

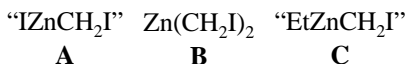
X-ray Crystal Structure of a Zinc Carbenoid Cyclopropanating Reagent: The $\text{IZnCH}_2\text{I}\cdot 18\text{-crown-6}$ and Benzo-18-crown-6 Complexes

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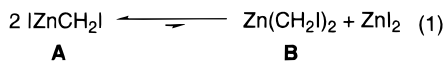
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The discovery by Simmons and Smith in the late 1950s that the reaction between an olefin and the reagent prepared by mixing the Zn/Cu couple with CH_2I_2 (tentatively assigned as reagent **A**)¹ has evolved into one of the most important methods for the formation of three-membered rings.^{2,3} Some years later, Wittig⁴ reported that treatment of zinc iodide with 2 equiv of diazomethane generated the bis(iodomethyl)zinc reagent (**B**). More recently, Denmark has further elaborated on the reactivity profile of $\text{Zn}(\text{CH}_2\text{I}_2)$ (prepared from 1 equiv of ZnEt_2 and 2 equiv of CH_2I_2) and confirmed the structure by X-ray crystallography and NMR spectroscopy.⁵ In 1966, Furukawa and co-workers⁶ reported that a more reactive reagent could be prepared by replacing the Zn/Cu couple/ CH_2I_2 system with $\text{ZnEt}_2/\text{CH}_2\text{I}_2$ (reagent **C**). Of these three reagents, only the structure of reagent **B** was unambiguously established by X-ray crystallography.



We have recently shown by low-temperature NMR of a chiral diether complex that the proposed Schlenk equilibrium of the Simmons–Smith reagent appears to lie to the left (eq 1),⁷ but the structural features and viability of IZnCH_2I (**A**) have never been established.



Our interest in the design and development of new stereoselective cyclopropanation reactions using iodomethylzinc reagents led us to further characterize IZnCH_2I , which has been postulated to be the Simmons–Smith reagent.⁸ We report herein the first two X-ray crystal structures of IZnCH_2I -derived complexes.

We found that the procedure of choice, to quantitatively generate IZnCH_2I , was to add CH_2I_2 (1 equiv) to a solution of EtZnI (prepared from 1 equiv of ZnEt_2 and 1 equiv of I_2) and a complexing agent. This procedure avoided the use of Zn/Cu

(1) (a) Simmons, H. E.; Smith, R. D. *J. Am. Chem. Soc.* **1958**, *80*, 5323–5324. (b) Simmons, H. E.; Smith, R. D. *J. Am. Chem. Soc.* **1959**, *81*, 4256–4264.

(2) (a) Simmons, H. E.; Cairns, T. L.; Vladuchick, S. A.; Hoiness, C. M. *Org. React.* **1973**, *20*, 1–131. (b) Furukawa, J.; Kawabata, N. *Adv. Organomet. Chem.* **1974**, *12*, 83–134. (c) Boersma, J. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: New York, 1984; Vol. 2, Chapter 16. (d) Zeller, K.-P.; Gugel, H. *Houben-Weyl: Methoden der Organischen Chemie*; Regitz, M., Ed.; Georg Thieme Verlag: Stuttgart, 1989; Band EXIXb, 195. (e) Hoveyda, A. H.; Evans, D. A.; Fu, G. C. *Chem. Rev.* **1993**, *93*, 1307–1370.

(3) This reagent has also been extensively used for homologation reactions in synthesis: (a) Knochel, P.; Singer, R. D. *Chem. Rev.* **1993**, *93*, 2117–2188. (b) Motherwell, W. B.; Nutley, C. J. *Contemp. Org. Synth.* **1994**, *1*, 219–241.

(4) Wittig, G.; Winkler, F. *Justus Liebigs Ann. Chem.* **1961**, 650, 18. (5) (a) Denmark, S. E.; Edwards, J. P.; Wilson, S. R. *J. Am. Chem. Soc.* **1992**, *114*, 2592–2602. (b) Denmark, S. E.; Edwards, J. P.; Wilson, S. R. *J. Am. Chem. Soc.* **1991**, *113*, 723–725.

(6) (a) Furukawa, J.; Kawabata, N.; Nishimura, J. *Tetrahedron Lett.* **1966**, 3353–3356. (b) Furukawa, J.; Kawabata, N.; Nishimura, J. *Tetrahedron* **1968**, *24*, 53–58.

(7) Charette, A. B.; Marcoux, J.-F. *J. Am. Chem. Soc.* **1996**, *118*, 4539–4549.

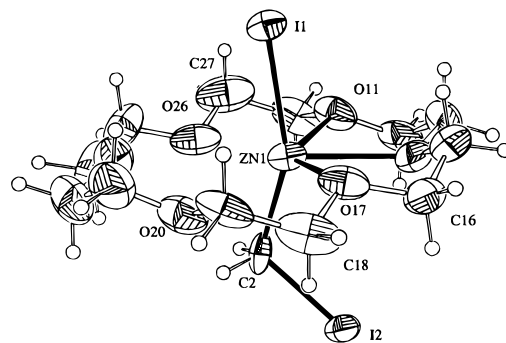


Figure 1. ORTEP drawing of the first molecule of the unit cell. Ellipsoids are drawn at the 40% probability level.

and allowed us to easily survey a variety of complexing agents to find suitable crystals for the X-ray diffraction study. Nice plates, corresponding to a mixture of $\text{IZnCH}_2\text{I}\cdot 18\text{-crown-6}$ (**1**) and $\text{ZnI}_2\cdot 18\text{-crown-6}$ (**2**), were formed if the solution containing 18-crown-6 (1 equiv) was left at 25 °C.⁹ The presence of the $\text{ZnI}_2\cdot 18\text{-crown-6}$ complex, formed by decomposition of $\text{IZnCH}_2\text{I}\cdot 18\text{-crown-6}$, was inevitable during the warming of the solution to get suitable crystals.¹⁰

Complex **1** crystallizes as a monomer with two independent molecules in the unit cell. An ORTEP drawing of one of the unambiguously elucidated structures is shown in Figure 1. Selected bond lengths and angles are presented in Table 1.

The zinc center resides in a highly distorted trigonal bipyramidal environment.¹¹ Quite interestingly, the threaded structure is not unusual for crown ether-derived complexes,¹² but this is one of the few structures in which the metal atom is not centrosymmetric.¹³ For example, the closely related $\text{ZnEt}_2\cdot 18\text{-crown-6}$ complex is centrosymmetric with zinc lying on the inversion center. The Zn–C bond length of 1.995 Å is comparable to those reported earlier. The Zn–O bond lengths (2.34(1), 2.56(1), and 2.60(1) Å) are slightly longer than those found in other alkylzinc halide–ether complexes, but these

(8) For a review, see: Charette, A. B.; Marcoux, J.-F. *Synlett.* **1995**, 1197–1207.

(9) Intensity data were measured on a Enraf-Nonius CAD-4 diffractometer by using copper K α radiation and the $\omega/2\theta$ scan technique. Crystals of $[\text{Zn}(\text{CH}_2\text{I})(\text{C}_{12}\text{H}_{24}\text{O}_6)]_{0.5}[\text{Zn}(\text{CH}_2\text{I})(\text{C}_{12}\text{H}_{24}\text{O}_6)]_{0.85}[\text{ZnI}_2(\text{C}_{12}\text{H}_{24}\text{O}_6)]_{0.15}$ belong to the monoclinic space group $P2_1/c$ with $a = 8.097(2)$ Å, $b = 49.52(2)$ Å, $c = 8.379(2)$ Å, $\beta = 117.96(2)^\circ$, $V = 2968(2)$ Å³, $Z = 4$, and $D_{\text{calc}} = 2.001$ mg/m³. Data were collected at 220 K, and the structure was solved by direct methods and refined to $R_f = 0.0728$ and $R_w = 0.1688$ for 5628 reflections with $I > 2\sigma(I)$. A full description of the structure is provided in the supporting information.

(10) To a solution of 18-crown-6 (260 mg, 0.98 mmol) and iodine (248 mg, 0.98 mmol) in freshly distilled dichloromethane (1.3 mL) cooled to –20 °C was added Et_2Zn (100 μL , 0.98 mmol) under argon. The resulting mixture was stirred at room temperature until the complete disappearance of the brown color and was recooled to –40 °C. Diiodomethane (79 μL , 0.98 mmol) was then slowly added, and the clear solution was rapidly warmed to 25 °C. Suitable crystals were slowly formed upon standing at room temperature.

(11) For examples of pentacoordinated zinc complexes, see: (a) Ansell, C. W. G.; Dancy, K. P.; McPartlin, M.; Tasker, P. A.; Lindoy, L. F. *J. Chem. Soc., Dalton Trans.* **1983**, 1789–1791. (b) Drew, M. G. B.; Hollis, S. J. *Chem. Soc., Dalton Trans.* **1978**, 511–516. (c) Markies, P. R.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F.; Spek, A. L. *J. Organomet. Chem.* **1992**, *430*, 1–13.

(12) Recent examples of threaded structure of 18-crown-6-complexes: (a) Pajerski, A. D.; BergStresser, G. L.; Parvez, M.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 4844–4845. (b) Paige, C. R.; Richardson, M. F. *Can. J. Chem.* **1984**, *62*, 332–335. (c) Kawasaki, Y.; Matsuura, Y. *Chem. Lett.* **1984**, 155–158. (d) Pears, D. A.; Stoddart, J. F.; Crosby, J.; Allwood, B. L.; Williams, D. J. *Acta Crystallogr., Sect. C* **1986**, *42*, 51–53. (e) Hazell, A. *Acta Crystallogr., Sect. C* **1988**, *44*, 88–92. (f) Drew, M. G. B.; Lee, K. C.; Mok, K. F. *Inorg. Chim. Acta* **1989**, *155*, 39–43.

(13) For selected examples of noncentrosymmetric complexes derived from 18-crown-6, see: (a) Doxsee, K. M.; Hagadorn, J. R.; Weakley, T. J. R. *Inorg. Chem.* **1994**, *33*, 2600–2606. (b) Atwood, J. L.; Bott, S. G.; Harvery, S.; Junk, P. C. *Organometallic* **1994**, *13*, 4151–4152. (c) Willey, G. R.; Lakin, M. T.; Alcock, N. W. *J. Chem. Soc., Chem. Commun.* **1992**, 1619–1620.

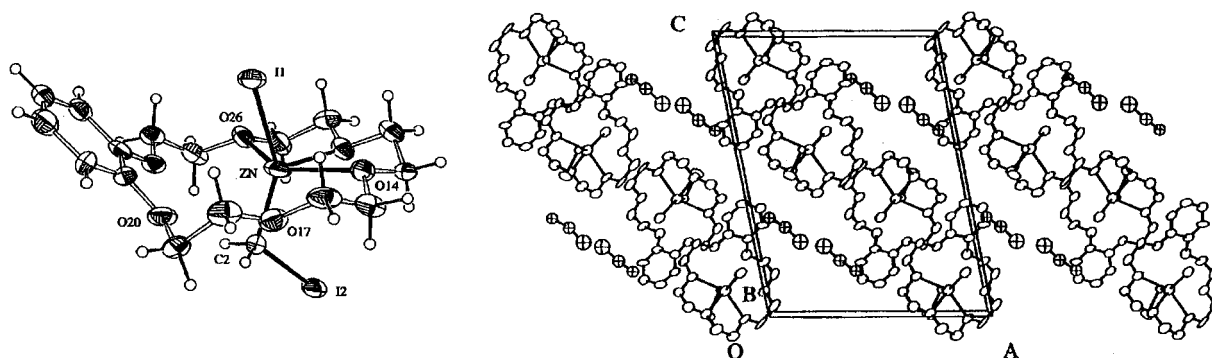


Figure 2. (Left) ORTEP view of $[\text{Zn}(\text{CH}_2\text{I})(\text{I})-(\text{C}_{16}\text{H}_{24}\text{O}_6)]$. Ellipsoids are drawn at the 40% probability level. (Right) View of the unit cell.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complexes **1** and **3**

Bond Lengths							
1		3		1		3	
Zn(1)–C(2)	1.995(9)	2.04(2)	Zn(1)–O(26)	3.060(12)	2.556(13)		
Zn(1)–I(2)	3.495(2)	3.469(3)	Zn(1)–O(11)	2.555(11)	2.243(14)		
I(2)–C(2)	2.104(8)	2.09(2)	Zn(1)–O(17)	2.601(11)	2.945(14)		
Zn(1)–O(14)	2.341(10)	2.387(11)	Zn(1)–O(23)	3.214(12)	3.209(12)		
Zn(1)–O(20)	3.052(11)	3.425(14)					
Bond Angles							
1		3		1		3	
C(2)–Zn(1)–I(1)		156.8(3)		146.1(6)			
Zn(1)–C(2)–I(2)		117.0(5)		114.1(10)			
O(26)–Zn(1)–O(11)		59.1(4)		69.0(4)			
O(11)–Zn(1)–O(14)		68.5(4)		70.9(5)			
O(14)–Zn(1)–O(17)		67.7(4)		64.4(4)			

values are not unusual.¹⁴ The bond angles I–Zn–C of 156.8(3)° and Zn–C–I of 117.5(6)° have normal values and do not seem to indicate any unusual interaction between I(2) and Zn. This is in contrast to two of four Zn–C–I values (107.9°, 106.9°, 116.4°, and 115.8°) observed by Denmark for the $\text{Zn}(\text{CH}_2\text{I})_2$ ·diether complex.^{4,15} One additional molecule was also present in the unit cell. Unfortunately, the molecule was centrosymmetric with Zn lying on the inversion center, and it was impossible to determine whether we had two molecules corresponding to IZnCH_2I ·18-crown-6 or a mixture of ZnI_2 ·18-crown-6 and $\text{Zn}(\text{CH}_2\text{I})_2$ ·18-crown-6.

To overcome this uncertainty, other substituted crown ether-derived complexes were prepared and crystallized to get suitable crystals for X-ray analysis. The IZnCH_2I ·benzo-18-crown-6 complex (**3**) was successfully crystallized into suitable single crystals.^{16,17} Colorless plates, corresponding to the chemical formula $[\text{Zn}(\text{CH}_2\text{I})(\text{I})(\text{C}_{16}\text{H}_{24}\text{O}_6)]_{0.7}[\text{Zn}(\text{I})_2(\text{C}_{16}\text{H}_{24}\text{O}_6)]_{0.3} \cdot \text{CH}_2\text{Cl}_2$, were formed if a solution of IZnCH_2I containing an equimolar amount of benzo-18-crown-6 in CH_2Cl_2 was cooled to room temperature.^{18,19}

The bond lengths and torsion angles observed are very close to those obtained for complex **1** except that some of the Zn–O bonds are much shorter. These latter values are more closely

(14) (a) Dekker, J.; Boersma, J.; van der Kerk, G. J. M. *J. Chem. Soc., Chem. Commun.* **1983**, 553–555. (b) Dekker, J.; Budzelaar, P. H. M.; Boersma, J.; van der Kerk, G. J. M.; Spek, A. L. *Organometallics* **1984**, *3*, 1403–1407. (c) Bellus, D.; Klingert, B.; Lang, R. W.; Rihs, G. *J. Organometal. Chem.* **1988**, *339*, 17–22. (d) Gruter, G.-J. M.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *Recl. Trav. Chim. Pays-Bas* **1993**, *112*, 425.

(15) We have also independently obtained an X-ray crystal structure of the related bis(iodomethyl)zinc complex, $[\text{Zn}(\text{CH}_2\text{I})_2(\text{C}_{12}\text{H}_{24}\text{O}_6)]_{0.75}[\text{Zn}(\text{CH}_2\text{I})(\text{I})(\text{C}_{12}\text{H}_{24}\text{O}_6)]_{0.25}$. The bond angles Zn–C–I observed for this complex are 119.0(8)° and 119.4(10)°. The details of this structure are provided in the supporting information. The wider torsion angles may be a consequence of the threaded structure of the complexes.

(16) These crystals also decomposed to the ZnI_2 ·benzo-18-crown-6 complex during the data collection. Although ethylene formation could not be detected by X-ray, the crystals swelled even at 173 K.

related to those found in the literature for zinc–ether complexes.¹³ The three-dimensional molecular assembly shown in Figure 2 indicates that no interaction between two IZnCH_2I or between IZnCH_2I and ZnI_2 is present in the unit cell. For example, both zinc atoms are 7.799(6) Å apart. Conversely, the intermolecular Zn–I(1) and Zn–I(2) distances are 6.749(5) and 6.191(4) Å, respectively. This absence of interactions (such as those present in the dimer-like structures for IZnCH_2I that have been contemplated in the past) may be a consequence of the oxygen-donating ability of the crown ether.²⁰ One CH_2Cl_2 molecule that does not interact with either IZnCH_2I , ZnI_2 , or the crown ether is also found per asymmetric unit.

In conclusion, the solid state structure of IZnCH_2I is reported for the first time. This reagent may be the actual Simmons–Smith reagent, but this remains to be established.²¹ The structural features of this reagent will serve as groundwork to gain further insight on the mechanism of stereoselective cyclopropanation reactions involving the various iodomethyl-zinc-derived reagents.

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Supporting Information Available: Description of the structure determination, refinement procedure, and tables of X-ray crystallographic data for the various complexes, including atomic coordinates, anisotropic thermal parameters, and fixed atom coordinates (68 pages). See any current masthead page for ordering and Internet access instructions.

JA953816M

(17) To the best of our knowledge, there is only one other X-ray crystal structure of a benzo-18-crown-6 complex: Simonov, Y. A.; Dvorkin, A. A.; Fonar, M. S.; Ganin, E. V.; Kotlyar, S. A. *J. Inclusion Phenom.* **1991**, *11*, 1.

(18) Crystals of $[\text{Zn}(\text{CH}_2\text{I})(\text{I})(\text{C}_{16}\text{H}_{24}\text{O}_6)]_{0.7}[\text{Zn}(\text{I})_2(\text{C}_{16}\text{H}_{24}\text{O}_6)]_{0.3} \cdot \text{CH}_2\text{Cl}_2$ belong to the monoclinic space group $P2_1/n$ with $a = 15.324(10)$ Å, $b = 8.431(5)$ Å, $c = 19.993(11)$ Å, $\beta = 101.23(5)^\circ$, $V = 2534(3)$ Å³, $Z = 4$, and $D_{\text{calcd}} = 1.904$ mg/m³. Data were collected at 173 K, and the structure was solved by direct methods and refined to $R_f = 0.1105$ and $R_w = 0.2698$ for 4825 reflections with $I > 2\sigma(I)$. A full description of the structure is provided in the supporting information. Decomposition of IZnCH_2I to ZnI_2 was unavoidable during both the crystallization due to the temperature and the collection of the data. This, and the presence of disordered CH_2Cl_2 molecules, explains the R value obtained.

(19) To a solution of benzo-18-crown-6 (100 mg, 0.32 mmol) and iodine (81 mg, 0.32 mmol) in freshly distilled dichloromethane (320 μL) cooled to -20°C was added Et_2Zn (33 μL , 0.32 mmol) under argon. The resulting mixture was stirred at room temperature until the complete disappearance of the brown color and was recooled to -40°C . Diiodomethane (26 μL , 0.32 mmol) was then slowly added, and the mixture was warmed to room temperature to produce unsuitable crystals. Subsequent addition of dichloromethane (400 μL) and warming the mixture to 35°C dissolved the crystals. The solution was then cooled to 25°C , and large crystals were formed in less than 15 min upon standing at that temperature.

(20) The aggregation state will obviously depend on the nature of the solvent. For a review of the various proposals, see ref 2a.

(21) Solutions of both complexes were effective cyclopropanating reagents. This is a consequence of the dynamic equilibrium between the complexed and uncomplexed forms of the reagent. Accordingly, the NMR spectra of these solutions indicate the presence of several species in solution.