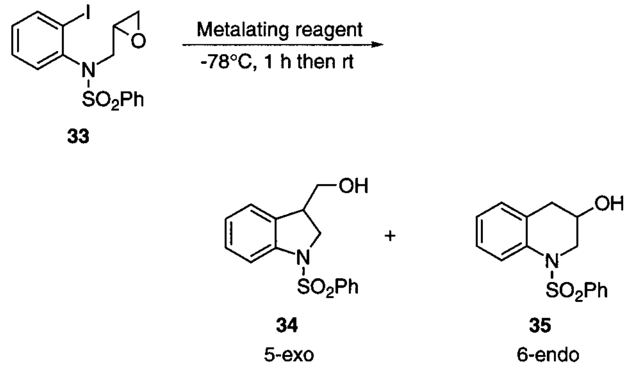


Table 8. Intramolecular Epoxide Opening Reaction



Entry	Metalating reagent	Yield (%) **34** + **35**	**34** : **35**
1	Me_3ZnLi	86	4:96
2	Me_4ZnLi_2	67	87:13
3	$Me_3Zn(CN)Li_2$	57	80:20
4	$Me_3Zn(SCN)Li_2$	92	97: 3
5	$Zn(SCN)_2$+3MeLi	80	81:19
6	$Me_2Cu(CN)Li_2$	50	12:88

the Cu atom but on the Li atom.[23,24] The structure of the newly designed zincates with the CN or SCN ligand has never been studied. Taking the tendency of zinc derivatives to form complexes with tetrahedral configuration (sp^3 hybridized structure) into account,[8,9] we cannot omit the possibility of the ligation of CN or SCN to the Zn atom. In addition, because studies to compare the reactivity of these reagents disclosed a different regioselectivity for intermolecular epoxide opening reaction and a different reactivity toward the halogen (or tellurium)−zinc exchange reaction, Michael addition reaction, and carbozincation reaction, these "newly designed" zincates should be distinguished from ordinary lithium trialkylzincates in *structure* and *reactivity*.

^{1}H NMR/Raman/React−IR(In Situ FTIR)/EXAFS Study of Newly Designed Zincates. From the preliminary ^{1}H NMR study, the methyl signals of Me_2Zn, Me_4ZnLi_2 (**2**), Me_3ZnLi (**1**), and MeLi in THF at −20 °C were observed as sharp singlets at −0.84, −1.44, −1.08, and −1.96 ppm, respectively (Figure 3, Tables 1 and 9). The high field shift of **2** from the value of **1** is considered to indicate the more anionic character of the newly designed zincates. Indeed, the crystal structure of **2** is known to be a tetracoordinated, dianionic zinc structure.[8,9] Furthermore, the methyl signals of the cyano- and thiocyano-substituted newly designed zincates, $Me_3Zn(CN)Li_2$ (**3**) and $Me_3Zn(SCN)Li_2$ (**4a**) were observed as sharp singlets (−1.20 ppm for **3** and −1.23 ppm for **4a**) together with the signal of the newly generated Me_4Si. The methyl signals of the free Me_3ZnLi (**1**) and MeLi were not observed in a THF solution of $Me_3Zn(CN)Li_2$ (**3**) or $Me_3Zn(SCN)Li_2$ (**4a**); however, we do not have enough evidence to neglect the possibility of a fast exchange on the NMR time scale.

Secondly, we measured the Raman spectra of $Me_3Zn(SCN)Li_2$ (**4a**) and LiSCN (Figure 6). In the spectrum of LiSCN (top

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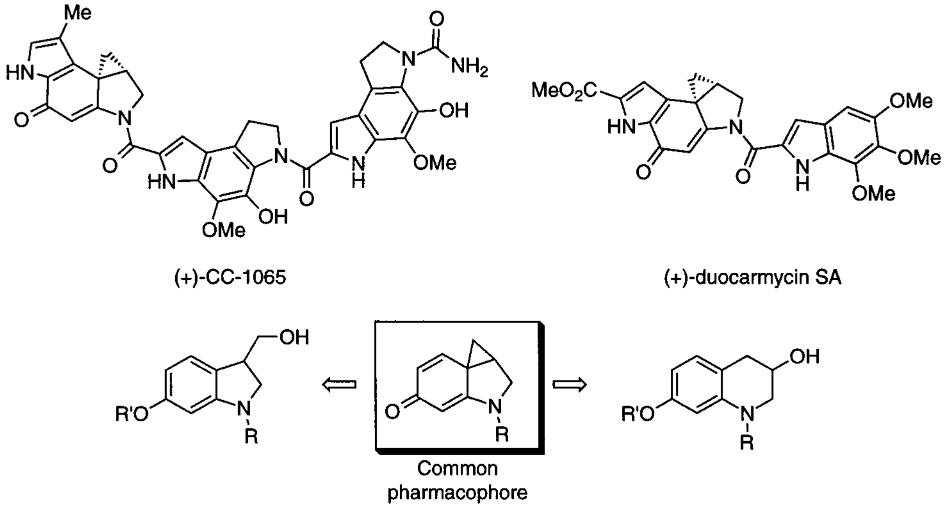

Figure 5.

Table 9. ^{1}H NMR of Zincates in THF (−20 °C)

entry	metal reagent	δ_{Me} (ppm)[a]
1	Me_2Zn	−0.84
2	Me_3ZnLi	−1.08
3	Me_4ZnLi_2	−1.44
4	$Me_3Zn(SCN)Li_2$	−1.23[b]
5	$Me_3Zn(CN)Li_2$	−1.20[b]
6	$Zn(SCN)_2$ + 3MeLi	−1.31

[a] The δ values are relative to β methylene proton (1.85 ppm) to THF. [b] The signal of tetramethylsilane newly generated in the mixture was observed at 0.00 ppm together with disappearance of the signal of Me_3SiNCS (0.40 ppm) or Me_3SiCN (0.38 ppm).

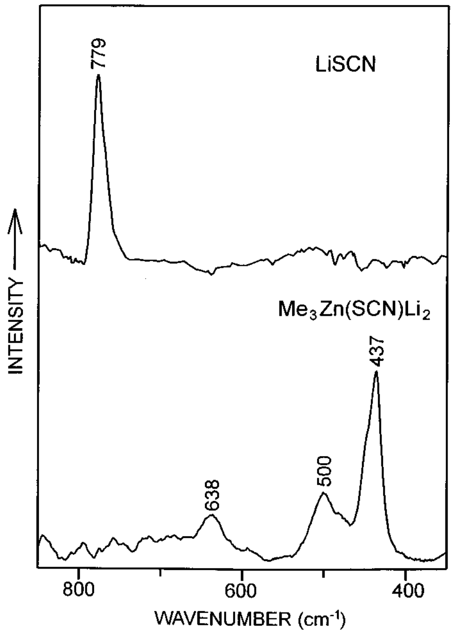

Figure 6. Raman spectra (514.5 nm excitation) of THF solutions of LiSCN (top) and $Me_3Zn(SCN)Li_2$ (bottom).

trace), a single strong band, which is assignable to the C−S stretching vibration of SCN on the Li atom or free SCN anion, appears at 779 cm^{-1}. On the other hand, $Me_3Zn(SCN)Li_2$ (**4a**) shows no band at 779 cm^{-1} (bottom trace). Namely, free LiSCN (or SCN^- ion) does not exist in a THF solution of $Me_3Zn(SCN)Li_2$ (**4a**).

In situ Fourier transform infrared (FTIR) spectroscopy has become an important technology for the investigation of chemical reactions in recent years.[6b,25] We then monitored the formation of $Me_3Zn(SCN)Li_2$ (**4a**) by the In Situ FTIR 1000 system (in situ FTIR) equipped with an immersible DiComp Attenuated Total Reflectance (ATR) probe in order to track the reaction of Me_3SiNCS with Me_4ZnLi_2 (**2**) in a THF solution (Figure 7). Infrared bands at 837, 855, and 1254 cm^{-1} in the spectrum of the starting material (Me_3SiNCS) were assigned to the methyl stretching vibration of the trimethylsilyl moiety, and diminished in intensity as the reaction proceeded. Furthermore, the bands at 863 and 1246 cm^{-1}, assigned to the methyl stretching vibration of the newly generated tetramethylsilane, increased in intensity. On the other hand, the reaction profile also shows the formation of a new zincate species as indicated by the decrease in intensity of the 2084 cm^{-1} isothiocyano band of the starting material (Me_3SiNCS) and the increase in intensity of the new (iso)thiocyano band at 2070 cm^{-1}. These present results, i.e., the ^{1}H NMR/Raman/in situ FTIR studies of the newly designed zincate solution, strongly support the existence of the *new* zincates. Although the implication from of the results the Raman/in situ FTIR spectroscopic experiments is that the (iso)thiocyano ligand must be incorporated somehow within the zincate cluster, there is no guarantee that the Zn−SCN covalent bonding exists.

In order to obtain direct information about the structures of the newly designed zincates, we measured the EXAFS spectra of the organozinc reagents and other organometallic reagents.[26] Extended X-ray absorption fine structure (EXAFS) spectroscopy probes the local structures, i.e., the nature, number, and distance of near neighbors which surround atoms or ions of *a chosen element* within *noncrystalline* systems.[27] The laboratory X-ray spectrometer employed for the XAFS measurements has been previously described[28] as well as the details of the analysis procedure.

The Fourier transform of the EXAFS data for THF solutions (~0.2 M) of Me_2Zn, Me_4ZnLi_2 (**2**), and Me_4ZnLi_2 + Me_3SiCN (**3**), and $Zn(CN)_2$ in the solid phase are shown in Figure 8. The spectra give a pseudoradial distribution function around the

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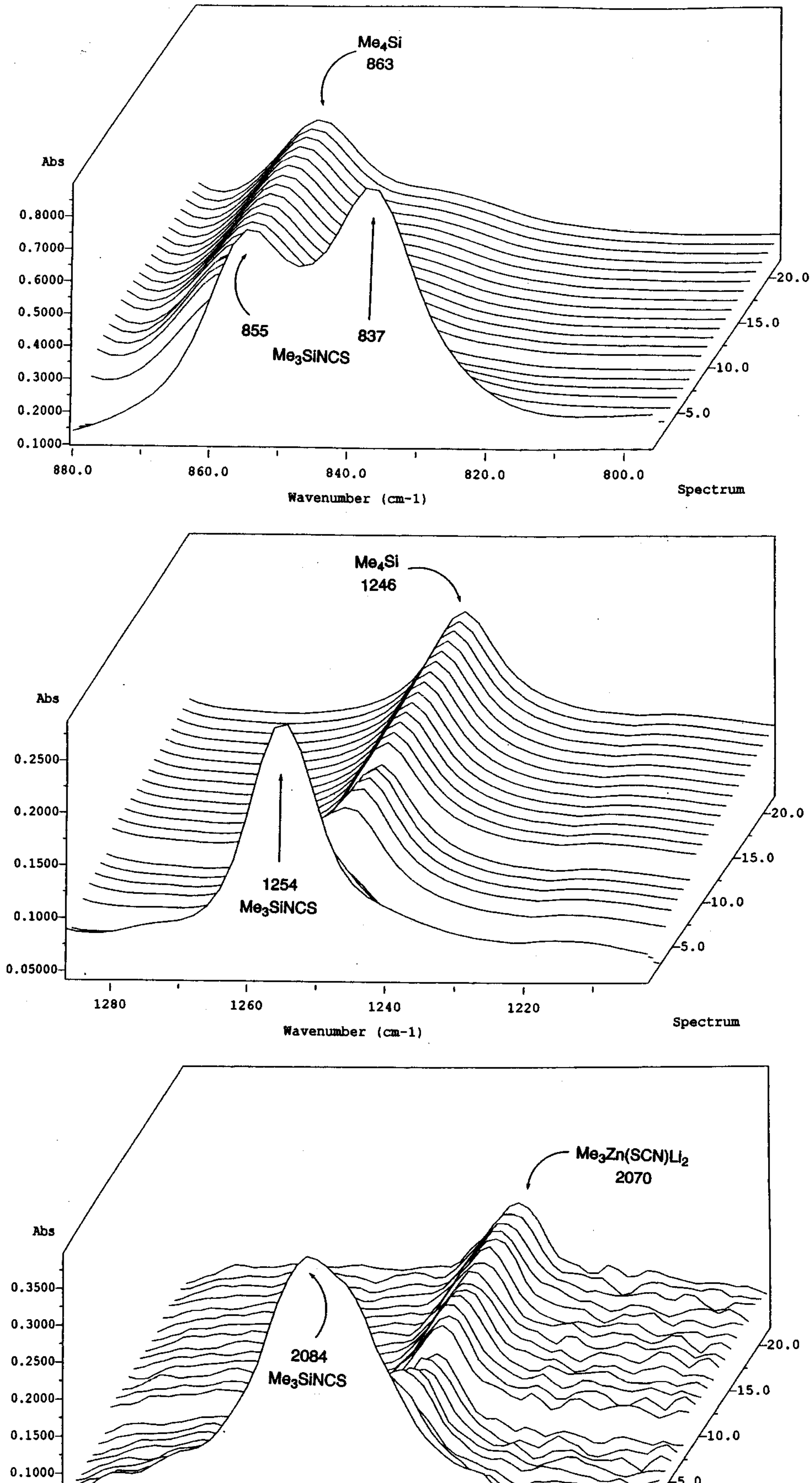

Figure 7. FTIR spectroscopic analysis of the reaction of Me_3SiNCS (1.0 M) with Me_4ZnLi_2 (1.0 M) in THF at −78 °C.

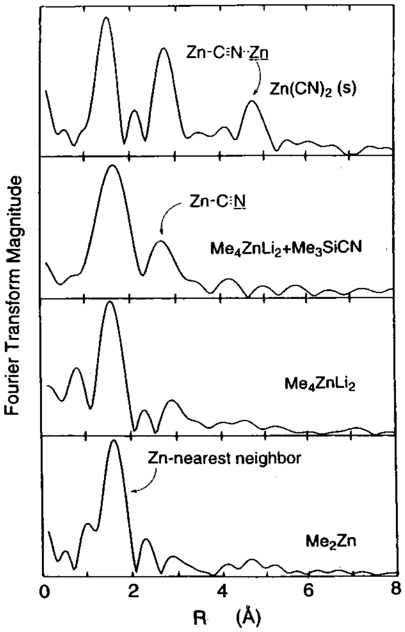

Figure 8. Fourier transform of the EXAFS spectra.

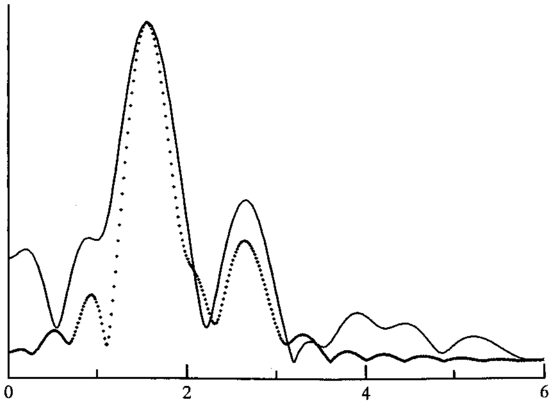

Figure 9. FEFF6 calculation of $Me_3Zn(CN)Li_2$.

absorbing atom (Zn). Peak positions in the Fourier transform are shifted by about 0.5 Å due to a phase shift. Only one and a similar principal feature is observed for both Me_2Zn and **2**. These peaks are attributed to the Zn−C nearest neighbors.

On the other hand, the Fourier transform for **3**, which was prepared by the reaction of Me_4ZnLi_2 (**2**) with Me_3SiCN in a THF solution, i.e., $Me_3Zn(CN)Li_2$ (**3**), shows a second feature in addition to the nearest neighbor peak. A new peak is considered to be attributed to *Zn*−C−*N* next nearest neighbors. To be more precise, the presence of the feature indicates that the CN ligand is on the Zn atom in $Me_3Zn(CN)Li_2$. FEFF6 calculations have been carried out using the following model; a Zn atom is surrounded by four tetrahedrally coordinated carbon atoms, one of which is CN and the others are methyl. The observed spectrum was almost reproduced when Zn−C nearest neighbors and *Zn*−C−*N* next nearest neighbors distances were set to 1.96 and 3.10 Å, respectively (Figure 9). CN distance is calculated to be 1.14 Å which is very close to the one observed in $Zn(CN)_2$.[29] Indeed, the Fourier transform for $Zn(CN)_2$ (s) of which cyanide is coordinated to the Zn atom, have similar peaks.

Moreover, a second outer-shell peak is also observed for $Zn(CN)_2$ (s). This peak can be assigned Zn···Zn (*Zn*−C−N−*Zn*) EXAFS, since the crystal structure of $Zn(CN)_2$ is known.[29] Also, the existence of this peak supports the fact that $Zn(CN)_2$ (s) is an oligomeric structure as previously reported.[29]

The EXAFS study of the $Me_3Zn(CN)Li_2$ (**3**) solution led us to the conclusion that the cyanide and all of the methyl groups are coordinated to the Zn atom in $Me_3Zn(CN)Li_2$, that is, the existence of a *four coordinated dianionic* zincate is confirmed.

Theoretical (DFT) Study of Newly Designed Zincates and Comparison with Experimental/Spectroscopic Data. The use of ab initio methods to obtain accurate data on the structures and properties of molecules has become a routine technique in the chemistry of heavy-atom molecules, as well as light-atom molecules.

In order to evaluate the four-coordinated dianionic structure of the newly designed zincates, we first carried out theoreticalcal culations based on the density-functional theory (DFT)[30] using the computer program MULLIKEN,[31] where a slightly modified version of the B3LYP function is implemented; in Mulliken the local correlation functional of Vosko, Wilk, and Nusair[32] is replaced by the functional of Perdew and Wang.[33] Hybrid density functional methods have been shown to give as good or better geometries as correlated ab initio methods for first-row transition-metal complexes.[34] The basis set for zinc was the double-ζ basis (62111111/3111/311) of Schäfer et al.,[35] enhanced with diffuse p, d, and f functions with exponents 0.174, 0.132, and 0.390, and 6-31G* for the other atoms.[36] The calculated Zn−C bond lengths of $ZnMe_2$ at B3LYP (1.955 Å) are in reasonable agreement with the X-ray distance of 1.928 Å.[37]

With this background, we studied theoretically the structures and the relative energies of the tetraorganozincates. Although the relative energies of the zincates depend to some degree on the substitutent (R), *the tri-coordinated monoanionic* zincates, **36b** and **37c**, are energetically favored over *the tetracoordinated dianionic* zincates, **36a** and **37a**, in both cases ($Me_3Zn(R)Li_2$; R = Me and CN) (Figure 10). Also, *the tetracoordinated dianionic* $Me_3Zn(SCN)Li_2$ (**38a**) calculations were carried out using the following model; a Zn atom is surrounded by four tetrahedrally coordinated carbon atoms, one of which is SCN and the others are methyls (Figure 11). Optimization with B3LYP causes a no-barrier rearrangement of the tetrahedral (dianionic) arrangement to the tricoordinated SCN-bridged structure (**38b**). In conclusion, the present DFT study predicted that *monomeric* lithium tetraorganozincates (symbolized as Me_3-

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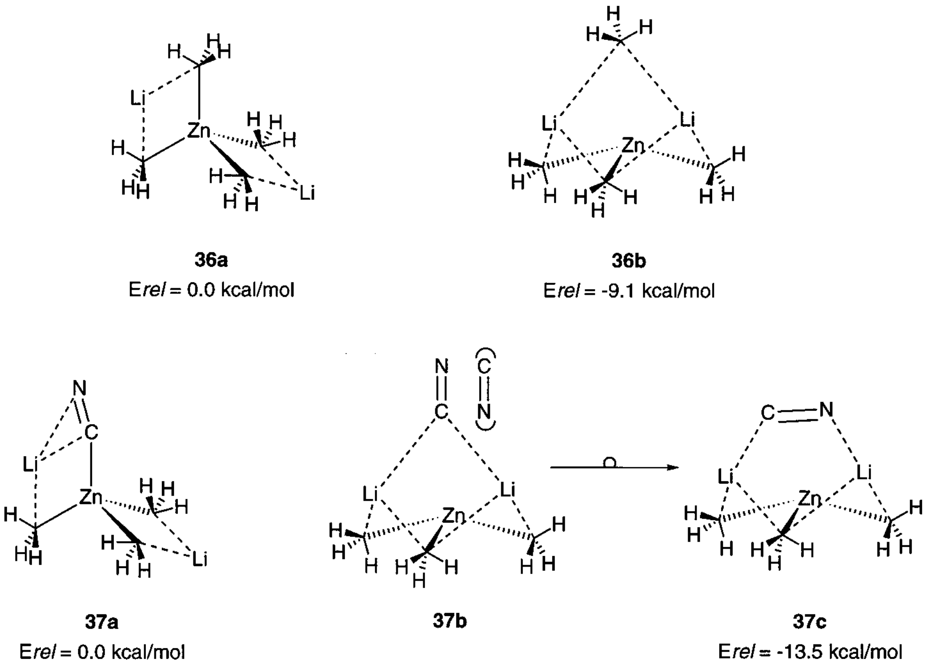


Figure 10. Relative energies for B3LYP-optimized isomers of $Me_3Zn(R)Li_2$ (R = Me, CN).

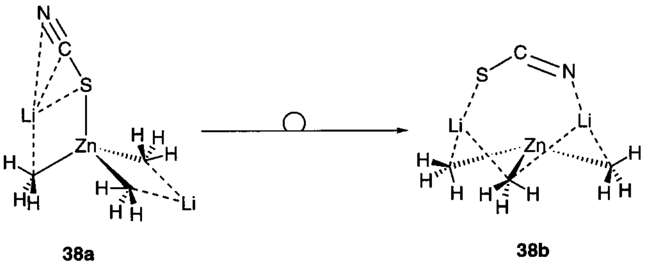


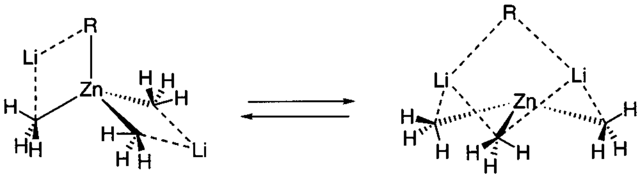
Figure 11.

$Zn(R)Li_2$; R = Me, CN, and SCN) prefer a *Zn(II) tricoordinate R-bridged structure* rather than *a tetracoordinated dianionic structure*.

All the results, including the ^1H NMR/Raman/in situ FTIR/EXAFS spectroscopies and DFT theoretical studies of the newly designed zincates, strongly support the fact that $Me_3Zn(R)Li_2$ (R = Me, CN, SCN) are *new category of zincate species*. Especially, EXAFS spectroscopy of the cyano-substituted zincate ($Me_3Zn(CN)Li_2$) supported the tetracoordinate, dianionic zinc structures and the CN ligand is directly coordinated to the Zn atom in these zincates. Also, X-ray studies of the zincates have disclosed that the crystal structure of the tetraalkylzincates and trialkylzincates are in a tetrahedral (sp^3 like) dianionic arrangement and a trigonal (sp^2 like) monoanionic arrangement about the Zn atom, respectively.[7,8] These observations are also identical with the experimental facts that newly designed zincates have higher reactivities (halogen (or tellurium)−zinc exchange, Michael addition, and carbozincation) and different chemoselectivities (epoxide ring opening reaction) compared to the triorganozincates. However, theoretical studies suggested an opposite result, that is, $Me_3Zn(R)Li_2$ is not a tetracoordinated zincate, dianionic Zn(II) salt, but a modified triorganozincate.

Why were two totally distinct results obtained? How do we understand these antipodal results? First, we do not have enough evidence to neglect the possibility of the existence of a dimer or polymer, while we carried out DFT calculations of model compounds due to computational simplicity on the supposition that these zincates exist as monomers. The tetracoordinated dianionic structure might be most stable in the zincate polymeric structure. Secondly, we considered the existence of an equilibrium between the tetracoordinated zincates (**39**) and the R-bridged tricoordinated zincates (**40**) as a reasonable explanation of these antipodal results. Since this equilibrium is sufficiently fast compare to the EXAFS or X-ray time scale, a tetracoordinated structure was considered to be observed in opposition to the real thermodynamic stability. Also, on the basis of the experimental data (the excellent chemical yields and chemoselectivity), newly designed zincates were expected to be differentiated from ordinary triorganozincates, R_3ZnLi. The thermodynamically most stable species is not always the real active species. Small amounts of tetracoordinated dianionic zincate in the reaction mixture may be active species and this equilibrium may be shifted to the left as the reaction proceeds (Scheme 4).

Scheme 4. Possible Equilibrium between Tetracoordinated Zincates And R-Bridged Tricoordinated Zincates



Presently, we can neither confirm the tricoordinated R-bridged structure nor omit the possibility of the tetracoordinated structure. However, it is evident that newly designed zincates are new species and effective reagents not only for the reaction of various kinds of electrophiles but also for the metalation of aromatic halides or tellurides.

Conclusion

We have shown the unique reactivities of various newly designed ate complexes of organozinc derivatives, $Me_3Zn(R)Li_2$ (R = Me, CN, SCN), arising from lithium trimethylzincate and anion species such as methyllithium, lithium cyanide, and lithium thiocyanate; these zincates proved to be effective for the chemoselective halogen (or tellurium)−zinc exchange, Michael addition, carbozincation, and epoxide ring opening reactions. We have also measured the ^{1}H NMR/Raman/in situ FTIR/extended X-ray absorption fine structure (EXAFS) spectra of the organozinc reagents and organometallic reagents, and carried out the density-functional theory (DFT) theoretical calculations of the newly designed zincates to obtain information about the structures of these newly designed zincates. Although it is very hard to come to a complete conclusion, we proposed some hypotheses. We believe the present idea would provide a new way for designing useful organozinc and organometallic reagents for organic synthesis.

Experimental Section

General Methods. Melting points were determined with a Yazawa micro melting point apparatus and uncorrected. ^{1}H NMR spectra were recorded on a Varian Gemini 2000 using tetramethylsilane as an internal standard. ^{1}H NMR spectra of zincates and other organometallic compounds were recorded on a JEOL GX-500. Chemical shifts are expressed in δ (ppm) values, and coupling constants are expressed in hertz (Hz). The following abbreviations are used: s = singlet, d = doublet, m = multiplet, and brs = broad singlet. Low-resolution mass spectra (MS) and high-resolution mass spectra (HRMS) were recorded on a JOEL JMS-O1SG-2 spectrometer. Tellurium (−40 mesh, 99.997%) was obtained from Aldrich Chemical Co. MeLi in Et_2O was obtained from Kanto Chemical, Co. Ltd. The concentration of MeLi was determined by titration prior to use.[38]

Preparation of Organozinc Derivatives. Preparation of Me_3ZnLi. Under Ar atmosphere, MeLi (1.02 M Et_2O solution, 1.10 mL, 1.125 mmol) was added to a mixture of dry THF (3 mL) and $ZnCl_2$ (1 M THF solution, 0.375 mL, 0.375 mmol) at 0 °C, and the mixture was stirred for 30 min at the temperature.

Preparation of Me_4ZnLi_2. Under Ar atmosphere, MeLi (1.02 M Et_2O solution, 1.50 mL, 1.50 mmol) was added to a mixture of dry THF (3 mL) and $ZnCl_2$ (1 M THF solution, 0.375 mL, 0.375 mmol) at 0 °C, and the mixture was stirred for 30 min at the temperature.

Preparation of $Me_3Zn(CN)Li_2$. Under Ar atmosphere, MeLi (1.02 M Et_2O solution, 1.50 mL, 1.50 mmol) was added to a mixture of dry THF (3 mL) and $ZnCl_2$ (1 M THF solution, 0.375 mL, 0.375 mmol) at 0 °C, and the mixture was stirred at the temperature. The mixture was cooled to −78 °C and TMSCN (39.2 mg, 0.375 mmol) was added dropwise to the mixture, and the mixture was stirred at 0 °C for 30 min.

Preparation of $Me_3Zn(CN)_2Li_3$ ($Zn(CN)_2$ + 3MeLi). Under Ar atomosphere, MeLi (1.02 M Et_2O solution, 1.10 mL, 1.125 mmol) was added to a mixture of $Zn(CN)_2$ (44.0 mg, 0.375 mmol) and dry THF (3 mL) at 0 °C, and the mixture was stirred for 30 min at the temperature.

Preparation of $Me_3Zn(SCN)Li_2$. Under Ar atmosphere, MeLi (1.02 M Et_2O solution, 1.50 mL, 1.50 mmol) was added to a mixture of dry THF (3 mL) and $ZnCl_2$ (1 M THF solution, 0.375 mL, 0.375 mmol) at 0 °C, and the mixture was stirred for 30 min at the temperature. The mixture was cooled to −78 °C and TMSNCS (49.7 mg, 0.375 mmol) was added dropwise and the whole was stirred at 0 °C for 30 min.

Preparation of $Me_3Zn(SCN)_2Li_3$ ($Zn(SCN)_2$ + 3MeLi). Under Ar atomosphere, MeLi (1.02 M Et_2O solution, 1.10 mL, 1.125 mmol) was added to a mixture of $Zn(SCN)_2$ (73.2 mg, 0.375 mmol) and dry THF (3 mL) at 0 °C, and the mixture was stirred for 30 min at the temperature.

General Procedure for Intermolecular Epoxide Opening Reaction. Under Ar atmosphere, a THF solution of a zincates (2 mmol) was prepared as described above. A solution of **5** (48.1 mg, 0.4 mmol) in THF (3 mL) was added dropwise to the THF solution of the zincate (2 mmol) at 0 °C. After allowing to warm to room temperature, the mixture was stirred for 4 h. The solvent was removed under reduced pressure and the residue was treated with NH_4Cl (30 mL) followed by extraction with CH_2Cl_2 (30 mL × 3). The CH_2Cl_2 layer was dried over $MgSO_4$, and the CH_2Cl_2 was removed under reduced pressure. The ratio of the two products were determined by analyzing the ^{1}H NMR spectrum of the mixture comparing with the authentic samples. 1-Phenyl-1-propanol (**6**): 300 MHz ^{1}H NMR ($CDCl_3$/TMS) δ (ppm) 0.90 (3H, t, J = 7.6 Hz), 1.71−1.86 (1H, m), 1.97 (1H, bs), 4.57 (1H, t, J = 6.6 Hz), 7.24−7.36 (5H, m). 2-Phenyl-1-propanol (**7**): 300 MHz ^{1}H NMR ($CDCl_3$/TMS) δ (ppm) 1.26 (3H, d, J = 7.1 Hz), 1.54 (1H, brs), 2.94 (1H, sextet, J = 7.1 Hz), 3.68 (2H, d, J = 6.9 Hz), 7.20−7.36 (5H, m).

General Procedure for Bromine−Zinc Exchange Reaction. Under Ar atmosphere, a THF solution of a zincate (1.1 mmol) were prepared as described above. The THF solution of the zincate (1.1 mmol) was cooled to 0 °C and bromobenzene (**8**) (165.3 mg, 1.0 mmol) in THF (3 mL) was added dropwise to the mixture. After the mixture was stirred for 2 h, benzaldehyde (0.21 mL, 2.0 mmol) was added and stirring was continued for 3 h at room temperature. The solvent was removed under reduced pressure, and the residue was treated with NH_4Cl (30 mL) followed by extraction with CH_2Cl_2 (30 mL × 3). The CH_2Cl_2 layer was dried over $MgSO_4$, and the CH_2Cl_2 was removed under reduced pressure. The residue was purified by SiO_2 column chromatography using AcOEt−hexane (1:5) as an eluent to give benzhydrol (**9**): mp 65−67 °C (recrystallized from *n*-hexane/ethyl acetate, colorless plates) (lit.[39] mp 68 °C); 300 MHz ^{1}H NMR ($CDCl_3$/TMS) δ (ppm) 2.21 (1H, d, J = 3.3 Hz), 5.85 (1H, brs), 7.2−7.5 (10H, m); MS *m/z* 184 (M^+).

4-Methoxybenzhydrol: mp 64 °C (recrystallized from *n*-hexane/ethyl acetate, colorless plates) (lit.[40] mp 67−68 °C). 300 MHz ^{1}H NMR ($CDCl_3$/TMS) δ (ppm): 2.50 (bs, 1H), 3.74 (s, 3H), 5.72 (s, 1H), 6.82 (d, 2H, J = 8.8Hz), 7.21−7.34 (m, 7H). MS *m/z*: 214 (M^+). HRMS: Calcd for $C_{14}H_{14}O_2$: 214.0994. Found: 214.1006.

4-Cyanobenzhydrol (13): mp 64 °C (recrystallized from *n*-hexane/ethyl acetate, colorless cubes) (lit.[41] mp 67−68 °C); 300 MHz ^{1}H NMR ($CDCl_3$/TMS) δ (ppm) 3.11 (bs, 1H), 5.79 (1H, s), 7.25−7.35 (5H, m), 7.47 (2H, d, J = 8.4Hz), 7.55 (2H, d, J = 8.4Hz); MS *m/z* 209 (M+); HRMS calcd for $C_{14}H_{14}O_2$ 209.0841, found 209.0829.

4-Acetylbenzhydrol (14): mp 113−114 °C (recrystallized from *n*-hexane/ethyl acetate, white powder); 300 MHz ^{1}H NMR ($CDCl_3$/TMS) δ (ppm) 2.56 (3H, s), 5.87 (1H, s), 7.29−7.36 (5H, m), 7.48 (2H, d, J = 8.5Hz), 7.91 (2H, d, J = 8.2Hz); MS *m/z* 226 (M^+ + H); HRMS calcd for $C_{15}H_{14}O_2$ 226.0994, found 226.0994.

4-Bromoacetophenone (15): 300 MHz ^{1}H NMR ($CDCl_3$/TMS) δ (ppm) 2.59 (3H, s), 7.61 (2H, d, J = 8.8 Hz), 7.83 (2H, d, J = 8.8 Hz); MS *m/z* 198 (M^+); HRMS calcd for $C_{15}H_{14}O_2$ 197.9680, found 197.9683.

Preparation of *n*-Butyl 2-Pyridinyl Telluride (19). Under Ar atomosphere, to a suspension of tellurium powder (273 mg, 214 mmol) in dry THF (8 mL), *n*-BuLi (1.39 M, 1.5 mL, 2.09 mmol) was added, and the mixture was stirred for 10 min. The mixture was cooled to −78 °C and 2-bromopyridine (317 mg, 2.01 mmol) was added at the temperature. The mixture was then allowed to warm to ambient temperature and then refluxed for 92 h. The mixture was diluted with H_2O (50 mL) and extracted with Et_2O (50 mL × 3). The ethereal extract was dried over $MgSO_4$. The solvent was removed, and the residue was purified by SiO_2 column chromatography using *n*-hexane/AcOEt (4:1) as a solvent to give *n*-butyl 2-pyridinyl telluride (**19**) (368 mg, 70%) as a viscous oil: 300 MHz ^{1}H NMR ($CDCl_3$/TMS) δ (ppm) 0.93 (3H, t, J = 7.3 Hz), 1.43 (2H, sext, J = 7.3 Hz), 1.89 (2H, quint, J = 7.5 Hz), 3.12 (2H, t, J = 7.5 Hz), 7.00−7.03 (1H, m), 7.28−7.34 (1H, m), 7.47 (1H, dd, J = 2.0, 7.7 Hz), 8.47 (1H, dd, J = 1.1, 4.0 Hz); MS *m/z* 265 (M^+); HRMS calcd for $C_9H_{13}NTe$ 265.0111, found 265.0111.

General Procedure for Tellulium−Zinc Exchange Reaction. Under Ar atmosphere, a THF solution of a zincate (0.57 mmol) was prepared as described above. The THF solution (0.57 mmol) of the zincate was cooled to −78 °C and **19** (110 mg, 0.42 mmol) in THF (3 mL) was added dropwise to the mixture. After the mixture was stirred for specified conditions, benzaldehyde (0.11 mL, 1.0 mmol) was added to the mixture. After the mixture was stirred for 3 h at room

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temperature, the solvent was removed under reduced pressure and the residue was treated with NH_4Cl (30 mL) followed by extraction with CH_2Cl_2 (30 mL × 3). The CH_2Cl_2 layer was dried over $MgSO_4$, and the CH_2Cl_2 was removed under reduced pressure. The residue was purified by SiO_2 column chromatography using AcOEt/hexane (3:1) as an eluent to give phenyl(2-pyridinyl)methanol (**20**) (62.9 mg, 81%) as a colorless oil: 300 MHz ^1H NMR ($CDCl_3$/TMS) δ (ppm) 5.75 (1H, s), 7.14−7.38 (7H, m), 7.61 (1H, t, *J* = 7.3 Hz), 8.54 (1H, d, *J* = 4.4 Hz); MS *m/z* 185 (M^+); HRMS calcd for $C_{12}H_{11}NO$ 185.0841, found: 185.0842.

Preparation of Methyl 4-(2-Iodophenylamino-*N*-phenylsulfonyl)-but-2-enoate (21, X = NSO_2Ph). Under Ar atmosphere, pyridine (22.0 g, 275 mmol) and benzenesulfonyl chlolide (11.7 g, 66 mmol) were added to a THF (5 mL) solution of 2-iodoaniline (12.0 g, 55 mmol) at 0 °C with stirring, and the mixture was stirred at room temperature for 6 h. After evaporation of the solvent, the residue was diluted with H_2O (100 mL) and extracted with $CHCl_3$ (100 × 3). The $CHCl_3$ layer was dried over $MgSO_4$, and the $CHCl_3$ was removed under reduced pressure. The solid obtained was recrystallized from ethyl acetate to give 2-iodo-*N*-phenylsulfonylaniline (18.0 g, 91%) as a colorless prisms: mp 113−114 °C (recrystallized from ethyl acetate, colorless prisms); 300 MHz ^1H NMR ($CDCl_3$/TMS) δ (ppm) 7.05 (1H, d, *J* = 8.0 Hz), 7.13 (1H, t, *J* = 8.0 Hz), 7.34 (1H, t, *J* = 7.4 Hz), 7.59 (1H, m), 7.67 (2H, m), 7.91 (1H, d, *J* = 8.0 Hz); MS *m/z* 359 (M^+). Anal. Calcd for $C_{12}H_{10}INO_2S$: C, 40.13; H, 2.81; N, 3.90; S, 8.93. Found: C, 40.02; H, 2.85; N, 3.89; S, 8.90.

Under Ar atomosphere, to a suspension of sodium hydride (145 mg, 3.6 mmol) in dry THF (5 mL), a THF (5 mL) solution of 2-iodo-*N*-phenylsulfonylaniline (1.0 g, 2.78 mmol) was added and stirred for 1 h at room temperature. The mixture was cooled to 0 °C and methyl 4-bromo-2-butenoate (1.0 g, 5.58 mmol) was added at the temperature. The mixture was then allowed to warm to ambient temperature and then stirred for 20 h. After reaction, the mixture was diluted with H_2O (50 mL), and the aqueous mixture was extracted with $CHCl_3$ (50 mL × 3). The $CHCl_3$ layer was dried over $MgSO_4$. The solvent was removed, and the residue was purified by SiO_2 column chromatography using *n*-hexane/AcOEt (3:1) as a solvent to give methyl 4-(2-iodophenylamino-*N*-phenylsulfonyl)but-2-enoate (**21**, X = NSO_2Ph): mp 89.0−89.5 °C (recrystallized from *n*-hexane/ethyl acetate, white powder); 300 MHz ^1H NMR ($CDCl_3$/TMS) δ (ppm) 3.75 (3H, s), 4.25 (1H, dd, *J* = 16.0, 8.0 Hz), 4.40 (1H, dd, *J* = 16.0, 8.0 Hz), 5.82 (1H, d, *J* = 16.0 Hz), 6.91 (1H, dt, *J* = 15.7, 6.6 Hz), 7.02 (1H, d, *J* = 7.7 Hz), 7.09 (1H, d, *J* = 8.0 Hz), 7.31 (1H, t, *J* = 8.0 Hz), 7.51 (2H, t, *J* = 7.1 Hz), 7.62 (1H, t, *J* = 7.1 Hz), 7.88 (1H, d, *J* = 8.0 Hz); MS *m/z* 457 (M^+); HRMS calcd for $C_{17}H_{16}NO_4SI$ 456.9844, found 456.9847.

Preparation of Methyl 4-(2-Iodophenyloxy)but-2-enoate (21, X = O). Under Ar atomosphere, to a suspension of sodium hydride (331 mg, 8.13 mmol) in dry THF (5 mL) was added a THF (5 mL) solution of 2-iodophenol (1.53 g, 6.25 mmol), and the mixture was stirred for 1 h at room temperature. The mixture was cooled to 0 °C and 4-bromo-2-butenoate (2.32 g, 12.5 mmol) was added at the temperature. The mixture was then allowed to warm to ambient temperature and then stirred for 20 h. The mixture was diluted with H_2O (50 mL) and the aqueous mixture was extracted with $CHCl_3$ (50 mL × 3). The $CHCl_3$ layer was dried over $MgSO_4$. The solvent was removed and the residue was purified by SiO_2 column chromatography using *n*-hexane/AcOEt (5:1) as a solvent to give methyl 4-(2-iodophenyloxy)but-2-enoate (1.2 g, 57%) as a colorless oil: 300 MHz ^1H NMR ($CDCl_3$/TMS) δ (ppm) 3.78 (3H, s), 4.75 (2H, d, *J* = 3.6 Hz), 6.40 (1H, dt, *J* = 15.7, 2.2 Hz), 6.74 (1H, d, *J* = 7.4 Hz), 6.78 (1H, m), 7.09 (1H, dt, *J* = 15.7, 3.6 Hz), 7.30 (1H, t, *J* = 8.2 Hz), 7.80 (1H, d, *J* = 7.7 Hz); MS *m/z* 318 (M^+); HRMS calcd for $C_{11}H_{11}O_3I$ 317.9753, found 317.9757.

General Procedure for Intramolecular Michael Addition Reaction. Under Ar atmosphere, a THF solution of a zincates (0.6 mmol) was prepared as described above. The THF solution of the zincate (0.6 mmol) was cooled to −78 °C and 4-(2-iodophenylamino-*N*-phenylsulfonyl)but-2-enoate (**21**, X = NSO_2Ph) (228.6 mg, 0.5 mmol) in THF (3 mL) was added dropwise to the mixture. The mixture was stirred at −40 °C for 4 h. The mixture was allowed to warm to room temperature and was stirred at room temperature for 8 h. The solvent was removed under reduced pressure and the residue was treated with NH_4Cl (30 mL) followed by extraction with $CHCl_3$ (50 mL × 3). The $CHCl_3$ layer was dried over $MgSO_4$ and $CHCl_3$ was removed under reduced pressure. The residue was purified by SiO_2 column chromatography using AcOEt/hexane (3:1) as an eluent to give methyl 1-(phenylsulfonyl)indoline-3-acetate (**22**, X = NSO_2Ph) as a yellow oil: 300 MHz ^1H NMR ($CDCl_3$/TMS) δ (ppm) 2.17 (1H, dd, *J* = 16.5, 9.8 Hz), 2.50 (1H, dd, *J* = 16.5, 5.2 Hz), 3.46−3.58 (1H, m), 3.65 (1H, dd, *J* = 11.0, 5.5 Hz), 3.66 (3H, s), 4.09 (1H, dd, *J* = 11.0, 8.8 Hz), 6.97 (1H, t, *J* = 6.6 Hz), 7.02 (1H, t, *J* = 6.7 Hz), 7.21 (1H, t, *J* = 7.2 Hz), 7.43 (2H, t, *J* = 7.4 Hz), 7.54 (1H, t, *J* = 7.4 Hz), 7.65 (1H, d, *J* = 8.5 Hz), 7.78 (2H, d, *J* = 5.5 Hz); MS *m/z* 331 (M^+); HRMS calcd for $C_{17}H_{17}NSO_4$ 331.0878, found 331.0868.

Methyl 2,3-dihydrobenzofuran-3-acetate (**22**, X = O): colorless oil; 300 MHz ^1H NMR ($CDCl_3$/TMS) δ (ppm) 2.59 (1H, dd, *J* = 16.5, 9.5 Hz), 2.80 (1H, dd, *J* = 16.5, 5.5 Hz), 3.72 (3H, s), 3.80−3.95 (1H, m), 4.25 (1H, dd, *J* = 9.3, 6.4 Hz), 4.75 (1H, t, *J* = 8.1 Hz), 6.80 (1H, d, *J* = 8.1 Hz), 6.86 (1H, t, *J* = 7.5 Hz), 7.14 (2H, t, *J* = 7.5 Hz); MS *m/z* 192 (M^+); HRMS calcd for $C_{11}H_{12}O_3$ 192.0787, found 192.0803.

Preparation of Allyl 2-Iodophenyl Ether (23). A mixture of 2-iodophenol (0.6 g, 2.7 mmol), allyl bromide (0.7 g, 3 equiv), K_2CO_3 (1.2 g, 3 equiv), and DMF (20 mL) was stirred at 80 °C for 48 h. After dilution with Et_2O (50 mL), the reaction mixture was washed with water and brine, dried over $MgSO_4$, and the Et_2O was removed under reduced pressure. The residue was purified by SiO_2 column chromatography using AcOEt/hexane (1:5) as an eluent to give allyl 2-iodophenyl ether (**23**) (0.70 g, 98%) as a colorless oil: 300 MHz ^1H NMR ($CDCl_3$/TMS) δ (ppm) 4.60 (2H, d, *J* = 5.0 Hz), 5.32 (1H, d, *J* = 10.7 Hz), 5.54 (1H, d, *J* = 17.3 Hz), 6.00−6.12 (1H, m), 6.72 (1H, t, *J* = 7.3 Hz), 6.80 (1H, d, *J* = 8.1 Hz), 7.27 (1H, t, *J* = 7.3 Hz), 7.78 (1H, d, *J* = 7.6 Hz); MS *m/z* 260 (M^+); HRMS calcd for $C_{11}H_{12}O_3$ 259.9698, found: 259.9711.

Reaction of 23 with Me_3ZnLi. Under Ar atmosphere, a THF solution of a zincates (1.0 mmol) was prepared as described above. The THF solution of the zincate (1.0 mmol) was cooled to −78 °C, and **23** (131 mg, 0.5 mmol) in THF (3 mL) was added dropwise to the mixture. After the mixture was allowed to warm to room temperature, it was stirred for 48 h. The solvent was removed under reduced pressure, and the residue was treated with NH_4Cl (30 mL) followed by extraction with CH_2Cl_2 (50 mL × 3). The CH_2Cl_2 layer was dried over $MgSO_4$ and CH_2Cl_2 was removed under reduced pressure. The residue was purified by SiO_2 column chromatography using AcOEt/hexane (1:10) as an eluent to give allyl phenyl ether (**25**) (136.8 mg, quant) as a colorless oil: 300 MHz ^1H NMR ($CDCl_3$/TMS) δ (ppm) 4.5−4.6 (2H, m), 5.2−5.3 (1H, m), 5.3−5.5 (1H, m), 6.0−6.2 (1H, m), 6.9−7.0 (3H, m), 7.31 (2H, t , *J* = 7.5 Hz).

Reaction of 23 with Me_4ZnLi_2. Under Ar atmosphere, a THF solution of a zincates (1.0 mmol) was prepared as described above. The THF solution of the zincate (1.0 mmol) was cooled to −78 °C and **23** (131 mg, 0.5 mmol) in THF (3 mL) was added dropwise to the mixture. After the mixture was allowed to warm to room temperature, it was stirred for 48 h. The solvent was removed under reduced pressure, and the residue was treated with NH_4Cl (30 mL) followed by extraction with CH_2Cl_2 (50 mL × 3). The CH_2Cl_2 layer was dried over $MgSO_4$, and the CH_2Cl_2 was removed under reduced pressure. The residue was purified by SiO_2 column chromatography using AcOEt/hexane (1:5) as an eluent to give 3-methyl-2,3-dihydrobenzofuran (**28**) (57.5 mg, 42%) as a colorless oil: 300 MHz ^1H NMR ($CDCl_3$/TMS) δ (ppm) 1.32 (3H, d, *J* = 7.5 Hz), 3.5−3.6 (1H, m), 4.07 (1H, dd, *J* = 7.4, 8.5 Hz), 4.68 (1H, dd, *J* = 8.5, 8.5 Hz), 6.79 (1H, d, *J* = 8.5 Hz), 6.87 (1H, t , *J* = 8.2 Hz), 7.2−7.1 (2H, m).

N,*N*-Diallyl-2-iodoaniline (**29**) was prepared from 2-iodoaniline and allyl bromide in the same manner as **23**. *N*,*N*-Diallyl-2-iodoaniline (**29**): colorless oil; 300 MHz ^1H NMR ($CDCl_3$/TMS) δ (ppm) 3.63 (4H, d, *J* = 6.1 Hz), 5.09−5.21 (4H, m), 6.78 (1H, t, *J* = 8.0 Hz), 7.02 (1H, d, *J* = 8.0 Hz), 6.27 (1H, t, *J* = 7.4 Hz), 7.86 (1H, d, *J* = 8.0 Hz); MS *m/z* 299 (M^+); HRMS calcd for $C_{11}H_{12}O_3$ 299.0171, found 299.0154.

N-Allyl-3-methylindoline (**32**): colorless oil, 300 MHz ^1H NMR ($CDCl_3$/TMS) δ (ppm) 1.31 (3H, d, *J* = 6.9 Hz), 2.85 (1H, t, *J* = 7.7 Hz), 3.25−3.33 (1H, m), 3.53−3.65 (2H, m), 3.74−3.82 (1H, m), 5.16−

5.31 (2H, m), 5.85−5.96 (1H, m), 6.52 (1H, d, *J* = 8.0 Hz), 6.70 (1H, t , *J* = 7.1 Hz), 7.04−7.10 (2H, m); MS *m/z* 173 (M^+); HRMS calcd for $C_{11}H_{12}O_3$ 173.1201, found 173.1203.

Preparation of *N*-(2,3-Epoxypropyl)-2-iodo-*N*-phenylsulfonylaniline (33). DEAD (1.13 mL, 7.2 mmol) was added to the mixture of 2-iodo-*N*-phenylsulfonylaniline (1.71 g, 4.8 mmol) and PPh_3 (1.9 g, 7.2 mmol) in dry THF (10 mL). 2,3-Epoxy-1-propanol (0.48 mL, 7.2 mmol) was added dropwise to the mixture at 0 °C over 10 min. The mixture was stirred at room temperature for 1 h. After evaporation of the solvent, the residue was purified by column chromatography using AcOEt/hexane (2:3) as an eluent to give *N*-(2,3-epoxypropyl)-2-iodo-*N*-phenylsulfonylaniline (**33**) (1.66 g, 80%): mp 76−77 °C (recrystallized from *n*-hexane/ethyl acetate, colorless prism); 300 MHz ^{1}H NMR ($CDCl_3$/TMS) δ (ppm) 2.30 (0.5H, dd, *J* = 2.5, 4.7 Hz), 2.42 (0.5H, dd, *J* = 2.5, 4.5 Hz), 2.72 (1H, dt, *J* = 4.1, 6.9 Hz), 3.20 (0.5H, bs), 3.32 (0.5H, bs), 3.73 (2H, m), 6.99 (0.5H, dd, *J* = 1.6, 8.0 Hz), 7.07 (1H, dt, *J* = 0.8, 7.4 Hz), 7.19 (0.5H, dd, *J* = 0.8, 7.4 Hz), 7.35 − 7.26 (1H, m), 7.51 (1H, t, *J* = 6.6 Hz), 7.62 (1H, t, *J* = 7.0 Hz), 7.78 (2H, d, *J* = 7.0 Hz), 7.92 (1H, ddd, *J* = 1.4, 8.0, 11.8 Hz); MS *m/z* 415 (M^+). Anal. Calcd for $C_{15}H_{14}INO_3S$: C, 43.39; H, 3.40; N, 3.37; S, 7.72; I, 30.56. Found: C, 43.47; H, 3.45; N, 3.46; S, 7.80; I, 30.61.

General Procedure for Intramolecular Epoxide Opening Reaction. Under Ar atmosphere, a THF solution of a zincate (0.375 mmol) was prepared as described above. The THF solution of the zincate (0.375 mmol) was cooled to −78 °C and **33** (104 mg, 0.25 mmol) in THF (3 mL) was added dropwise to the mixture. After the mixture was allowed to warm to room temperature, it was stirred for 12 h. The solvent was removed under reduced pressure, and the residue was treated with NH_4Cl (30 mL) followed by extraction with CH_2Cl_2 (50 mL × 3). The CH_2Cl_2 layer was dried over $MgSO_4$ and the CH_2Cl_2 was removed under reduced pressure. The residue was purified by SiO_2 column chromatography using AcOEt/hexane (2:3) as an eluent to give a mixture of 1-phenylsulfonylindoline-3-methanol (**34**) and 3-hydroxy-1-phenylsulfonyl-1,2,3,4-tetrahydroquinoline (**35**). The ratio of the two products were determined by analyzing the ^{1}H NMR spectrum of the mixture and comparing with the authentic samples. 1-Phenylsulfonylindoline-3-methanol (**34**): colorless oil; 300 MHz ^{1}H NMR ($CDCl_3$/TMS) δ (ppm) 3.33−3.45 (2H, m), 3.58 (1H, dd, *J* = 5.1, 10.3 Hz), 3.89 (1H, dd, *J* = 5.1, 11.0 Hz), 4.01 (1H, dd, *J* = 9.1, 11.0 Hz), 7.01 (1H, t, *J* = 7.3 Hz), 7.13 (1H, d, *J* = 7.3 Hz), 7.25 (1H, t, *J* = 4.0 Hz), 7.45 (2H, t, *J* = 7.7 Hz), 7.55 (1H, t, *J* = 7.7 Hz), 7.69 (1H, d, *J* = 8.4 Hz), 7.82 (2H, d, *J* = 8.4 Hz); MS *m/z* 289 (M^+); HRMS calcd for $C_{15}H_{15}NO_3S$ 289.0773, found 289.0783. 3-Hydroxy-1-phenylsulfonyl-1,2,3,4-tetrahydroquinoline (**35**): colorless oil; 300 MHz ^{1}H NMR ($CDCl_3$/TMS) δ (ppm) 1.77 (1H, bs), 2.53 (1H, dd, *J* = 6.3, 16.2 Hz), 2.77 (1H, dd, *J* = 6.0, 15.7 Hz), 3.65 (1H, dd, *J* = 7.7, 14.3 Hz), 4.02−4.07 (2H, m), 7.05−7.09 (1H, m), 7.44 (1H, t, *J* = 7.7 Hz), 7.53−7.68 (1H, m), 7.71 (1H, dd, *J* = 1.8, 7.0 Hz); MS *m/z* 289 (M^+); HRMS calcd for $C_{15}H_{15}NO_3S$ 289.0773, found 289.0784.

X-ray Absorption Measurements and Data Analysis. The EXAFS experiments were performed by an in-house EXAFS system which has been described in detail previously.[42] Basically it consists of a 12 kW rotating anode X-ray generator, a spectrometer with a curved Ge(311) crystal monochromator, and a scintillation counter. The X-ray source with a silver target was operated at 25 kV to avoid possible contamination of the third-order reflection. The resolution of the spectrometer near the Zn absorption edge is about 4 eV with a 200 mm slit used.

The EXAFS function χ(k) was subtracted in a manner described in detail in ref 42 and then was Fourier transformed with a k^3 weighing factor.

Raman Measurements. Raman spectra were excited with the 514.5-nm line of a Coherent Innova 70 argon ion laser using 50 mW of radiant power at the sample. The spectra were recorded on a Jasco NR-1800 triple spectrometer equipped with a liquid nitrogen cooled CCD detector. Samples were kept at 24 °C during the collection of Raman spectra. Raman frequencies were calibrated using the spectrum of liquid indene. Wavenumbers of Raman bands were reproducible to within ±0.5 cm^{-1}.

IR Spectroscopic Analyses. Samples were recorded using a ReactIR 1000 from ASI Applied Systems fitted with an immerscible DiComp ATR (Attenuated Total Reflectance) probe optimized for maximum sensitivity. The spectra were acquired in 128 scans per spectrum at a gain of 1 and a resolution of 2 using system ReactIR 2.1 software. A representative reaction was carried out as follows: The IR probe was inserted through a nylon adapter and O-ring seal into an oven-dried, cylindrical two necked flask fitted with magnetic stir bar. Following evacuation under full vacuum and flushing with Ar, the flask was charged with a solution of Me_3SiNCS (132 mg, 1.0 mmol) in THF (1 mL) and cooled in acetone/dry ice bath to −78 °C. Following the recording of a background spectrum, a 1M THF solution of Me_4ZnLi_2 (**2**) (1 mL, 1.0 mmol) was added neat with stirring. IR spectra were recorded every 4 min over the course of the reaction. To account for mixing and temperature equilibration, spectra recorded in the first 4 min were discarded. Data manipulation and statistical analyses were carried out using the system 2.1 ReactIR software.

Acknowledgment. We thank Prof. Dr. Yasuo Udagawa for helpful discussions of EXAFS, Prof. Dr. Takashi Miura for useful discussions of Raman, and Mr. Hitoshi Ohfune for technical assistance of the EXAFS measurements. We are also grateful to Mr. Manabu Shilai for carrying out a part of preparation of pyridinyltellurium compounds.

JA973855T

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