TMS, 200 MHz) δ 1.24 (d, J = 6.3 Hz, 3 H), 2.50 (t, J = 6.6 Hz, 4 H), 2.82–3.02 (m, 2 H), 3.02–3.20 (m, 2 H), 3.30–3.42 (m, 4 H), 3.42–3.48 (m, 1 H), 3.48–3.56 (m, 4 H), 3.56–3.68 (m, 8 H), 3.68–3.72 (m, 1 H), 3.84–3.90 (m, 1 H), 4.02–4.08 (m, 2 H), 4.16 (dq, J = 3.0 Hz, 6.6 Hz, 1 H), 4.30–4.36 (m, 1 H), 4.36–4.40 (m, 1 H), 7.10–7.35 (m, 18 H), 7.42–7.58 (m, 2 H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$/TMS, 50 MHz) δ 10.88, 49.53, 56.39 (d, $J_{C\text{-}P}$ = 7.4 Hz), 69.79, 70.18, 70.35, 70.58, 71.46, 72.26, 72.42, 73.77, 75.00, 75.41, 75.51, 75.72, 75.87, 97.38 (d, $J_{C\text{-}P}$ = 24.6 Hz), 127.03, 127.23, 127.36, 127.49, 127.65, 127.81, 128.23, 128.54, 132.16 (d, $J_{C\text{-}P}$ = 18.3 Hz), 132.63 (d, $J_{C\text{-}P}$ = 19.1 Hz), 13.32 (d, $J_{C\text{-}P}$ = 20.1 Hz), 134.86 (d, $J_{C\text{-}P}$ = 22.0 Hz), 137.77 (d, $J_{C\text{-}P}$ = 9.2 Hz), 138.07 (d, $J_{C\text{-}P}$ = 9.7 Hz), 138.98 (d, $J_{C\text{-}P}$ = 10.1 Hz), 140.32 (d, $J_{C\text{-}P}$ = 8.3 Hz); $^{31}P\{^{1}H\}$ NMR ($CDCl_3/H_3PO_4$, 81 MHz) −25.51, −17.24. Anal. Calcd for $C_{48}H_{55}NO_5P_2Fe$: C, 68.33; H, 6.57; N, 1.66. Found: C, 68.51; H, 6.66; N, 1.62.

Preparation of the π-Allylpalladium(II) Complex of 8b. To a small glass vessel were added 27.4 mg (0.0304 mmol) of **8b** and 5.6 mg (0.0153 mmol) of di-μ-chlorobis(π-allyl)dipalladium(II) and then dissolved in 0.3 mL of $CDCl_3$. The solution was rinsed into an NMR tube (5 ϕ) with $CDCl_3$, and the total volume was adjusted to 0.7 mL with $CDCl_3$: ^{1}H NMR ($CDCl_3$/TMS, 400 MHz) δ 1.0–1.4 (broad, 3 H), 1.72–1.88 (m, 1 H), 1.93 (s, 3 H), 2.15–2.39 (m, 2 H), 2.39–2.75 (m, 5 H), 3.50 (t, J = 5.4 Hz, 4 H), 3.55–3.80 (m, 21 H), 3.86–4.17 (broad, 4 H), 4.31 (m, 1 H), 4.35 (m, 1 H), 4.37 (m, 1 H), 4.44 (m, 2 H), 4.40–4.56 (broad, 1 H), 4.65 (m, 1 H), 6.16 (broad, 1 H), 7.15–7.82 (m, 20 H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$/TMS, 50 MHz) δ 9.77, 30.85, 34.20, 54.03, 54.32, 58.84, 68.90, 70.13, 70.51, 70.58, 70.71, 71.24 (d, $J_{C\text{-}P}$ = 5.7 Hz), 72.99 (d, $J_{C\text{-}P}$ = 5.3 Hz), 73.24 (d, $J_{C\text{-}P}$ = 6.1 Hz), 73.93 (d, $J_{C\text{-}P}$ = 10.1 Hz), 77.21, 77.90, 78.05, 97.43 (d, $J_{C\text{-}P}$ = 14.8 Hz), 123.57 (t, $J_{C\text{-}P}$ = 5.4 Hz), 127.58 (d, $J_{C\text{-}P}$ = 10.2 Hz), 128.09, 128.34, 128.71 (d, $J_{C\text{-}P}$ = 10.7 Hz), 129.19 (d, $J_{C\text{-}P}$ = 10.3 Hz), 129.61 (d, $J_{C\text{-}P}$ = 10.2 Hz), 130.13, 131.48, 131.70, 131.78, 132.26, 132.43, 132.62, 132.85, 133.55, 133.79, 135.59, 135.87, 135.91; $^{31}P\{^{1}H\}$ NMR ($CDCl_3/H_3PO_4$, 81 MHz) 23.34 (AB q, J_{AB} = 38.7 Hz, $\Delta\nu$ = 110 Hz).

$^{1}H\{^{1}H\}$ Nuclear Overhauser Effect Experiment. A sample of the π-allylpalladium(II) complex was prepared as above, and the solution was degassed by the freeze–thaw method and sealed. The $^{1}H\{^{1}H\}$ NOE experiment was performed at 400 MHz. The decoupler was set to the resonance of internal π-allyl proton (δ 6.16) and turned on for 10 s. This pre-irradiation period was followed by a short (0.05 s) switching time to prevent the occurrence of unwanted decoupling, immediately followed by a 45° acquisition pulse and a 4-s acquisition. Reference spectra were obtained in a similar manner with the decoupler frequency set to irradiate an empty region of the spectrum. Eight transients were acquired with the decoupler on resonance followed by eight reference transients. A total of 512 transients were collected. Percent NOE enhancements were determined by integration of the difference spectra as totals of the enhancements for all equivalent protons.

General Procedure for the Palladium-Catalyzed Asymmetric Allylation. In a small glass vessel, 0.011 mmol of a chiral ligand and 0.005 mmol of $Pd_2(dba)_3{\cdot}CHCl_3$ were dissolved in a solvent (1 mL for Table II, entries 8 and 11, and Table III; 2 mL for Table I and Table II, entries 1–7, 9, 10, and 12–16) and stirred for 1 h at room temperature. The solution was added to 2.0 mmol of potassium fluoride (spray-dried) placed in 20-mL Schlenk tube under an argon atmosphere. The suspension was stirred for 30 min before the addition of 1.0 mmol of β-diketone **2**, followed by stirring for 15 min. The mixture was cooled to a given reaction temperature before the addition of 1.5 mmol of allyl acetate and was kept stirring at the temperature for a given reaction time. The reaction was quenched by 6 N hydrochloric acid and extracted with ether. The ether extracts were washed with sodium bicarbonate solution and brine, dried over magnesium sulfate, and evaporated. The residue was analyzed by GLC to determine the conversion. Product **3** was isolated by MPLC (silica gel, hexane/ethyl acetate) and bulb-to-bulb distillation.

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Solution- and Solid-State Structural Studies of (Halomethyl)zinc Reagents

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Abstract: (Halomethyl)zinc cyclopropanation reagents have been investigated by solution NMR and X-ray crystallographic methods. Treatment of glycol–ether complexes of diethylzinc with chloroiodomethane or diiodomethane quantitatively produced glycol–ether complexes of bis(chloromethyl)zinc and bis(iodomethyl)zinc, respectively. Similarly, treatment of acetone solutions of diethylzinc with either dihalomethane produced the corresponding bis(halomethyl)zinc species. The bis(chloromethyl)zinc complexes displayed characteristic NMR resonances at 2.4–2.7 ppm (^{1}H) and 29.5–29.8 ppm (^{13}C) for the methylene unit, while the bis(iodomethyl)zinc complexes displayed characteristic resonances at 1.35–1.40 ppm (^{1}H) and −16.4 to −19.6 ppm (^{13}C). The first X-ray crystallographic analysis of an (iodomethyl)zinc compound, bis(iodomethyl)zinc complex **9**, is also reported. Some key features of the structure include Zn–C bond lengths of 1.92–2.02 Å, C–I bond lengths of 2.13–2.21 Å, and Zn–C–I bond angles of 106.9–116.4°. In addition, bis(iodomethyl)zinc complexes were demonstrated to lose one methylene upon concentrating in vacuo, and the iodomethylzinc iodide complexes were established to exist predominantly as the bis(iodomethyl)zinc/zinc iodide pair in acetone solution.

Introduction

The Simmons–Smith[1] cyclopropanation of olefins is arguably the most important application of organozinc reagents in organic synthesis.[2] Several factors make this reaction synthetically useful, including (1) stereospecificity (strict retention of olefin geometry); (2) broad generality with regard to olefin structure; (3) modest tolerance of other functional groups, including carbonyls; and (4) the syn-directing effect of proximal oxygen functions. The strong directing effect of oxygen substituents was recognized early on[3] and has both preparative[4] and mechanistic[5] significance. This

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† Author to whom correspondence should be addressed concerning the X-ray structure determination.

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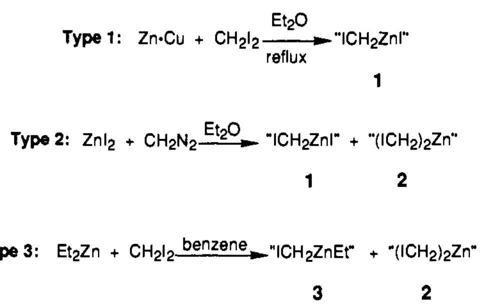
0002-7863/92/1514-2592\$03.00/0

Scheme I



feature of the Simmons–Smith reaction has recently been extended to include chiral auxiliary-directed cyclopropanations of chiral acetals,[6] ketals,[7] enol ethers,[8] and vinyl boronates.[9]

There are a variety of methods for generating "Simmons–Smith" reagents, all of which generate species containing an (iodomethyl)zinc moiety.[2,10] These methods can be categorized into three general classes (Scheme I): type 1, oxidative addition of a dihalomethane to zinc metal, as typified by the original Simmons–Smith procedure;[1,11] type 2, the reaction of a zinc(II) salt with a diazoalkane, first reported by Wittig and co-workers;[12] type 3, an alkyl exchange reaction between an alkylzinc and an 1,1-dihaloalkane, often referred to as the Furukawa procedure.[13]

Type 1 reagent generation, which is believed to afford "ICH_2ZnI" (**1**), has been used most often in synthetic contexts due to the ease with which the reagent precursors can be handled. Although the initial method of preparation of the Zn–Cu couple was difficult and not easily reproducible,[1] several simpler and highly reproducible methods soon followed.[14] Treatment of Zn–Cu couple with CH_2I_2 in Et_2O followed by heating to reflux generates the active reagent. Other modifications include the use of $Zn/CuCl/CH_2I_2$,[14c] Zn–Ag couple/CH_2I_2,[15a] $Zn/TiCl_4/CH_2Br_2$,[15b] and $Zn/AcCl/CuCl/CH_2Br_2$.[15c] Type 2 reagent generation has been utilized much less frequently, presumably due to the experimental difficulties associated with handling and drying large quantities of diazoalkanes. First reported by Wittig in 1959,[12a] the method consists of the treatment of an ethereal suspension of a zinc(II) salt ($ZnCl_2$, $ZnBr_2$, ZnI_2, $Zn(OBz)_2$) with CH_2N_2[12] or an aryldiazomethane.[16] A potential advantage of this technique is that the reagent can be generated at subambient temperatures. In addition, Wittig showed that treatment of ZnI_2 with 2 equiv of CH_2N_2 generates a species with two active methylenes that was formulated as bis(iodomethyl)zinc, $(ICH_2)_2Zn$ (**2**). Type 3 (halomethyl)zinc generation was originally reported by Furukawa and co-workers in 1966.[13a] This method consists of the treatment of a solution of Et_2Zn with CH_2I_2. Advantages of the Furukawa procedure include *rapid* formation of the reagent under mild conditions (room temperature or below); strict control of the *stoichiometry* of the reactants; *compatibility* with a wider range of substrates, including enol ethers; and the use of *noncoordinating solvents*, if desired (vide infra). Treatment of Et_2Zn with substituted diiodides, such as benzylidene and ethylene iodide, also gives rise to active cyclopropanating reagents.[17] It is not at all clear that the reagents formed by each of the methods described above are identical. However, many of the reactivity differences may be explained by the presence of byproducts due to the method of preparation or the reaction conditions required to generate the reagent. The comparable reactivity of these reagents implies closely related methylene transfer reagent structures. Similarly, aluminum-based[18] and samarium-based[19] cyclopropanation reagents have also been proposed to contain analogous "(iodomethyl)metal" linkages. Interestingly, the samarium reagents react only with allylic alcohols or enolates,[19] while the aluminum reagents react only with isolated olefins.[18]

Despite the synthetic importance of this reaction, detailed mechanistic understanding and structural characterization of the cyclopropanating species are lacking.[2,20] Evidence for the persistence of the (iodomethyl)zinc moiety in solution comes mainly from product distribution analysis. Early studies by Simmons demonstrated that hydrolysis of the reagent generated from Zn–Cu couple/CH_2I_2 affords CH_3I as the major product, while treatment with I_2 regenerates CH_2I_2.[10] Identical experiments by Wittig on the reagent derived from ZnI_2/CH_2N_2 gave similar results.[12] Importantly, the rate of reaction of cyclohexene with a filtered solution of "ICH_2ZnI" (**1**) was shown to be first order in olefin, indicating that the (iodomethyl)zinc moiety acts as the methylene transfer species, rather than as a precursor to free carbene.[10] In a series of extensive studies by Simmons and co-workers,[10] it was concluded that the active reagent is $(ICH_2)_2Zn/ZnI_2$ (**4**), resulting from the Schlenk-type equilibrium depicted in eq 1. Rickborn came to the same conclusion based upon his investigations on oxygen-directed cyclopropanations.[5d] To the best of our knowl-

$$2\ \underset{\mathbf{1}}{\text{"}ICH_2ZnI\text{"}} \rightleftharpoons \underset{\mathbf{4}}{\text{"}(ICH_2)_2Zn\text{-}ZnI_2\text{"}} \qquad (1)$$

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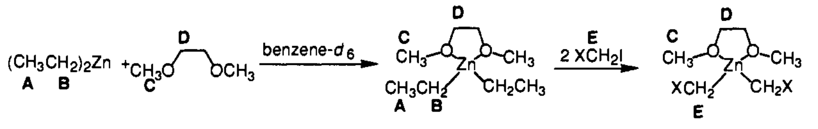
Table I. NMR Data for **5**–**7**[a]



5

6 X=I
7 X=Cl

entry	species	^{1}H NMR (δ, ppm)					^{13}C NMR (δ, ppm)				
		A	B	C	D	E	A	B	C	D	E
1	CH_2I_2					2.95					−54.00
2	$ClCH_2I$					4.11					1.19
3	$(CH_3CH_2)_2Zn$	1.12[b]	0.10[b]				10.40	6.78			
4	$(CH_3OCH_2)_2$			3.11	3.32				58.61	72.17	
5	**5**	1.31[b]	0.25[b]	3.01	3.14		11.46	4.84[c]	58.35	71.52	
6	**6**			3.02	2.97	1.40			59.83	70.61	−19.67[d]
7	**7**			3.03	3.04	2.71			59.28	70.82	29.60[e]
8	**6**/DME			3.06	3.14	1.40			59.30	71.35	−20.00

[a] All values are in ppm downfield relative to TMS = 0.00 δ. Referenced to benzene-d_6: 7.15 ppm (^{1}H), 128.00 ppm (^{13}C). [b] $^3J_{HH}$ = 8.1 Hz. [c] $^1J_{CH}$ = 124 Hz. [d] $^1J_{CH}$ = 133 Hz. [e] $^1J_{CH}$ = 132 Hz.

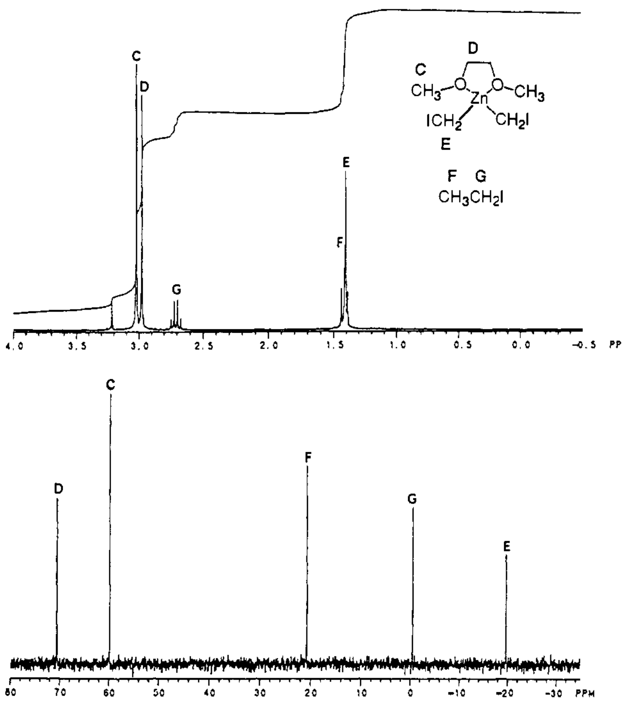


Figure 1. ^{1}H and ^{13}C NMR spectra of $(ICH_2)_2Zn$ complex **6**.

edge, the only spectroscopic study of (halomethyl)zinc compounds is a 1981 report by Fabisch and Mitchell,[21] describing NMR spectra of the reagent derived from Zn–Cu couple and CH_2 in THF-d_8. The data reported are consistent with an initial formation of $BrCH_2ZnBr$ followed by its equilibration to $(BrCH_2)_2Zn/ZnBr_2$ (i.e., the bromo analogue of eq 1).

Regardless of the actual structure of the reagent, the Simmons–Smith reaction has proven to be an extremely versatile and general reaction. In addition to a variety of isolated olefins, enol ethers[22a] and enamines[22b–d] also have been found to be excellent substrates under the proper conditions, as have steroidal enones.[23a] Simmons–Smith reagents thus have been demonstrated to cyclopropanate olefins ranging from electron rich to electron deficient, though the reaction is most successful with the former. Certain vinylmetal species (Al, Si, Ge, Sn, B) can also be cyclopropanated with some success with the Simmons–Smith reagent.[24] Knochel has recently demonstrated the utility of ICH_2ZnI for C_1 homolgation in combination with organocopper reagents.[25]

Continued current interest in cyclopropanes[26] combined with the burgeoning field of catalytic asymmetric synthesis using organozinc reagents[27] prompted us to study the structure of (halomethyl)zinc compounds. We report herein our spectroscopic studies of (chloromethyl)zinc and (iodomethyl)zinc cyclopropanation reagents in full, including the first X-ray crystallographic structure analysis of an (iodomethyl)zinc compound.[28]

Results

NMR Studies of Bis(halomethyl)zinc Reagents. The one previous NMR study of (halomethyl)zinc reagents[21] reported the NMR spectra of the reagent generated from Zn–Cu couple and CH_2Br_2 in THF-d_8. Although the spectra apparently showed signals corresponding to a number of species, the major resonance at 2.1–2.3 ppm (^{1}H) and 14.4 ppm (^{13}C) was assigned to the THF

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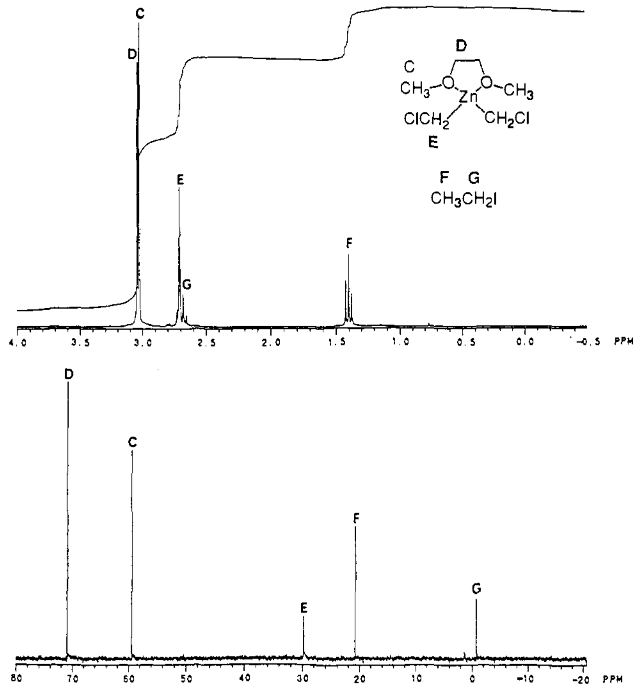


Figure 2. ^1H and ^{13}C NMR spectra of $(ClCH_2)_2Zn$ complex **7**.

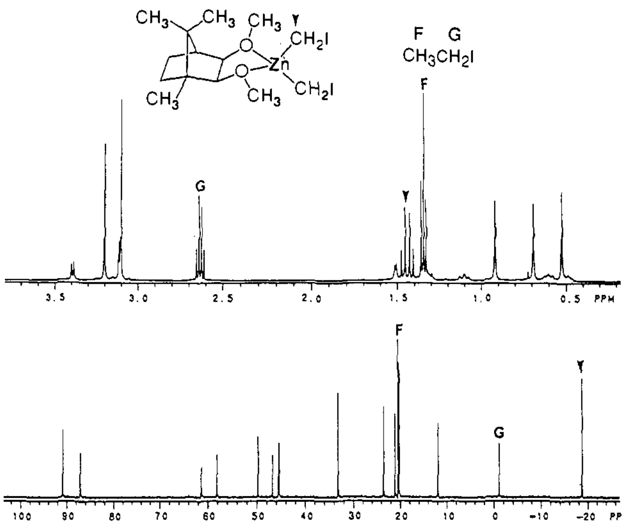
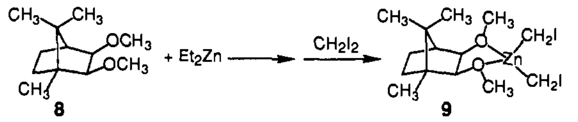


Figure 3. ^1H and ^{13}C NMR spectra of bis(iodomethyl)zinc complex **9**.

Scheme II



complex of $BrCH_2ZnBr$. Interestingly, on standing, the signal for this species disappeared and a new signal at 3.1 ppm (^1H) was observed. This latter signal was assigned as the THF complex of $(BrCH_2)_2Zn$.

Our initial goal was the generation and identification of a variety of (halomethyl)zinc species and their ligand complexes. Complications of Schlenk equilibria (eq 1) and the desire to generate ligand-free (halomethyl)zinc species suggested the Furukawa procedure[13] as an attractive method of reagent preparation. However, in our hands, treatment of 0.40–1.0 M solutions of Et_2Zn in benzene-d_6 or toluene-d_8 with 1–2 equiv of either $ClCH_2I$ or CH_2I_2 at 0 °C to room temperature resulted in rapid exothermic reactions and precipitation of solids. The spectra obtained of these suspensions showed several sets of multiplets in the 0.5–2.0 ppm range, the only identifiable species being ethyl iodide. Notably, none of the samples thus prepared showed more than traces of residual dihalomethane.

In light of the complexity of the reaction of Et_2Zn with $ClCH_2I$ and CH_2I_2 in aromatic solvents, we were gratified to discover that 1,2-dimethoxyethane (DME) complexes of $(ICH_2)_2Zn$ and $(ClCH_2)_2Zn$ could be generated quite cleanly in benzene-d_6. The relevant NMR spectroscopic data are collected in Table I.

Treatment of a 0.80–1.0 M solution of Et_2Zn in benzene-d_6 with 1 equiv of DME generated complex **5**.[29,30] Entries 1–5 of Table I list the spectroscopic data for CH_2I_2, $ClCH_2I$, Et_2Zn, DME, and the 1:1 complex of Et_2Zn/DME (**5**) in benzene-d_6 and serve as references for the subsequent entries. The complexation of DME and Et_2Zn was evident from the expected[29] downfield shifts of the Et_2Zn signals and upfield shifts of the DME signals in the ^1H NMR spectra. Bis(iodomethyl)zinc complex **6** was formed cleanly upon addition of 2 equiv of CH_2I_2 to **5** (entry 6, Table I). The key (iodomethyl)zinc methylene resonance of **6** (Figure 1) was observed at 1.40 ppm (^1H) and −19.67 ppm (^{13}C) as sharp singlets.[31] Compared to CH_2I_2 (entry 1), these resonances represent a significant upfield shift in the ^1H spectrum ($\Delta\delta$ = 1.55 ppm) and a dramatic downfield shift in the ^{13}C spectrum ($\Delta\delta$ = 34.33 ppm). Particularly notable were the strong upfield shifts of the DME methylenes in **6** relative to free DME. In the ^1H NMR spectrum this upfield shift was 0.35 ppm, while in the ^{13}C NMR spectrum this upfield shift was 1.56 ppm. The only other signals observed were those due to the ethyl iodide byproduct. No ethylzinc resonances were observed.

Bis(chloromethyl)zinc complex **7** was generated by the addition of 2 equiv of $ClCH_2I$ to **5** (entry 7, Table I). The (chloromethyl)zinc methylene resonance (Figure 2) was observed at 2.71 ppm (^1H) and 29.60 ppm (^{13}C). As was observed for **6**, the methylene resonance was shifted upfield relative to $ClCH_2I$ in the ^1H NMR spectrum ($\Delta\delta$ = 1.40 ppm) and downfield in the ^{13}C NMR spectrum ($\Delta\delta$ = 28.41 ppm). Upfield shifts of the DME methylenes were similar to those observed for **6**, though of smaller magnitude.

The persistence of the (halomethyl)zinc moieties in solution was clearly evident from the one-bond C–H coupling constants for the zinc-bound methylenes. One-bond C–H coupling constants of 133 and 132 Hz were observed for **6** and **7**, respectively. These coupling constants are typical for sp^3-hybridized carbon atoms; compare CH_3I (152 Hz) and CH_3Cl (151 Hz).[32]

The dynamic nature of the complexation of DME to $(ICH_2)_2Zn$ was demonstrated by treatment of a 2:1 mixture of DME/Et_2Zn in benzene-d_6 with 2 equiv of CH_2I_2. Reagent formation was uneventful, and the spectra obtained displayed a single set of peaks for the DME signals in both the ^1H and ^{13}C spectra (entry 8). The signals for the (iodomethyl)zinc methylene were the same as those observed for **6**, but the DME signals corresponded to the average of the values obtained for free DME and **6**.

The spectra obtained for $(ICH_2)_2Zn$ complex **9**, derived from the chiral glycol ether **8** (Scheme II), were particularly interesting. In the ^1H NMR spectrum (Figure 3), the zinc-bound methylene protons were observed at 1.49 ppm as a doublet of doublets ($^2J_{HH}$ = 10.6 Hz), indicating the diastereotopicity of the methylene protons due to the chiral environment of the ether ligand. These protons are diastereotopic, and thus distinguishable by ^1H NMR, only when the zinc reagent is bound to the chiral ligand.

In the ^{13}C NMR spectrum, on the other hand, the zinc-bound carbon nucleii resonated at −18.50 ppm as a single, sharp line,

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[29] (a) Thiele, K.-H. *Z. Anorg. Allg. Chem.* **1962**, *319*, 183. (b) Thiele, K.-H. *Z. Anorg. Allg. Chem.* **1963**, *322*, 71. (c) Noltes, J. G.; van den Hurk, J. W. G. *J. Organomet. Chem.* **1964**, *1*, 377.

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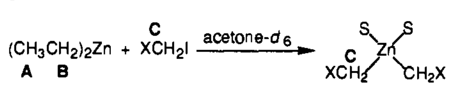
[31] Due care must be taken to prevent sample contamination by traces of water, which results in the formation of CH_3I and broadening of the ICH_2Zn resonances.

[32] Weigert, F. J.; Winokur, M.; Roberts, J. D. *J. Am. Chem. Soc.* **1968**, *90*, 1566. Compare CH_3X (151–152 Hz).

Table II. Spectral Data for **10** and **11**[a]



10 X=I
11 X=Cl

entry	species	¹H NMR (δ, ppm) A	B	C	¹³C NMR (δ, ppm) A	B	C
1	$(CH_2CH_2)_2Zn$	1.02	0.02		11.53	4.75	
2	$(CH_3CH_2)_2Zn$/DME	1.05	0.03		11.47	4.11	
3	**10**			1.34			−16.62
4	**10**/DME			1.34			−18.30
5	**11**			2.55			*b*
6	**11**/DME			2.56			*b*

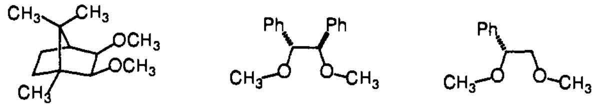
[a] All values are in ppm downfield relative to TMS = 0.00 δ. Referenced to acetone-d_6: 2.04 ppm (¹H), 29.80 ppm (¹³C) (center signal of each multiplet). [b] This signal was obscured by the acetone CD_3 multiplet, thus must be approximately 29.8 ppm, consistent with the value obtained for **7**.

despite the fact that the carbon atoms in **9** are diastereotopic as well. The assignment of the doublet of doublets at 1.49 ppm in the ¹H NMR spectrum to the (iodomethyl)zinc protons was unequivocally established by a HETCOR spectrum which displayed the expected correlation of this multiplet and the singlet at −18.50 ppm in the ¹³C NMR spectrum. The difference in time scales of the two spectra (500 MHz, ¹H; 125.8 MHz, ¹³C) cannot explain this phenomenon, because if an exchange process was being observed in the ¹³C spectrum that was too slow to be observed in the ¹H spectrum, the protons of the zinc-bound methylenes would have appeared as two doublets of doublets, since all H/H relationships are diastereotopic. In addition, the ¹H NMR spectrum of this sample obtained at 300 MHz displayed the iodomethylene AB quartet with the same pattern and same chemical shift as that observed in the spectrum acquired at the higher field. A possible explanation of this phenomenon is contained in the Discussion.

The effect of other coordinating ligands on the behavior of (halomethyl)zinc species was of interest in the context of planned chiral ligand modified reagents. Unfortunately, efforts to obtain spectra of amine-coordinated (halomethyl)zinc reagents were thwarted by the reaction of the reagent with the amine ligands.[12] However, it was discovered that both $(ClCH_2)_2Zn$ and $(ICH_2)_2Zn$ could be prepared as reasonably stable acetone solutions, and thus the spectra of these compounds in acetone-d_6 were obtained. The spectroscopic data are collected in Table II, along with data for the reagents prepared in the presence of 1 equiv of DME. For comparison, the spectroscopic data for Et_2Zn in acetone-d_6 and a 1:1 mixture of Et_2Zn and DME in acetone-d_6 are also provided (entries 1 and 2).

Although these spectra were not as clean as those obtained for **6** and **7** in benzene-d_6,[33] the bis(halomethyl)zinc reagent was by far the major component in these samples (>90%). The data obtained for $(ICH_2)_2Zn$ solvate **10** are qualitatively consistent with that obtained for **6**. The (iodomethyl)zinc protons resonated at 1.34 ppm (¹H) and −16.62 ppm (¹³C) (entry 3). The addition of 1 equiv of DME resulted in an upfield shift of the zinc-bound carbon (−18.30 ppm), while the proton spectrum was unchanged (entry 4). Note that a similar effect was observed in the spectra of Et_2Zn (entries 1 and 2). The resonance of the (chloromethyl)zinc methylene protons in **11** was observed at 2.55 ppm (¹H) (entry 5) and was unchanged upon addition of 1 equiv of DME (entry 6). Unfortunately, the methyl multiplet (at 29.8 ppm) of the acetone-d_6 solvent obscured the carbon resonance of this species.

Finally, it should be noted that the signals due to the DME in the ¹H and ¹³C NMR spectra containing this ligand (entries 2, 4, and 6) were virtually the same as those in the spectra of the free ligand in acetone-d_6, suggesting that the bis(halomethyl)zinc reagents were predominantly acetone solvates (i.e., **10** and **11**, S = acetone-d_6) rather than DME complexes (**6**, **7**).



8 **12** **13**

Figure 4. Glycol ether ligands **8**, **12**, and **13**.

Table III. NMR Data for "Dried" Reagents[a]

$$Et_2Zn + \text{ether} + 2 \text{ equiv of } C_2H_2 \xrightarrow{\text{hexane}} \xrightarrow{\text{(evaporate)}} \xrightarrow{\text{acetone-}d_6} \text{“}ICH_2ZnI\text{”}$$

entry	ligand	¹H NMR (ppm) δ(ZnC*H*₂)	¹³C NMR (ppm) δ(Zn*C*H₂)
1	Et_2O	1.34	−17.20
2	DME	1.33–1.40[b]	−17.0 to −18.1[b]
3	**8**	1.34–1.41[c]	−17.2 to −17.4[c]
4	**12**	1.46	−17.0
5	**13**	1.44	−17.6

[a] All spectra were obtained in acetone-d_6 at 300 MHz (¹H) or 75.5 MHz (¹³C). Referenced to acetone-d_6: 2.04 ppm (¹H), 29.80 ppm (¹³C) (center peak of each multiplet). [b] Range of three samples. [c] Range of two samples.

NMR Studies of "Dried" Reagents. During their investigations into the nature of "ICH_2ZnI", Simmons and co-workers[10a] reported that treatment of Zn–Cu couple with CH_2I_2 in refluxing Et_2O followed by filtration of the reagent and evaporation of the volatile components affords an unstable oily residue. Evidence was obtained which indicated this residue to be an etherate of either ICH_2ZnI or $(ICH_2)_2Zn/ZnI_2$. In the hope of obtaining a crystalline (iodomethyl)zinc derivative, we attempted to prepare solvent-free etherate complexes of $(ICH_2)_2Zn$[12] in a similar manner by use of the Furukawa method for reagent generation and discovered that solutions of $(ICH_2)_2Zn$/ether complexes lose one methylene to form "ICH_2ZnI" complexes upon evaporation of the solvent. A brief investigation designed to determine the structure of these "dried" reagents is described below.

The protocol used initially to generate a "dried" Furukawa reagent consisted of the treatment of a cooled (0 °C) solution of Et_2Zn in Et_2O with 2 equiv of CH_2I_2. After the mixture was stirred for 30–60 min, the volatile components were removed in vacuo (0.2 Torr), affording a thick colorless oil. This material was found to be soluble in acetone or DME, but only sparingly soluble in Et_2O and insoluble in hydrocarbon solvents. The NMR spectra of acetone-d_6 solutions of this material displayed the signals expected for Et_2O and a broadened resonance at 1.34 ppm (¹H) and −17.2 ppm (¹³C). Samples prepared similarly in DME afforded white foams, the NMR spectra of which displayed a single resonance for the iodomethylzinc methylene that ranged from 1.33 to 1.40 ppm (¹H) and −17.0 to −18.1 ppm (¹³C) in addition to signals attributable to DME. Integration of the ¹H spectra initially afforded Et_2O/"ICH_2Zn" in ratios of 2:1 and DME/"ICH_2Zn" in ratios of 1:1, indicative of "ICH_2ZnI" complexes. However, these ratios tended to vary from sample to sample, presumably due to the volatile nature of the complexing ethers. In addition, the similarity of these spectra to those of the in situ generated $(ICH_2)_2Zn$ reagents (vide supra) suggested that $(ICH_2)_2Zn$ complexes were in solution. Therefore, independent confirmation of the empirical formulas of these species was sought.

The use of nonvolatile glycol ethers as complexing agents for the zinc species provided the first such confirmation. Thus, treatment of hexane or benzene solutions of each of the ligands **8**, **12**, or **13** (Figure 4) with 1 equiv of Et_2Zn followed by 2 equiv of CH_2I_2 generated homogeneous solutions of the $(ICH_2)_2Zn$ complexes.

Removal of the volatile components in vacuo afforded white powders which were soluble only in acetone or DME. The NMR

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(33) The minor peaks observed in these spectra were apparently due to some reaction with the acetone-d_6 solvent. Similar peaks (multiplets in the 1.0–1.5 ppm range) were observed in spectra of Et_2Zn in acetone-d_6 and thus may not be related to bis(halomethyl)zinc formation or reactivity.

spectroscopic data of acetone-d_6 solutions of these materials are collected in Table III. As can be seen by inspection of the table, each of these materials had very similar spectroscopic features, the key methylene resonance being observed at 1.34–1.44 ppm (^{1}H) and −17.0 to −18.1 ppm (^{13}C). Importantly, integration of the ^{1}H NMR spectra of each of the complexes derived from **8**, **12**, and **13** clearly indicated a 1:1 ratio of ligand/iodomethylzinc. As was observed for the in situ generated reagents in acetone-d_6, the signals for the ligands in these samples were nearly identical to those in the spectra of the free ligands in acetone-d_6, indicating that these species are more properly represented in acetone solvates (i.e., **10**, S = acetone-d_6).

Further confirmation for the conversion of the $(ICH_2)_2Zn$ complexes to "ICH_2ZnI" was obtained by two independent methods: iodimetric titration and elemental analysis. Formation of $(ICH_2)_2Zn$ in Et_2O followed by removal of the volatile components in vacuo afforded the "ICH_2ZnI etherate" complex, the spectra of which had been obtained earlier. Iodimetric titration of acetone or DME solutions of this material indicated that 55–60% of the zinc–carbon bonds remained. Thus, approximately half of the "ICH_2Zn" moieties had been consumed during the evaporation of the volatile components, consistent with the conversion of "$(ICH_2)_2Zn$" to "ICH_2ZnI". In addition, formation of a hexane solution of $(ICH_2)_2Zn$ complex **9** at 0 °C followed by removal of all volatiles in vacuo afforded a white solid. Elemental analysis of this material provided an empirical formula of $C_{13}H_{24}I_2O_2Zn$, which corresponded to **8**·ICH_2ZnI.

It is important to note that this conversion of "$(ICH_2)_2Zn$" to "ICH_2ZnI" was not simply due to the slow decomposition of $(ICH_2)_2Zn$ over time. This was demonstrated by the fact that solutions of $(ICH_2)_2Zn$ in DME or Et_2O could be maintained at room temperature for over 1 h (the time typically required for preparation of the samples described above) with very little decomposition. Iodimetric titration of solutions thus prepared indicated that greater than 90% of the "ICH_2Zn" was intact after 1 h at room temperature.

Extension of this study to the (chloromethyl)zinc analogue failed when it was discovered that the evaporation to dryness of solutions of **12**/$(ClCH_2)_2Zn$ or **13**/$(ClCH_2)_2Zn$ afforded **12**/$ZnCl_2$ and **13**/$ZnCl_2$, respectively. The spectra of these compounds contained signals only for the ligands; no "$ClCH_2Zn$" resonances were observed. This observation suggests that (chloromethyl)zinc species are inherently more reactive than (iodomethyl)zinc species. In support of this view, we have found that the $ClCH_2I/Et_2Zn$ reagent system cyclopropanates olefins more rapidly than the CH_2I_2/Et_2Zn system.[34]

X-ray Crystallographic Analysis of 9. Organozinc compounds have been the subject of a number of X-ray crystallographic studies.[35-39] By far, monoalkylzinc species have been studied the most intensely, due to their high degree of crystallinity. These analyses have provided valuable insight into the chemistry of species ranging from alkylzinc alkoxides[35f] and Reformatskii reagents[38] to chiral zinc Lewis acids.[27a,b] X-ray crystal structure analyses of diorganozinc compounds are much less common,[36,37] and X-ray crystal structures of diorganozinc reagents complexed to ethers are rare.[36a,37b] To the best of our knowledge, the only

Table IV. Crystal and Experimental Data for **9**

crystal system	triclinic
space group	$P1$ (C_1^1)
a, Å	7.367 (3)
b, Å	11.108 (4)
c, Å	11.728 (5)
α, deg	105.42 (4)
β, deg	91.67 (3)
γ, deg	94.57 (3)
V, Å^3	921.0 (9)
Z	2
ρ(calcd), g/cm^3	1.968
temp, °C	−75
color, habit	colorless, columnar
dimensions, {inversion form}, mm	{0,1,−1}, 0.06; {0,1,1}, 0.10; {0,0,1}, 0.28
diffractometer	Enraf-Nonius CAD4
μ, cm^{-1}	46.81
transmission factor range	0.581–0.400 (numerical)
2θ limit, deg (octants)	50.0 ($-h,\pm k,\pm l$)
no. intens measd (unique)	3579 (3504)
no. intens > $2.58\sigma(I)$	3248
R	0.044
R_w (for $w = 3.42/\sigma^2(F_o) = pF_o^2$)	0.069 (p = 0.03)
density range in ΔF map, e/Å^3	+3.58 to −1.44

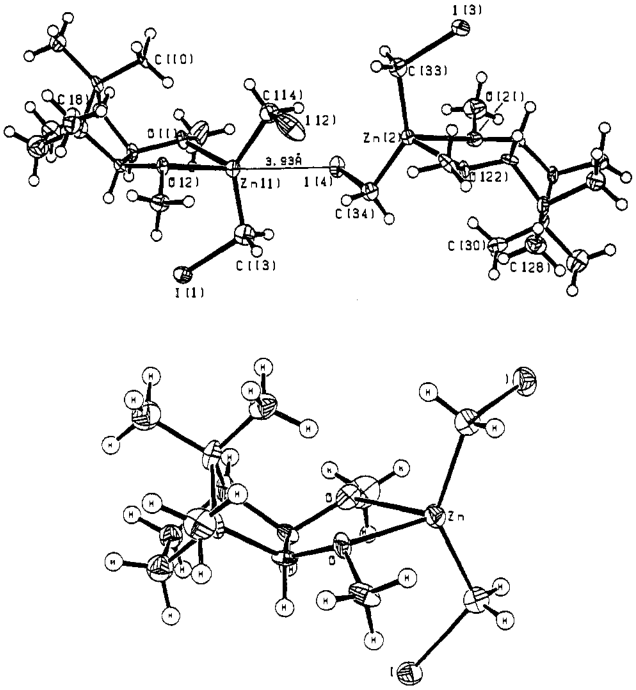

Figure 5. ORTEP representations of unit cell contents of **9**.

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Table V. Selected Bond Lengths, Bond Angles, and Nonbonded Distances for **9**

	Bond Lengths, Å		
Zn(1)–O(1)	2.103 (10)	Zn(2)–C(33)	2.01 (2)
Zn(1)–O(2)	2.20 (1)	Zn(2)–C(34)	2.02 (2)
Zn(2)–O(21)	2.20 (1)	I(1)–C(13)	2.21 (2)
Zn(2)–O(22)	2.231 (10)	I(2)–C(14)	2.16 (2)
Zn(1)–C(13)	1.92 (2)	I(3)–C(33)	2.15 (2)
Zn(1)–C(14)	1.98 (2)	I(4)–C(34)	2.13 (2)
	Bond Angles, deg		
O(1)–Zn(1)–C(13)	109.5 (6)	O(21)–Zn(2)–C(33)	106.5 (6)
O(2)–Zn(1)–C(14)	104.3 (5)	O(22)–Zn(2)–C(34)	106.3 (5)
O(1)–Zn(1)–O(2)	72.7 (4)	O(21)–Zn(2)–O(22)	71.7 (4)
O(1)–Zn(1)–C(14)	104.6 (6)	O(21)–Zn(2)–C(33)	107.4 (5)
O(2)–Zn(1)–C(13)	107.9 (6)	O(1)–Zn(2)–C(34)	108.2 (5)
C(13)–Zn(1)–C(14)	138.4 (7)	C(33)–Zn(2)–C(34)	137.5 (6)
I(1)–C(13)–Zn(1)	116.4 (9)	I(3)–C(33)–Zn(2)	115.8 (7)
I(2)–C(14)–Zn(1)	107.9 (8)	I(4)–C(34)–Zn(2)	106.9 (7)
	Nonbonded Distances, Å		
Zn(1)–I(4)	3.929 (2)	Zn(1)–I(2)	3.350 (3)
Zn(2)–I(2)	4.342 (3)	Zn(2)–I(3)	3.525 (2)
Zn(1)–I(1)	3.513 (2)	Zn(2)–I(4)	3.329 (2)

previous X-ray crystal structure analysis of an (α-haloalkyl)zinc compound is that of ($CF_3CCl_2ZnCl \cdot 2DMF$), reported recently by Lang and co-workers.[39] This interesting compound has been used to alkylate aldehydes and carbon monoxide[40] but, not surprisingly, does not seem to react readily with olefins.[40b] The dearth of structural information on (iodomethyl)zinc reagents prompted us to seek a crystalline derivative of $(ICH_2)_2Zn$.

Attempts to prepare amine complexes of (halomethyl)zinc species were thwarted by the reaction of the amine (TMEDA, Et_3N, pyridine, 2,2′-bipyridine) with the (halomethyl)zinc moiety,[12] as mentioned earlier in the context of our NMR spectroscopic studies. However, hexane solutions of a variety of glycol ether complexes of $(ICH_2)_2Zn$ were found to precipitate crystals upon cooling to −20 °C or below. An extensive screening of such complexes showed that $(ICH_2)_2Zn$ complex **9** gave crystalline samples most frequently upon cooling to −20 °C. Treatment of a cooled (0 °C) 0.2 M hexane solution of **8** with 1 equiv of Et_2Zn followed by 2 equiv of CH_2I_2 afforded a homogeneous solution of $(ICH_2)_2Zn$ complex **9**. Further cooling to −20 °C induced crystallization, and recrystallization was accomplished by warming the reaction mixture to 0 °C and then slowly recooling to −20 °C. Attempts to isolate the crystals free from solvent resulted in decomposition to an amorphous white solid. This material, when evaporated to dryness, afforded $(ICH_2)_2Zn/ZnI_2$ (vide supra). However, a suitable single crystal could be removed directly from the reaction flask as a suspension in Paratone-N (Exxon) oil. These crystals are stable at −20 °C in the presence of solvent for 2–3 days.

Complex **9** crystallizes as a monomer with two independent molecules in the unit cell (Table IV). The two molecules of the unit cell are related by a pseudo-inversion center, ignoring the bridgehead methyl groups (C(8) and C(28)). ORTEP representation of the unit cell contents are depicted in Figure 5, and key bond lengths and bond angles are collected in Table V.

The two molecules have very similar structural characteristics. Molecule A (Zn(1)) has zinc–carbon bond lengths of 1.92 (2) and 1.98 (2) Å, while these same bonds in molecule B (Zn(2)) are 2.01 (2) and 2.02 (2) Å. These values compare favorably with the range of bond lengths of previously reported monomethyl- and monoethylzinc crystal structures (1.89–1.99 Å)[35] and the dialkylzinc crystal structures (Zn–C = 1.96–2.01 Å).[37]

The zinc–oxygen bond lengths of 2.103 (10), 2.20 (1), 2.20 (1), and 2.231 (10) Å are long compared to those found in $(C_6F_5)_2Zn(THF)_2$ (2.093 (2), 2.113 (3) Å)[36b] and (η^1-fluorenyl)$_2$Zn(THF)$_2$ (2.095 (4), 2.114 (5) Å).[41] Other than the unusual Et_2Zn–18-crown-6 structure,[37a] there are no tetracoordinate di*alkyl*zinc ether complexes with which to directly compare the zinc–oxygen bond lengths obtained for **9**.[42] Finally, the carbon–iodine bond lengths of 2.13 (2)–2.21 (2) Å are typical for sp^3-carbon (2.14–2.21 Å).[43]

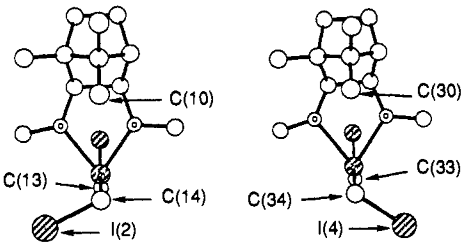

Figure 6. ChemDraw representations of molecules A (left) and B (right).

The geometry around zinc is clearly a distorted tetrahedron, with extremely small O–Zn–O bond angles of 71.7 (4)° and 72.7 (4)°. This can be compared to the extremely narrow bite angle (75.0°) in the recently reported X-ray structure of $Me_2Zn(t\text{-}BuDAB)_2$.[37d] The C–Zn–C bond angles of 137.5 (6)° and 138.4 (7)° are in line with the corresponding angle in the $Me_2Zn(t\text{-}BuDAB)_2$ complex[37d] (137.3 (3)°) and are slightly larger than the C–Zn–C bond angle in $(C_6F_5)_2Zn(THF)_2$[36b] (132.1 (2)°). The O–Zn–C bond angles of 104.6 (6)–108.2 (5)° approximate the 109.5° characteristic of a tetrahedron.

The oxygen atoms exhibit a distorted tetrahedral geometry (Σ angles = 341.2–346.4°), consistent with other DME/transition-metal complexes.[44] The zinc-bound oxygen atoms of THF complexes of alkylzinc species typically are very nearly planar (Σ angles >358°), but this may be a consequence of the higher basicity of the THF oxygen atom. Unfortunately, the lack of structural data concerning acyclic bis(dialkyl ether)zinc complexes prevents a direct comparison of the features of **9**. However, constraining the chelate ring size to five is obviously not the reason that the oxygen atoms do not adopt a planar geometry, as evidenced by the C–O–Zn bond angles in the five-membered rings (116.6 (8)°, 118.1 (8)°, 119.6 (8)°, 121.4 (8)°), which could easily accommodate the 120° angle preferred by a planar oxygen atom.

The orientations of the iodomethyl groups are strongly influenced by the glycol ether ligand structure; this is clearly evident when the molecules are viewed normal to the chelate ring (Figure 6). Each endo iodomethyl group (C(13), C(33)) bisects an O–Zn–O angle, thus placing the iodine atoms (I(1), I(3)) directly underneath the five-membered chelate rings. In contrast, the exo iodomethyl groups (C(14), C(34)) cannot adopt this conformation due to steric interactions with the C(10) and C(30) methyl groups. Thus, each exo C–I bond is anticlinal to one of the Zn–O bonds. Since the two molecules are related to one another by a pseudo-inversion center, the exo iodomethyl group in molecule A swings toward the bridgehead methyl, while the exo iodomethyl group molecule B swings away from the bridgehead methyl of the enantiomerically pure ligand.

The differing orientations of the iodomethyl groups have a dramatic effect on the individual iodine atoms' proximity to the zinc atoms. In molecule A, the endo iodine atom (I(1)) is 3.513 (2) Å away from Zn(1); similarly, in molecule B the endo iodine atom (I(3)) is 3.525 (2) Å away from Zn(2). The exo iodine atoms are much closer to the Zn atoms, however. Iodine I(2) is only 3.350 (3) Å away from Zn(1), while iodine I(4) is 3.329 (2) Å away from Zn(2). These latter values fall within the sum of the van der Waals radii for zinc (1.40 Å) and iodine (1.95–2.12

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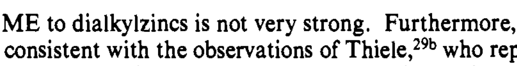
Å).[45] Accordingly, the Zn–C–I bond angles for the exo iodomethyl groups (106.9 (7)°, 107.9 (8)°) are noticeably smaller than those for the endo iodomethyl groups (115.8 (7)°, 116.4 (9)°). The Zn–C–I bond angles for **9** compare favorably with those found in previously reported (iodomethyl)metal crystal structures: $(ICH_2)Fe(I)(PO\text{-}i\text{-}Pr)_3(CO)$,[46] Fe–C–I = 120 (1)°; $(ICH_2)Pt(I)(PPh_3)_2$,[47] Pt–C–I = 110.5 (9)°; $N(CH_2CH_2O)_3GeCH_2I$,[48] Ge–C–I = 115.9 (9)°; $\{Ir(\mu\text{-}C_5H_4NS)(CO)\}_2(CH_2I)(I)$,[49] Ir–C–I = 115.0 (7)°. None of these compounds are reported to be cyclopropanating agents. These close contacts between the exo iodine atoms and the zinc atoms are consistent with the mechanism by which Simmons has proposed the methylene is transferred to olefins: i.e., an internal activation of the methylene by formation of a bond between the iodine and zinc atoms.[10,50]

Cyclopropanations with 6 and 9. As might be expected from the electrophilic nature of (halomethyl)zinc reagents,[2] the glycol ether complexes of $(ICH_2)_2Zn$ **6** and **9** reacted with olefins at a much slower rate than when the reagent was generated in noncoordinating solvents. In addition, hexane solutions of chiral glycol ether (**8**, **12**, **13**) complexes of $(ICH_2)_2Zn$ reacted with cinnamyl alcohol to provide a racemic cyclopropyl derivative. Thus, the equilibrium concentration of uncomplexed $(ICH_2)_2Zn$ was apparently reacting much faster than the complexed $(ICH_2)_2Zn$ resulting in no enantiofacial discrimination.

Discussion

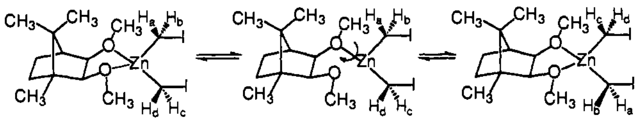
Solution Structure of Bis(halomethyl)zinc Species. The NMR spectroscopic studies described above clearly demonstrate that bis(halomethyl)zinc species are formed by the addition of either CH_2I_2 or $ClCH_2I$ to Et_2Zn and that these species are stabilized by coordinating ligands. An intriguing aspect of the DME-complexed species **6** and **7** in benzene-d_6 is the dynamic nature of the complexation. The fact that the DME signals in the NMR spectra of a 2:1 mixture of DME/$(ICH_2)_2Zn$ displayed resonances corresponding to the average of **6** and free DME indicated that although ligand exchange was rapid, the binding constant was high. This result is to be compared with the finding of Allen et al.,[30b] who, on the basis of NMR spectra of mixtures of DME and $(CH_3)_2Zn$ in cyclohexane, determined that the equilibrium constant of eq 2 is only 1.0 ± 0.3, suggesting that coordination of DME to dialkylzincs is not very strong. Furthermore, our result is consistent with the observations of Thiele,[29b] who reported that dialkylzinc species are not easily separated from ethereal solvents. The observed stability of **6** and **7** further suggested that coordination of DME to bis(halomethyl)zinc reagents is in fact quite strong. This stronger binding to DME may be a result of increased Lewis acidity of the zinc center due to the halogenated alkyl groups.



(2)

The NMR spectra of **9** deserve some comment. The diastereotopic zinc-bound methylene carbon atoms were indistinguishable under the conditions of our spectroscopic analysis, and this is manifested by the appearance of a single ICH_2Zn signal in the ^{13}C NMR spectrum and a single AB quartet in the ^1H NMR spectrum. There are two explanations for the observation of a single signal for the two diastereotopic carbon atoms in **9**. The first is trivial in that both nucleii are accidentally isochronous. This explanation is difficult to accept since the two groups are in such different steric environments (see the X-ray crystallographic analysis above). A second explanation invokes an interchange of the two iodomethyl groups while the $(ICH_2)_2Zn$ unit is still bound to the ligand. This can be accomplished by decomplexation of one oxygen followed by rotation about the remaining Zn–O bond (Scheme III). As shown, such a process results in the interchange of the carbon atoms and the two pairs of protons a/c and b/d. This process cannot result in the interchange of a/b or c/d, and hence the observation of a doublet of doublets for these protons. A similar process would also explain the observed exchange of DME ligands for **6** in the presence of excess DME. Coordination of an unbound DME molecule to **6** (to form a 2:1 complex of DME and $(ICH_2)_2Zn$) followed by dissociation of the initially complexed DME molecule results in the exchange of the ligands. Precedence for exchange via an intermediate of this type is found in the work of Thiele,[29b] who reported that the 2:1 complex of $(CH_3)_2Zn$ and DME is an isolable, distillable material.

Scheme III



"Dried" Reagents. Although the empirical formulas of the "dried" (iodomethyl)zinc species were firmly established, neither titration nor microanalysis could distinguish which species ("$(ICH_2)_2Zn/ZnI_2$" or "ICH_2ZnI") predominated in the Schlenk equilibrium (eq 1). On the basis of the similarity of the spectra of the "dried" reagents to the in situ generated $(ICH_2)_2Zn$ complexes described earlier, we believe that the species observed in acetone solution were $(ICH_2)_2Zn/ZnI_2$ solvates; i.e., the Schlenk equilibrium of eq 1 lies far to the right. This is in contrast to the results of extensive studies on EtZnI,[51] for which it has been determined that the Schlenk equilibrium strongly favors EtZnI rather than Et_2Zn/ZnI_2. It has been noted, however, that the similarity of the NMR spectra of Et_2Zn and EtZnI in ethereal solvents makes identification based on chemical shifts difficult.[30c,51d,e]

On the other hand, the NMR study by Fabisch and Mitchell on $BrCH_2ZnBr/(BrCH_2)_2Zn$[21] suggests that the (halomethyl)zinc species does not behave like the ethylzinc species. As was mentioned earlier, these workers observed that the ^1H NMR signal at 2.1–2.3 ppm assigned to a complex of THF and $BrCH_2ZnBr$ was slowly replaced (upon warming, over time) by a new signal at 3.1 ppm, which they assigned to $(BrCH_2)_2Zn$. This assignment was made by analogy to the spectra of $BrCH_2HgBr$ and $(BrCH_2)_2Hg$. The ^1H NMR spectrum of $BrCH_2HgBr$ is reported[52a] to exhibit a single resonance at 2.17 ppm, while $BrCH_2HgCl$ resonates at 2.07 ppm,[52a] indicating a small dependence on the halide attached to the Hg atom. The methylene protons of $(BrCH_2)_2Hg$, on the other hand, resonate at 3.18 ppm,[52b] a significant downfield shift and nearly identical to the shift observed by Fabisch and Mitchell[21] for the $BrCH_2Zn$ reagent. Further confirmation of the significant chemical shift difference between (halomethyl)mercury halides and (halomethyl)mercury alkyls comes from the comparison of the ^1H NMR resonances of $ClCH_2HgCl$ and $ClCH_2HgBr$ (2.54 and 2.59 ppm, respectively)[52a] to those of a series of (chloromethyl)mercury alkyl compounds (3.20–3.30 ppm[52c]).

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Table VI. Selected Dihedral Angles (deg) for **9**

O(2)–Zn(1)–C(13)–I(1)	40 (1)
O(22)–Zn(2)–C(33)–I(3)	37.8 (9)
O(1)–Zn(1)–C(14)–I(2)	146.2 (9)
O(2)–Zn(1)–C(14)–I(2)	70.7 (7)
I(1)–C(13)–Zn(1)–C(14)	179.5 (8)
O(1)–Zn(1)–C(13)–I(1)	−37 (1)
O(21)–Zn(2)–C(33)–I(3)	−37.8 (9)
O(22)–Zn(2)–C(34)–I(4)	−159.8 (9)
O(21)–Zn(2)–C(34)–I(4)	−84.3 (7)
I(3)–C(33)–Zn(2)–C(34)	−179.5 (7)

Additional support for the contention that the results of the EtZnI studies cannot be extended to other alkylzinc halide systems comes from the work of Evans and Phillips.[53] On the basis of ^{19}F NMR studies of $(C_6F_5)_2Zn$ and C_6F_5ZnI, it was determined that a substantial amount of $(C_6F_5)_2Zn/ZnI_2$ exists in solutions of C_6F_5ZnI and that the equilibrium constant is solvent dependent.

By analogy to the (halomethyl)mercury compounds and the $BrCH_2ZnBr/(BrCH_2)_2Zn$ system, the resonance of the methylene protons in ICH_2ZnI would be expected to be in the 0.3–0.5 ppm range; our observation of resonances in the 1.3–1.4 ppm range for the spectra described in Table III strongly suggest that the species being observed was $(ICH_2)_2Zn$.

The study described in this section demonstrated that Simmons–Smith-type reagents with the empirical formula "ICH_2ZnI" exist predominantly as $(ICH_2)_2Zn/ZnI_2$ pairs in acetone solution, thus supporting the supposition of Simmons et al.[10a] that $(ICH_2)_2Zn/ZnI_2$ is the active reagent in the Simmons–Smith reaction. The obtention of such species from $(ICH_2)_2Zn$ complexes strongly supports the hypothesis that methylene transfer reactions of bis(halomethyl)zinc reagents are more rapid than those of mono(halomethyl)zinc reagents.[34] Furthermore, the inability to obtain "dried" $ClCH_2Zn$ reagents substantiates the observation[34,54] that $ClCH_2Zn$ reagents are inherently more reactive than ICH_2Zn reagents, although a rationale for this effect is still lacking.

X-ray Crystal Structure of 9. The most important structural features of **9** are of course the (iodomethyl)zinc moieties. As mentioned previously, the endo and exo iodomethyl groups adopt radically different conformations in the solid state. The endo iodomethyl groups are perhaps easiest to explain, as their conformations are nicely accommodated by the gauche effect.[55] For molecule A, the O(2)–Zn(1)–C(13)–I(1) and O(1)–Zn(1)–C(13)–I(1) dihedral angles are 40 (1)° and −37 (1)°, respectively (Table VI). Likewise, for molecule B the O(22)–Zn(2)–C(33)–I(3) and O(21)–Zn(2)–C(33)–I(3) dihedral angles are 37.8 (9)° and −37.8 (9)°, respectively. The fact that each endo C–I bond is gauche to two Zn–O bonds undoubtedly adds to the favorable energetics of this conformation.

The rationale for the orientations of the exo iodomethyl groups is apparently more subtle. These groups are prevented from bisecting the O–Zn–O angles by steric interactions between I(2) and C(10) (molecule A) and between I(4) and C(30) (molecule B); thus, each exo iodomethyl group must adopt another conformation. This conformation can be seen to be an anticlinal relationship between each exo C–I bond and one of the Zn–O bonds. The O(1)–Zn(1)–C(14)–I(2) dihedral angle of 146.2 (9)° (molecule A) is almost perfectly anticlinal, but the O(22)–Zn(2)–C(34)–I(4) dihedral angle of −159.8 (9)° is well on its way toward antiperiplanarity. The larger dihedral angle for O(22)–Zn(2)–C(34)–I(4) compared to that for O(1)–Zn(1)–C(14)–I(2) may be related to the close contact of 3.929 (2) Å between I(4) and Zn(1). Although too long to be a bonding interaction, this close contact may represent an attractive interaction that is best accommodated by the larger O(22)–Zn(2)–C(34)–I(4) dihedral angle. Bonding between alkyl halides and transition metals has been observed previously.[56]

Although supporting evidence is lacking, it is interesting to speculate that the smaller Zn–C–I bond angles and shorter Zn–I distances of the exo iodomethyl groups imply that these iodomethyl groups are more reactive than the endo iodomethyl groups. In turn, this would imply that the coordination of the ether oxygens decelerates methylene transfer reactions in two ways: (1) Zn is coordinatively saturated while two ether molecules are bound to $(ICH_2)_2Zn$, thus slowing the "bending back" of the iodomethyl groups postulated to be part of the methylene transfer process. (2) The iodomethyl groups are also stabilized by virtue of the gauche effect, thus making them less inherently reactive. The stabilization of the ICH_2Zn moieties is also manifested in the slower rate of cyclopropanation by glycol ether complexes of $(ICH_2)_2Zn$ described above, and this in turn results in nonselective cyclopropanation via uncomplexed $(ICH_2)_2Zn$.

Summary

This study served to further elucidate the chemistry of (halomethyl)zinc reagents. In particular, it was demonstrated that highly reactive bis(halomethyl)zinc reagents are stabilized by chelation to ethers or to acetone, presumably due to saturation of the empty orbitals on zinc which are otherwise necessary for activation of the carbon–iodine bond. The dramatic rate enhancement of cyclopropanation for olefins with proximal oxygen substituents is an example of a complex-induced proximity effect,[57] rather than an inherent activation of the reagent. Finally, the first X-ray crystallographic analysis of an (iodomethyl)zinc complex revealed the structural parameters for such species and provided insight into the stabilization provided by ether complexation.

Experimental Section

General Experimental Procedures. ^{1}H and ^{13}C NMR spectra were recorded at 300 MHz ^{1}H (75.5 MHz ^{13}C) or 500 MHz ^{1}H (125.8 MHz ^{13}C) in the indicated solvents. Data are reported in the following order: chemical shifts are given in δ; multiplicities are indicated as br (broadened), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), or exch (exchangeable); coupling constants, J, are reported in hertz. Infrared spectra were recorded on an IBM FTIR-32 spectrometer. Peaks are reported (cm^{-1}) with the following relative intensities: s (strong, 67–100%), m (medium, 40–67%), w (weak, 20–40%), and br (broad). Mass spectra were obtained by the University of Illinois Mass Spectroscopy Center on a Varian MAT CH-5 spectrometer with ionization voltages of 70 and 10 eV. Data are reported in the form m/z (intensity relative to base = 100). Optical rotations were obtained on a Jasco DIP-360 digital polarimeter and are reported as follows: $[\alpha]^{\text{temperature}}_{\text{wavelength}}$ (concentration in g/100 mL, solvent). Elemental analyses were performed by the University of Illinois Microanalytical Service Laboratory.

Analytical thin-layer chromatography was performed on Merck silica gel plates with F-254 indicator. Visualization was accomplished by UV light, iodine, or *p*-anisaldehyde solution. Solvents for extraction and chromatography were technical grade and distilled from the indicated drying agents: dichloromethane (CH_2Cl_2), pentane, hexane, from $CaCl_2$; diethyl ether (Et_2O), *tert*-butyl methyl ether (TBME), from $CaSO_4$/$FeSO_4$; ethyl acetate (EtOAc), from K_2CO_3. Column chromatography was performed by the method of Still[58] with 32-63-μm silica gel (Woelm). Analytical gas chromatography (GC) was performed using a Hewlett-Packard HP-5 capillary column. The injector temperature was 225 °C, the detector temperature was 300 °C, and the column head pressure was 17.5 psi. Temperature programs are reported in the following form: initial temperature [time (min))], temperature ramp rate (deg/min), final temperature [time (min)]. Retention times (t_R) and integrated ratios were obtained from a Hewlett-Packard 3393A recorder. Bulb-to-bulb ("Kugelrohr") distillations were done on a Buchi GKR-50 Kugelrohr, and boiling points (bp) correspond to uncorrected air bath temperatures.

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All reactions were performed under a dry argon atmosphere in oven- and/or flame-dried glassware. "Brine" refers to a saturated aqueous solution of NaCl. The following compounds were prepared by literature methods: (*R*)-(1*l*,2*l*,3*u*,4*u*)-2,3-dihydroxy-4,7,7-trimethylbicyclo[2.2.1]heptane,[59] (*R*)-(1*l*,2*l*)-1,2-dihydroxy-1,2-diphenylethane,[60] (*R*)-(1*l*,2*l*)-1,2-dimethoxy-1,2-diphenylethane (**12**),[61] (*R*)-1,2-dimethoxy-2-phenylethane (**13**).[62]

(*R*)-(1*l*,2*l*,3*u*,4*u*)-2,3-Dimethoxy-4,7,7-trimethylbicyclo[2.2.1]heptane (8). A 60% suspension of sodium hydride in mineral oil (705 mg, 17.6 mmol, 3.0 equiv) was washed with hexane (3 × 20 mL), dried in vacuo, and suspended in DME (30 mL). The suspension was cooled to 0 °C (ice/H_2O), and a solution of (*R*)-(1*l*,2*l*,3*u*,4*u*)-2,3-dihydroxy-4,7,7-trimethylbicyclo[2.2.1]heptane (1.00 g, 5.8 mmol) in DME (25 mL) was added dropwise over a 15-min period. The reaction mixture was allowed to warm to room temperature, and CH_3I (825 μL, 13.2 mmol, 2.26 equiv) was added slowly via syringe. The reaction mixture was stirred for 10 h at room temperature, quenched by the addition of CH_3OH (2 mL), poured into saturated NH_4Cl (75 mL), and extracted with Et_2O (3 × 80 mL). The extracts were washed with a 10% solution of $NaHCO_3$ (1 × 75 mL) and brine (1 × 75 mL), combined, dried (K_2CO_3), filtered through a pad of silica gel, and concentrated to afford a pale yellow oil. Purification by silica gel chromatography (hexane/EtOAc, 20:1) and bulb-to-bulb distillation afforded 1.058 g (91%) of **8** as a clear liquid. Data for **8**: bp 145–150 °C (25 Torr); ^{1}H NMR (500 MHz, $CDCl_3$) 3.38 (s, 3 H, $\mathrm{H_3C}$(11)), 3.34 (d, J = 6.85, 1 H, HC(3)), 3.33 (s, 3 H, $\mathrm{H_3C}$(12)), 3.10 (d, J = 6.85, 1 H, HC(2)), 1.78 (d, J = 4.86, 1 H, HC(1)), 1.62 (tt, J = 4.4, 12.5, 1 H, HC(6)), 1.41 (dt, J = 4.2, 2.5, 1 H, HC(5)), 1.04 (s, 3 H), 0.91 (m, 1 H, HC(5)), 0.87 (m, 1 H, HC(6)), 0.86 (s, 3 H), 0.73 (s, 3 H); ^{13}C NMR (125.8 MHz, $CDCl_3$) 90.71 (C(3)), 87.03 (C(2)), 60.62 (C(12)), 58.03 (C(11)), 49.12 (C(4)), 47.59 (C(1)), 46.38 (C(7)), 33.79 (C(5)), 24.06 (C(6)), 21.04; 20.43; 11.32; IR (CCl_4) 2953 (s), 2824 (s), 1458 (m), 1393 (m), 1370 (m), 1287 (w), 1242 (w), 1194 (m), 1144 (s), 1105 (s), 1082 (m), 1042 (m), 1007 (m), 997 (w); MS (70 eV) 198 (M^+, 14), 166 (34), 153 (14), 151 (23), 134 (16), 123 (17), 121 (45), 119 (22), 115 (23), 113 (60), 99 (44), 98 (19), 88 (100), 86 (43), 85 (73); TLC R_f 0.48 (hexane/EtOAc, 8:1); $[\alpha]^{24}_{D}$ −98° (c = 2.87, CCl_4). Anal. Calcd for $C_{12}H_{22}O_2$ (198.31): C, 72.68; H, 11.18. Found: C, 72.70; H, 11.18.

NMR Spectra of (1,2-Dimethoxyethane)diethylzinc (5). In an oven-dried Wilmad 528PP NMR tube fitted with a septum securely wrapped with Teflon tape, DME (52.0 μL, 0.50 mmol) was added to degassed benzene-d_6 (500 μL) and the resultant mixture cooled to 0 °C and treated with Et_2Zn (51.2 μL, 0.50 mmol, 1.00 equiv). The sample was warmed to room temperature, and the spectra were acquired. The multiplicities and coupling constants reported for the ^{13}C spectrum were obtained from a proton-coupled spectrum. Data for **5**: ^{1}H NMR (300 MHz, benzene-d_6) 3.14 (s, 4 H, H_2CO), 3.02 (s, 6 H, H_3CO), 1.31 (t, J = 8.13, 6 H, $\mathrm{H_3C}$(2)), 0.25 (q, J = 8.13, 4 H, $\mathrm{H_2C}$(1)); ^{13}C NMR (75.5 MHz, benzene-d_6) 71.52 (t, $^1J_{\mathrm{C-H}}$ = 144, CH$_2$O), 58.35 (q, $^1J_{\mathrm{C-H}}$ = 142, CH$_3$O), 11.46 (q, $^1J_{\mathrm{C-H}}$ = 124, C(2)), 4.84 (t, $^1J_{\mathrm{C-H}}$ = 118, C(1)).

General Procedure for NMR Spectra of $(XCH_2)_2Zn$/DME Reagents. In an oven-dried Wilmad 528PP NMR tube fitted with a septum securely wrapped with Teflon tape, DME (52.0 μL, 0.50 mmol, 1.00 equiv) was added to a cooled (0 °C) solution of Et_2Zn (51.2 μL, 0.50 mmol) in 500 μL of degassed solvent (benzene-d_6 for Table I, acetone-d_6 for Table II) followed by the dihalomethane (2.00 equiv). The sample was shaken several times, maintained at 0 °C for 5 min, and warmed to room temperature, and the spectra were acquired. The multiplicities and coupling constants reported for the ^{13}C spectra were obtained from a proton-coupled spectrum.

General Procedure for NMR Spectra of $(XCH_2)_2Zn$ in Acetone-d_6. To a cooled (0 °C) acetone-d_6 solution of Et_2Zn in an NMR tube was added the dihalomethane (2.00 equiv). The sample was shaken several times, maintained at 0 °C for 5 min, and warmed to room temperature, and the spectra were acquired.

NMR Spectra of (1,2-Dimethoxyethane)bis(iodomethyl)zinc (6). From a solution of DME (52.0 mL, 0.50 mmol, 1.00 equiv), Et_2Zn (51.2 μL, 0.50 mmol), and CH_2I_2 (81 μL, 1.01 mmol, 2.01 equiv) in degassed benzene-d_6 (500 μL) was obtained a solution of **6**. Data for **6**: ^{1}H NMR (300 MHz, benzene-d_6) 3.02 (s, 4 H, H_2CO), 2.97 (s, 6 H, H_3CO), 1.40 (s, 4 H, H_2CZn); ^{13}C NMR (75.5 MHz, benzene-d_6) 70.61 (t, $^1J_{\mathrm{C-H}}$ = 146, CH$_2$O), 59.83 (q, $^1J_{\mathrm{C-H}}$ = 143, CH$_3$O), −19.67 (t, $^1J_{\mathrm{C-H}}$ = 133, CH$_2$Zn).

NMR Spectra of (1,2-Dimethoxyethane)bis(chloromethyl)zinc (7). From a solution of DME (52.0 mL, 0.50 mmol, 1.00 equiv), Et_2Zn (51.2 μL, 0.50 mmol), and $ClCH_2I$ (73 μL, 1.00 mmol, 2.00 equiv) in degassed benzene-d_6 (500 μL) was obtained a solution of **7**. Data for **7**: ^{1}H NMR (300 MHz, benzene-d_6) 3.04 (s, 6 H, H_3CO), 3.03 (s, 4 H, H_2CO), 2.71 (s, 4 H, H_2CZn); ^{13}C NMR (75.5 MHz, benzene-d_6) 70.82 (t, $^1J_{\mathrm{C-H}}$ = 144, CH$_2$O), 59.28 (q, $^1J_{\mathrm{C-H}}$ = 144, CH$_3$O), 29.60 (t, $^1J_{\mathrm{C-H}}$ = 132, CH$_2$Zn).

NMR Spectra of ((*R*)-(1*l*,2*l*,3*u*,4*u*)-2,3-Dimethoxy-4,7,7-trimethylbicyclo[2.2.1]heptane)bis(iodomethyl)zinc (9). In a 5-mL two-neck flask, a solution of **8** (90 mg, 0.45 mmol, 1.00 equiv) in benzene-d_6 (500 μL) was degassed (freeze/thaw × 3). The sample was cooled to 0 °C and treated with Et_2Zn (46.5 μL, 0.45 mmol). The reaction mixture was transferred via syringe to an oven-dried Wilmad 528 PP NMR tube fitted with a septum securely wrapped with Teflon tape. The flask was rinsed with degassed benzene-d_6 (100 μL), which was added to the NMR tube. To this clear solution was added CH_2I_2 (73.0 μL, 0.90 mmol, 2.00 equiv). The sample was shaken several times, maintained at 0 °C for 5 min, and warmed to room temperature, and the spectra were acquired. Data for **9**: ^{1}H NMR (500 MHz, benzene-d_6) 3.44 (d, J = 6.6, 1 H, HC(3)), 3.25 (s, 3 H, $\mathrm{H_3C}$(11)), 3.16 (m, 1 H, HC(2)), 3.15 (s, 3 H, $\mathrm{H_3C}$(12)), 1.55 (d, J = 4.89, 1 H, HC(1)), 1.49 (dd, J = 10.6, 4 H, $\mathrm{H_2CZn}$), 1.38 (m, 1 H, HC(6)), 1.15 (dt, J = 4.2, 12.5, 1 H, HC(5)), 0.97 (s, 3 H), 0.74 (s, 3 H), 0.72–0.56 (m, 2 H, HC(5), HC(6)), 0.57 (s, 3 H); ^{13}C NMR (125.8 MHz, benzene-d_6) 91.14 (C(3)), 87.36 (C(2)), 61.58 (C(12)), 58.32 (C(11)), 49.99 (C(4)), 47.04 (C(1)), 45.72 (C(7)), 33.42 (C(5)), 23.72 (C(6)), 21.34; 20.41; 12.13, −18.50 ($\mathrm{CH_2Zn}$).

NMR Spectra of Bis(acetone-d_6)bis(iodomethyl)zinc (10). From a solution of Et_2Zn (51.2 μL, 0.50 mmol) and CH_2I_2 (81 μL, 1.00 mmol, 2.00 equiv) in degassed acetone-d_6 (500 μL) was obtained a solution of **10**. Data for **10**: ^{1}H NMR (300 MHz, acetone-d_6) 1.34 (s, 4 H, H_2CZn); ^{13}C NMR (75.5 MHz, acetone-d_6) −16.62 (CH$_2$Zn).

NMR Spectra of Bis(acetone-d_6)bis(iodomethyl)zinc (10) in the Presence of DME. From a solution of Et_2Zn (51.2 μL, 0.50 mmol), DME (52.0 μL, 0.50 mmol, 1.00 equiv), and CH_2I_2 (81 μL, 1.00 mmol, 2.00 equiv) in degassed acetone-d_6 (500 μL) was obtained a solution of **10**. Data for **10** + DME: ^{1}H NMR (300 MHz, acetone-d_6) 3.52 (s, 4 H, H_2CO), 3.32 (s, 6 H, H_3CO), 1.34 (s, 4 H, H_2CZn); ^{13}C NMR (75.5 MHz, acetone-d_6) 71.18 (CH$_2$O), 58.34 (CH$_3$O), −18.30 (CH$_2$Zn).

NMR Spectra of Bis(acetone-d_6)bis(chloromethyl)zinc (11). From a solution of Et_2Zn (51.2 μL, 0.50 mmol) and $ClCH_2I$ (73.0 μL, 1.00 mmol, 2.00 equiv) in degassed acetone-d_6 (500 μL) was obtained a solution of **11**. Data for **11**: ^{1}H NMR (300 MHz, acetone-d_6) 2.55 (s, 4 H, H_2CZn); ^{13}C NMR (75.5 MHz, acetone-d_6) ~29.8 (CH$_2$Zn, this signal was obscured by the acetone heptet).

NMR Spectra of Bis(acetone-d_6)bis(chloromethyl)zinc (11) in the Presence of DME. From a solution of Et_2Zn (51.2 μL, 0.50 mmol), DME (52.0 μL, 0.50 mmol, 1.00 equiv), and $ClCH_2I$ (73 μL, 1.00 mmol, 2.00 equiv) in degassed acetone-d_6 (500 μL) was obtained a solution of **11**. Data for **11** + DME: ^{1}H NMR (300 MHz, acetone-d_6) 3.50 (s, 4 H, H_2CO), 3.30 (s, 6 H, H_3CO), 2.56 (s, 4 H, H_2CZn); ^{13}C NMR (75.5 MHz, acetone-d_6) 71.00 (CH$_2$O), 57.87 (CH$_3$O), ~29.8 (CH$_2$Zn, this signal was obscured by the acetone heptet).

NMR Spectra of Bis(acetone-d_6)bis(iodomethyl)zinc (10) Derived from Bis(diethyl ether)bis(iodomethyl)zinc ("Dried Reagent"). In a 10-mL two-neck flask, Et_2O (3 mL) was cooled to 0 °C and Et_2Zn (1.00 mL, 1.0 mmol, 1.0 M in hexane) was added via syringe. To this solution was added CH_2I_2 (169 μL, 2.10 mmol, 2.10 equiv). The reaction mixture was stirred for 30 min at 0 °C and carefully concentrated (0.2 Torr). After the bulk of the volatiles had evaporated, the reaction vessel was warmed to room temperature and maintained at 0.2 Torr for 1 h. The resulting white solid was dissolved in acetone-d_6 and transferred to an NMR tube (Wilmad 528PP). Data for **10** + Et_2O: ^{1}H NMR (300 MHz, acetone-d_6) 3.36 (q, J = 6.8, 2 H, H_2CO), 1.34 (s, 3 H, H_2CZn), 1.00 (t, J = 6.8, 3 H, H_3CO); ^{13}C NMR (75.5 MHz, acetone-d_6) 64.92 (CH$_2$O), 14.50 (CH$_3$O), −17.20 (CH$_2$Zn).

NMR Spectra of Bis(acetone-d_6)bis(iodomethyl)zinc (10) Derived from 6 ("Dried Reagent"). In a 10-mL two-neck flask, DME (3 mL) was cooled to 0 °C and Et_2Zn (1.0 M in hexane, 1.0 mmol) was added via syringe. To this solution was added CH_2I_2 (169 μL, 2.10 mmol, 2.10 equiv). The reaction mixture was stirred for 30 min at 0 °C and carefully concentrated (0.2 Torr). After the bulk of the volatiles had evaporated, the reaction vessel was warmed to room temperature and maintained at 0.2 Torr for 1 h. The resulting white solid was dissolved in acetone-d_6 and the solution transferred to an NMR tube (Wilmad 528PP). Data for **10** + DME: ^{1}H NMR (300 MHz, acetone-d_6) 3.54 (s, 4 H, H_2CO), 3.30 (s, 6 H, H_3CO), 1.33 (s, 2 H, H_2CZn); ^{13}C NMR (75.5 MHz,

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acetone-d_6) 70.85 (CH_2O), 58.74 (CH_3O), −18.07 (CH_2Zn).

General Procedure of NMR Spectra of L/ICH_2ZnI (L = 8, 12, or 13) Complexes in Acetone-d_6 ("Dried Reagents"). A solution of the ligand (0.50 mmol) in hexane (2 mL) was degassed (three freeze/thaw cycles) and cooled to 0 °C. To this solution was added Et_2Zn (1.0 M in hexane, 0.50 mL, 0.50 mmol). The reaction mixture was stirred for 15 min at 0 °C and treated with CH_2I_2 (81 μL, 1.00 mmol, 2.00 equiv). The reaction mixture was cooled to −78 °C, and a white solid precipitated out of solution. The reaction mixture was warmed to 0 °C and carefully concentrated at 0.2 Torr. After the bulk of the volatiles had evaporated, the reaction vessel was warmed to room temperature and maintained at 0.2 Torr for 1 h. The resulting white solid was dissolved in acetone-d_6 (500 μL) and transferred to an NMR tube (Wilmad 528PP).

NMR Spectra of Bis(acetone-d_6)bis(iodomethyl)zinc (10) Derived from ((*R*)-1,2-Dimethoxy-1-phenylethane)bis(iodomethyl)zinc ("Dried Reagent"). From 13 (99 mg, 0.50 mmol, 1.0 equiv) was obtained a white solid. Data for 10 + 13: ^{1}H NMR (300 MHz, acetone-d_6) 7.32 (m, 5 H, Ph), 4.38 (dd, *J* = 4.1, 7.7, 1 H, HC(1)), 3.55 (dd, *J* = 7.7, 10.6, 1 H, HC(2)), 3.39 (dd, *J* = 4.1, 10.6, 1 H, HC(2)), 3.30 (s, 3 H, H_3CO), 3.19 (s, 3 H, H_3CO), 1.44 (s, 2 H, H_2CZn); ^{13}C NMR (75.5 MHz, acetone-d_6) 129.05, 128.60, 127.82, 127.75 (Ph), 82.13 (C(1)), 76.36 (C(2)), 58.07 (CH_3O), 55.87 (CH_3O), −17.21 (CH_2Zn).

NMR Spectra of Bis(acetone-d_6)bis(iodomethyl)zinc (10) Derived from ((1*R*,2*R*)-1,2-Dimethoxy-1,2-diphenylethane)bis(iodomethyl)zinc ("Dried Reagent"). From 12 (48 mg, 0.20 mmol, 1.0 equiv) was obtained a white solid. Data for 10 + 12: ^{1}H NMR (300 MHz, acetone-d_6) 7.18–7.03 (m, 10 H, Ph), 4.44 (s, 2 H, HC(1), HC(2)), 3.23 (s, 6 H, H_3CO), 1.46 (br s, 2 H, H_2CZn); ^{13}C NMR (75.5 MHz, acetone-d_6) 138.54, 128.43, 128.05, 127.94 (Ph), 87.63 (C(1), C(2)), 56.91 (CH_3O), −17.03 (CH_2Zn).

NMR Spectra of Bis(acetone-d_6)bis(iodomethyl)zinc (10) Derived from ((*R*)-(1*l*,2*l*,3*u*,4*u*)-2,3-Dimethoxy-4,7,7-trimethylbicyclo[2.2.1]heptane)bis(iodomethyl)zinc (9) ("Dried Reagent"). From 8 (99 mg, 0.50 mmol, 1.0 equiv) was obtained a white solid. Data for 10 + 8: ^{1}H NMR (300 MHz, acetone-d_6) 3.42 (d, *J* = 6.85, 1 H, HC(3)), 3.35 (s, 3 H, $H_3C(11)$), 3.30 (s, 3 H, $H_3C(12)$), 3.22 (d, *J* = 6.86, 1 H, HC(2)), 1.80 (d, *J* = 4.91, 1 H, HC(1)), 1.58 (m, 1 H, HC(6)), 1.37 (m, 1 H, HC(5)), 1.34 (br, 2 H, H_2CZn), 0.98 (s, 3 H), 0.90–0.84 (m, 2 H, HC(5), HC(6)), 0.82 (s, 3 H), 0.69 (s, 3 H); ^{13}C NMR (75.5 MHz, acetone-d_6) 89.97 (C(3)), 86.54 (C(2)), 60.06 (C(12)), 57.30 (C(11)), 48.40 (C(4)), 46.82 (C(1)), 46.11 (C(7)), 33.10 (C(5)), 23.21 (C(6)), 20.44, 20.10, 10.84, −17.21 (CH_2Zn). Anal. Calcd for $C_{13}H_{24}I_2O_2Zn$ (8/ICH_2ZnI, 531.52): C, 29.38; H, 4.55; I, 47.75; Zn, 12.30. Found: C, 29.41; H, 4.63; I, 47.45; Zn, 12.46.

Procedure for the Recrystallization of ((*R*)-(1*l*,2*l*,3*u*,4*u*)-2,3-Dimethoxy-4,7,7-trimethylbicyclo[2.2.1]heptane)bis(iodomethyl)zinc (9). In a flame-dried 10-mL two-neck flask, a solution of 8 (99 mg, 0.50 mmol) in hexane (3 mL) was degassed (three freeze/thaw cycles) and cooled to 0 °C. To this solutioin was added Et_2Zn (1.0 M in hexane, 500 μL, 0.50 mmol, 1.0 equiv). The reaction mixture was stirred for 10 min at 0 °C, and CH_2I_2 (81 μL, 1.00 mmol, 2.00 equiv) was added via syringe. The reaction mixture was allowed to warm to room temperature, and stirring was continued for 15 min. Stirring was then halted, and the reaction mixture was slowly cooled to 0 °C. Small white needles formed over a 10–20-min period. The reaction flask was maintained at 0 °C for 45 min and then placed into a −20 °C freezer. Additional crystals formed immediately. After 2 h, the flask was removed from the freezer and the reaction mixture was warmed to room temperature, with stirring, over a 30-min period. Stirring was once again halted, and the reaction flask was cooled to −20 °C over a 25-min period, resulting in the deposition of colorless crystals.

X-ray Crystallographic Analysis of ((*R*)-(1*l*,2*l*,2*u*,4*u*)-2,3-Dimethoxy-4,7,7-trimethylbicyclo[2.2.1]heptane)bis(iodomethyl)zinc (9). A single crystal suitable for analysis was removed from the reaction vessel with the aid of a spatula tipped with Paratone-N (Exxon) oil. The crystal was mounted using this oil to a thin glass fiber and then cooled to −75 °C with the (−3,0,1) scattering planes roughly normal to the spindle axis. The reflections were observed on an Enraf-Nonius CAD4 automated κ-axis diffractometer equipped with a graphite monochromator (Table IV). The variable-scan option was used at 3–16°/min. The three standard intensities monitored every 90 min showed less than 5% decay; no correction for decay was applied. Data were corrected for anomalous dispersion,[63a] absorption,[63b] and Lorentz and polarization effects. An analytical approximation to the scattering factors[63c] was used. There was no change in the appearance of the sample during the experiment.

The structure was solved by direct methods;[64a] iodine and zinc atom positions for two independent molecules were deduced from an E-map. Subsequent least-squares difference Fourier calculations[64b] revealed positions for the remaining non-hydrogen atoms. Hydrogen atoms were included as fixed contributors in "idealized" positions. In the final cycle of full-matrix least-squares refinement, an isotropic parameter for extinction was varied, common isotropic thermal parameters were refined for the methyl and non-methyl hydrogen atoms, independent isotropic thermal coefficients were refined for carbon atoms C-(5,6,13,14,25,26,33,34), and the remaining atoms were refined with anisotropic thermal coefficients. Correlations between refined parameters for atoms I(2) and I(4) were less than 0.6, and no other correlations exceeded 0.5. Successful convergence was indicated by the maximum shift/error for the last cycle. However, thermal parameters for the isotropically refined carbon atoms listed above converged to imaginary values when refined anisotropically, and there were clearly some correlations between atoms related by the pseudo-inversion center. The three highest peaks in the final difference Fourier map were near iodine atoms I(2) and I(4). The orientation of these peaks with respect to molecule A suggested that atom I(2) was slightly disordered, but attempts to resolve a low-percentage (<10%) disorder model for this atom were not successful. There were no other peaks above background, and the final map had no other significant features. The final analysis of variance between observed and calculated structure factors showed a minor dependence on sin θ.

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Registry No. 5, 65466-93-5; 6, 131457-21-1; 7, 131457-22-2; 8, 131457-19-7; 9, 131457-20-0; 10 (S = acetone-d_6), 139043-14-4; 10 (S = Et_2O), 139043-17-7; 11 (S = acetone-d_6), 139043-15-5; 12, 62860-43-9; 13, 32345-80-5; DME, 110-71-4; $(Et)_2Zn$, 557-20-0; XCH_2I (X = I), 75-11-6; XCH_2I (X = Cl), 593-71-5; $ICH_2ZnI(OC(CD_3)_2)_2$, 139043-16-6; (*R*)-(1*l*,2*l*,3*u*,4*u*)-2,3-dihydroxy-4,7,7-trimethylbicyclo[2.2.1]heptane, 59599-25-6.

Supplementary Material Available: Tables of final atomic positional parameters, anisotropic thermal parameters, bond lengths and angles, and torsion angles (8 pages); listing of observed and calculated structure factors for 9 (22 pages). Ordering information is given on any current masthead page.

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