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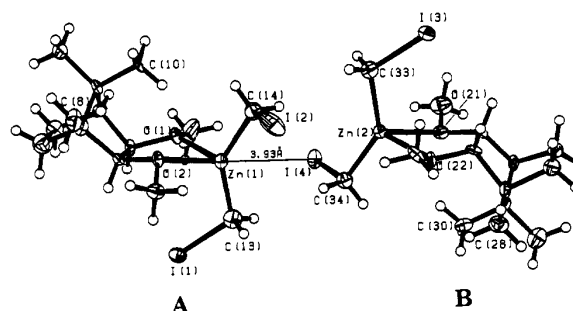
### Solution and Solid-State Structure of the "Wittig–Furukawa" Cyclopropanation Reagent<sup>†</sup>

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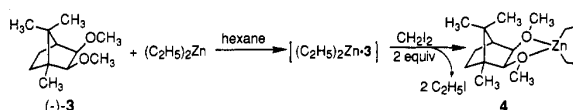
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The Simmons–Smith cyclopropanation of olefins is arguably the most important application of organozinc reagents in organic synthesis.<sup>1</sup> The reaction proceeds under mild conditions<sup>2</sup> and is characterized by broad generality, olefin stereospecificity,<sup>1,2</sup> and a high degree of relative stereoselectivity [with allylic alcohols (ethers),<sup>3–5</sup> acetals,<sup>6</sup> and enol ethers<sup>7</sup>]. Indeed, the strong directing effect of hydroxyl groups was recognized early on<sup>3</sup> and has both preparative<sup>4</sup> and mechanistic significance.<sup>5</sup> Despite the synthetic importance of this reaction, a detailed mechanistic understanding and a structural characterization of the cyclopropanating species are lacking. Early studies by Simmons provided indirect evidence for the existence of a "ZnCH<sub>2</sub>I" moiety in the active cyclopropanation agent.<sup>1,2</sup> Wittig came to similar conclusions from extensive investigations with the reagents prepared from CH<sub>2</sub>N<sub>2</sub>/ZnX<sub>2</sub>.<sup>8</sup> Since then, much effort has been expended in the development of new synthetic modifications but the structure of the reagents remains unclear.<sup>1,9</sup> Continued current interest



**Figure 1.** ORTEP view of the two independent molecules of **4** (35% probability ellipsoids).

#### Scheme 1



**Table I.** Selected Bond Lengths and Angles for **4**

Bond Lengths, Å					
Zn(1)–O(1)	2.103 (10)	Zn(1)–C(13)	1.92 (2)	I(1)–C(13)	2.21 (2)
Zn(1)–O(2)	2.20 (1)	Zn(1)–C(14)	1.98 (2)	I(2)–C(14)	2.16 (2)
Zn(2)–O(21)	2.20 (1)	Zn(2)–C(33)	2.01 (2)	I(3)–C(33)	2.15 (2)
Zn(2)–O(22)	2.231 (10)	Zn(2)–C(34)	2.02 (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(34)	107.4 (5)		
O(2)–Zn(1)–C(13)	107.9 (6)	O(22)–Zn(2)–C(33)	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(1)	3.513 (2)	Zn(2)–I(3)	3.525 (2)
Zn(2)–I(2)	4.342 (3)	Zn(1)–I(2)	3.350 (3)	Zn(2)–I(4)	3.329 (2)

<sup>†</sup> Dedicated to Professor Dr. Albert Eschenmoser on the occasion of his 65th birthday.

<sup>‡</sup> Correspondence author for inquiries concerning the X-ray structure determination.

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in cyclopropanes<sup>10</sup> combined with the burgeoning field of catalytic asymmetric synthesis using organozinc reagents<sup>11</sup> prompted us to study the structure of (halomethyl)zinc compounds. We report herein spectroscopic studies of the bis(halomethyl)zinc cyclopropanation reagents as well as the first X-ray crystal structure analysis of an (iodomethyl)zinc compound.

We chose to study bis(halomethyl)zinc reagents (ICH<sub>2</sub>)<sub>2</sub>Zn (**1**) and (ClCH<sub>2</sub>)<sub>2</sub>Zn (**2**) (prepared by the method of Furukawa<sup>12</sup> from Et<sub>2</sub>Zn and CH<sub>2</sub>I<sub>2</sub> or ICH<sub>2</sub>Cl<sup>13</sup>) for three reasons: (1) the reaction mixtures were expected to be homogeneous, (2) the amount of each educt could be precisely controlled, and (3) generation of (ICH<sub>2</sub>)<sub>2</sub>Zn from Et<sub>2</sub>Zn avoids potential "Schlenk-type" equilibria (with ICH<sub>2</sub>ZnI and ZnI<sub>2</sub>) thought to be important in the reagent derived from Zn(Cu) and CH<sub>2</sub>I<sub>2</sub>.<sup>1</sup>

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Table II. NMR Data for 4–6<sup>a</sup>

compd	<sup>1</sup> H NMR, ppm (δΔ) <sup>b</sup>			<sup>13</sup> C NMR, ppm (δΔ) <sup>b</sup>		
	XCH <sub>2</sub> Zn	CH <sub>3</sub> O	CH(H <sub>2</sub> O)	XCH <sub>2</sub> Zn	CH <sub>3</sub> O	CH(H <sub>2</sub> O)
4	1.49	3.15, 3.25	3.16, 3.44	-18.50	58.32, 61.58	87.36, 91.14
5	1.40	3.00 (-0.11)	2.95 (-0.37)	-19.67 <sup>c</sup>	59.98 (1.37)	70.45 (-1.72)
6	2.75	3.03 (-0.08)	3.04 (-0.28)	29.58 <sup>d</sup>	59.38 (0.77)	70.82 (-1.35)

<sup>a</sup> NMR spectra for 4–6 were taken in benzene-*d*<sub>6</sub> at 500 (<sup>1</sup>H) and 125 MHz (<sup>13</sup>C). <sup>b</sup> δΔ = δ<sub>obs</sub> - δ<sub>DME</sub>. Negative values are upfield shifts. <sup>c</sup> <sup>1</sup>J<sub>CH</sub> = 133 Hz. <sup>d</sup> <sup>1</sup>J<sub>CH</sub> = 132 Hz.

Initial efforts to study the reagent in nonpolar solvents (hexane, toluene) were hampered by the instability of this species at ambient temperatures.<sup>1,2,12</sup> Gratifyingly, addition of 1 equiv of a glycol bisether (L) provided reasonably stable, homogeneous solutions of (ICH<sub>2</sub>)<sub>2</sub>Zn·L.<sup>14</sup> After a brief survey of various candidates, we found that the complex 4, formed from 1 and the (1*S*,2*R*,3*S*)-bornanediol-derived bisether (-)-3<sup>15</sup> (Scheme I), deposited crystals suitable for X-ray analysis. Complex 4 is, to the best of our knowledge, the first (iodomethyl)zinc compound to be characterized crystallographically and spectroscopically.<sup>16</sup>

Complex 4 crystallizes as a monomer with two independent molecules in the unit cell.<sup>17</sup> Ignoring the C(8) and C(28) methyl groups at the bridgehead of the ligand, the two subunits are related by a pseudoinversion center. No intermolecular contacts were evident; the shortest separation between the independent molecules was (3.93 Å),<sup>18</sup> as depicted in Figure 1. The noteworthy bond lengths and angles are collected in Table I. The two molecules are very similar in their bonding details. Molecule A [Zn(1)] has Zn–C 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. This range compares favorably with the range of Zn–C bond lengths reported for other Zn–Me and Zn–Et compounds (1.89–1.98 Å).<sup>19</sup> The C–I bond lengths are normal for sp<sup>3</sup> carbon atoms<sup>20</sup> and the Zn–C–I bond angles [107.4 (8)–116.1 (9)°] are comparable to those found in the previous X-ray analyses of M–CH<sub>2</sub>I compounds, [Pt(CH<sub>2</sub>I)(PPh<sub>3</sub>)<sub>2</sub>]<sup>21</sup> [Pt–C–I = 110.5 (9)°], [Fe(CH<sub>2</sub>I)(P(O-*i*-Pr)<sub>3</sub>)(CO)<sub>2</sub>]<sup>22</sup> [Fe–C–I = 120 (1)°] and N(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>GeC–H<sub>2</sub>I [Ge–C–I = 115.9 (9)°].<sup>23</sup> The normal linear geometry of dialkylzincs<sup>9</sup> is clearly perturbed into a distorted tetrahedron (C–Zn–C angles ca. 138° and O–Zn–O angles ca. 72°) as a result of complexation.<sup>24</sup> The conformation of the Zn(CH<sub>2</sub>I)<sub>2</sub> units can be understood in terms of the generalized anomeric effect.<sup>25</sup>

Both iodomethyl groups are staggered about the Zn–C bonds but in a different way. In the endo iodomethyl groups, the C–I bonds bisect the O–Zn–O angles whereas in the exo groups they are gauche (+sc and –sc) because of steric interactions with the C(10) and C(30) methyl groups of the ligand. An intriguing consequence of this conformation is the distinctly smaller Zn–C–I angles and shorter Zn–I distances for the exo compared to the endo iodomethyl groups (Table I). This close contact (within the van der Waals radii)<sup>18</sup> is reminiscent of the internal activation proposed by Simmons in the methylene-transfer step.<sup>2</sup>

The <sup>1</sup>H NMR spectrum of 4 in benzene-*d*<sub>6</sub> displayed the diastereotopic iodomethylene protons as a single AB quartet at 1.49 ppm, while in the <sup>13</sup>C NMR spectrum, the corresponding carbons appeared as a single peak at -18.50 ppm, despite the fact that these nuclei in 4 are also diastereotopic. This equivalence of the iodomethyl groups on the NMR time scale is due to dynamic complexation of the zinc unit. To gain further insight into the nature of bis(halomethyl)zinc species in solution, a spectroscopic investigation of the dimethoxyethane complexes (ICH<sub>2</sub>)<sub>2</sub>Zn·DME (5) and (ClCH<sub>2</sub>)<sub>2</sub>Zn·DME (6) was undertaken.<sup>26a</sup> Treatment of a 1:1 mixture of Et<sub>2</sub>Zn and DME in benzene-*d*<sub>6</sub> at 0 °C with 2 equiv of CH<sub>2</sub>I<sub>2</sub> quickly and cleanly generated 5, while treatment with 2 equiv of ICH<sub>2</sub>Cl generated 6 in a similar manner.<sup>13</sup> Relevant spectral data are collected in Table II. Particularly notable are the chemical shifts of the zinc-bound methylenes. In 5, this unit appeared at 1.40 (<sup>1</sup>H) and -19.67 ppm (<sup>13</sup>C), while in 6 it appeared at 2.75 (<sup>1</sup>H) and 29.58 ppm (<sup>13</sup>C). These data, along with the <sup>1</sup>J<sub>CH</sub><sup>27</sup> for 5 and 6 suggest that the C–X and C–Zn bonds are still intact in solution.<sup>8b</sup> Complexation of the bis-(halomethyl)zinc species was evident from the significant changes in chemical shifts for the DME ligand (δΔ, Table II).<sup>26b</sup> This association between DME and 1 was dynamic at room temperature. When a 2:1:2 mixture of DME/Et<sub>2</sub>Zn/CH<sub>2</sub>I<sub>2</sub> was examined by <sup>1</sup>H and <sup>13</sup>C NMR, only one type of DME molecule was observed corresponding to the average of free DME and 5.

As might be expected from the electrophilic nature of the Simmons–Smith and Furukawa reagents,<sup>1,2,12</sup> 4 and 5 are less reactive toward olefins than is (ICH<sub>2</sub>)<sub>2</sub>Zn. This deceleration due to DME complexation can be understood as a saturation of the empty orbitals on zinc, which are otherwise necessary to polarize the C–I bond. Accordingly, the remarkable rate acceleration and stereodirecting effects of allylic alcohols and ethers<sup>3–5</sup> should be interpreted as a complexation-induced proximity effect<sup>28</sup> and not an intrinsic activation of the reagent.<sup>26</sup> The structural information from this study provides valuable insights into the nature of the cyclopropanating species, which is necessary for the development of new stereoselective methylene-transfer reagents.

**Acknowledgment.** We are grateful to the National Institutes of Health (GM-30938) and the National Science Foundation (Presidential Young Investigator Award CHE 8451321) for support of this project. Matching funds were provided by the Upjohn Co. and Stuart Pharmaceuticals. S.E.D. acknowledges support from the Alexander von Humboldt Foundation for a

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Senior Scientist Award (1990).

**Supplementary Material Available:** Procedure for the preparation of **4**, listings of crystal and positional parameters, bond lengths, angles, van der Waals contacts, and torsional angles, and ORTEP diagrams (28 pages). Ordering information is given on any current masthead page.

### Cleavage of the N–N Bond in a High-Oxidation-State Tungsten or Molybdenum Hydrazine Complex and the Catalytic Reduction of Hydrazine

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In spite of a vast amount of research on nitrogenases<sup>1</sup> and isolable transition-metal dinitrogen complexes,<sup>2</sup> few details are known about how the N–N bond of dinitrogen is cleaved to give ammonia. Explanations involving enzymes focus on bound diazene and hydrazine as intermediates.<sup>1</sup> Synthetic and mechanistic studies on low-oxidation-state "Chatt-type" complexes,  $M(N_2)_2L_4$  ( $M = Mo$  or  $W$ ;  $L$  = a phosphine), and related derivatives suggest that (i) a single metal center is sufficient for reducing dinitrogen stoichiometrically to ammonia if an open coordination site is available; (ii) a hydrazido(2-) complex ( $M=NNH_2$ ) is a key intermediate; and (iii) the N–N bond is cleaved either in a  $M=NNH_3$  or  $M=NHNH_2$  intermediate to give a  $M=N$  or  $M=NH$  species, respectively.<sup>3</sup> We report here some results which suggest that the N–N bond is cleaved in coordinated hydrazine in relatively high oxidation state complexes having the  $MCp^*Me_3$  core.

Complexes of the type  $MCp^*Me_3(OTf)$  ( $M = Mo^4$  or  $W^5$ ;  $OTf = OSO_2CF_3$ ;  $Cp^* = \eta^5-C_5Me_5$ ) react with 1 equiv of hydrazine to give what are postulated to be  $\eta^2$ -hydrazine complexes (**1a** and **1b**; eq 1).<sup>6</sup> A monomeric structure containing  $\eta^2$ -hydrazine is proposed on the basis of the following: (i) the structure of  $[WCp^*Me_3(\eta^2-NHNH_2)]^+$  is similar to the structure shown in eq 1;<sup>7</sup> (ii) <sup>15</sup>N NMR studies suggest that the hydrazine ligand in  $[WCp^*Me_3(NH_2NH_2)]^+$  is bound in an  $\eta^2$  fashion;<sup>8</sup> (iii) two  $\eta^2$ - $NH_2NRR'$  complexes have been structurally characterized;<sup>9</sup>

Table I. Stoichiometric Reductions To Give Ammonia

complex	NH <sub>3</sub> yield, equiv	conversion, %
$[Mo](N_2H_4)^+ b,c$	1.80 (3) <sup>d</sup>	90 <sup>e</sup>
$[W](N_2H_4)^+ c$	1.84 (2)	92
$N_2H_4^{a,c}$	0.12 (4)	6
$[Mo](OTf)^c$	0.05 (2)	<3
$[W](OTf)^c$	0.05 (2)	<3
$[W](NNH_2)^{a,b}$	1.80 (3)	90

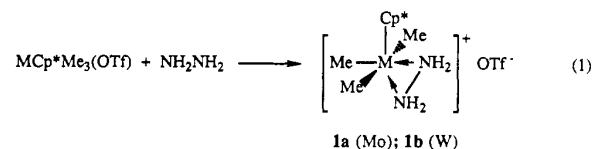
<sup>a</sup> Zn/Hg with base distillation. <sup>b</sup> Zn/Hg without base distillation. <sup>c</sup>  $CoCp_2$  with base distillation. <sup>d</sup> Number of experiments. <sup>e</sup> Variation  $\pm 3\%$  between experiments.

Table II. Catalytic Reductions of Hydrazine to Ammonia

complex	added N <sub>2</sub> H <sub>4</sub> , equiv	NH <sub>3</sub> yield, equiv	conversion, %
$[Mo](N_2H_4)^+$	2 (2) <sup>a</sup>	5.70 (6) <sup>b</sup>	95
	3 (4)	6.88 (8)	86
	4 (3)	8.70 (10)	87
$[W](N_2H_4)^+$	2 (2)	5.88 (6)	98
	3 (4)	7.28 (8)	91
	4 (3)	8.30 (10)	83
$[W](NNH_2)$	3 (2)	6.72 (8)	84
	6 (1)	10.92 (14)	78

<sup>a</sup> Number of experiments. <sup>b</sup> Maximum yield possible.

and (iv) conductivity studies on **1b** in nitromethane suggest that it is a 1:1 electrolyte analogous to  $[WCp^*Me_3(\eta^2-NH_2NH_2)]^+ \cdot$ .<sup>10,18</sup>



Both **1a** and **1b** are reduced by zinc amalgam or cobaltocene in THF in the presence of 2,6-lutidine hydrochloride (lutHCl) to give ammonia in >90% yield (Table I).<sup>11</sup> Since  $[WCp^*Me_3(\eta^2-NH_2NH_2)]^+$  is reduced by sodium amalgam in the absence of lutHCl to give  $WCp^*Me_3(NH)^{12}$  and ammonia in at least 70% yield, we propose that the N–N bond is cleaved in  $WCp^*Me_3(NH_2NH_2)$ . In the absence of added protons, an attractive mechanism for N–N cleavage is overall migration of an  $H_\alpha$  proton to  $N_\beta$ , either in an  $\eta^1$ -hydrazine ligand (eq 2) or (equivalently) as shown in eq 3.<sup>13</sup> In the presence of protons, the  $N_\beta$  electron pair could be protonated in  $\eta^1$ -hydrazine (eq 2) or in one of the amido ligands in  $WCp^*Me_3(NH_2)_2$ . In all scenarios, ammonia would be formed smoothly since the required two electrons are provided by the metal.

Hydrazine can be reduced catalytically to ammonia in high yield by  $[WCp^*Me_3(NH_2NH_2)]^+$  or  $[MoCp^*Me_3(NH_2NH_2)]^+$  under conditions analogous to those employed for stoichiometric reductions (Table II). Catalytic reduction of hydrazine to ammonia

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(6) Experimental details, NMR or EPR data, and elemental analyses can be found in the supplementary material. Hydrazine was obtained from Aldrich and dried with  $CaH_2$ .

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(8) A  $-80^\circ C$  <sup>15</sup>N NMR spectrum of  $[WCp^*Me_3(\eta^2-^{15}NH_2-^{15}NH_2)]^+PF_6^-$ , prepared by treating  $[WCp^*Me_3]^+PF_6^-$  with <sup>15</sup>NH<sub>2</sub><sup>15</sup>NH<sub>2</sub>, shows a single nitrogen resonance at  $\delta$  29.7 (vs liquid NH<sub>3</sub>) with  $J_{NH} = 80$  and 83 Hz and  $J_{NW} < 5$  Hz.

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(10)  $[WCp^*Me_3(\eta^2-NH_2NH_2)]^+$  loses methane slowly in nitromethane to give  $[WCp^*Me_3(\eta^2-NHNH_2)]^+$ , which is stable in nitromethane.  $\Delta_0$  (units  $\Omega^{-1} mol^{-1} cm^{-2}$ ) was determined to be 83 for  $[Cp^*WMe_3(\eta^2-NH_2NH_2)]OTf$  and 93 for  $[Cp^*WMe_3(\eta^2-NH_2NH_2)]PF_6$ .<sup>6</sup>

(11) (a) Reductions were carried out in THF at room temperature under N<sub>2</sub> using 12 equiv of Zn/Hg and 16 equiv of lutidine hydrochloride. The reaction mixture was stirred for approximately 15 h. See supplementary material for a complete description of the workup procedure. The ammonia was quantified by the indophenol method.<sup>11b</sup> (b) Chaney, A. L.; Marbach, E. P. *Clin. Chem. (Winston-Salem, N.C.)* **1962**, *8*, 130.

(12) Addition of 1 or 2 equiv of ammonia to  $MCp^*Me_3(OTf)$  yields  $[MCp^*Me_3(NH_3)]^+OTf^-$  or  $[MCp^*Me_3(NH_3)_2]^+OTf^-$ , respectively ( $M = Mo$  or  $W$ ). Each is deprotonated by excess NEt<sub>3</sub> to give  $MCp^*Me_3(NH_2)$ . In the presence of NEt<sub>3</sub>,  $WCp^*Me_3(NH_2)$  reacts with  $FeCp_2^+PF_6^-$  to yield  $WCp^*Me_3(NH)$  in high yield, we propose via  $[WCp^*Me_3(NH_2)]^+$ . So far  $[WCp^*Me_3(NH_2)]^+$  has not been observed at room temperature by NMR.

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