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Communications

A *gem*-Organodizinc Species Assembled in a Tetrameric Cage

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Summary: Treatment of both polymeric [{(2-pyridyl)(SiMe$_3$)C}SbCl]$_\infty$ and the implied stibene (Sb═C) containing red oil, formed as a result of Me$_3$SiCl elimination from [{(2-pyridyl)(SiMe$_3$)$_2$C}$_2$SbCl], with excess Et$_2$Zn in the presence of tmeda results in the geminal organodizinc chiral cage tetramer [Zn{C(SiMe$_3$)(2-pyridyl)}]$_4$ possessing three-coordinate metal centers, [(tmeda)Et(Cl)Zn] and [(tmeda)Et$_2$Zn].

Main group metal chemistry of the bulky alkyl ligand (2-pyridyl)(SiMe$_3$)$_2$C$^-$ (R) has been extensively investigated.[1-5] The effect of steric hindrance at the ligating C-center combined with the potential for stabilizing N-donation to any metal(loid) center has led to monomeric, subvalent, hypervalent, electron-deficient, low-coordinate, and ionic species.

Another important aspect of the ligand is the potential for the low-energy β-elimination of SiMe$_3$Cl from ligated metal(loid) chlorides. In exploring this process, we recently reported the synthesis and characterization of two C-centered *geminal* organodimetallics: (i) the distibine polymer [{(2-pyridyl)(SiMe$_3$)C}SbCl]$_\infty$, **1**,[6] formed from the mild thermolysis of RSbCl$_2$, and (ii) an Al(III)/Sb(III) metallocycle, **2** (Figure 1), formed from the addition of Me$_3$Al across an implied C═Sb double bond arising from the low-temperature elimination of Me$_3$SiCl from R$_2$SbCl.[7] In attempting the analogous reaction with Et$_2$Zn, surprisingly, we did not isolate the expected Sb/Zn species but the completely novel *gem*-organodizinc complex **3**, Scheme 1. We have also found that it is possible to obtain the same product from the low-temperature addition of Et$_2$Zn to a solution of **1**.

There is significant interest in *geminal* organodimetallic species due to their potential in developing new reaction pathways in fine organic syntheses.[8] However, while a few 1,1 dilithio and dimagnesio complexes[9] have been examined, crystallographically no *gem*-organodizinc species have been previously structurally authenticated. Indeed, only recently has the structure of a 1:2 organozinc species been reported, notably that of dimeric *o*-phenylenezinc.[10]

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(1) van den Ancker, T. R.; Raston, C. L. *J. Organomet. Chem.* **1995**, *500*, 289 and references therein.

(2) Engelhardt, L. M.; Kynast U.; Raston, C. L.; White, A. H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 681.

(3) Jones, C.; Engelhardt, L. M.; Junk, P. C.; Hutchings, D. S.; Patalinghug, W. C.; Raston C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1991**, 1560.

(4) Papsergio, R. I.; Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans* **1987**, 3085.

(5) Henderson, M. J.; Papasergio, R. I.; Raston, C. L.; White, A. H.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1986**, 672.

(6) Andrews, P. C.; Raston, C. L.; Skelton, B. W.; Tolhurst, V.-A.; White, A. H. *Chem. Commun.* **1998**, in press.

(7) Andrews, P. C.; Raston, C. L.; Skelton, B. W.; White, A. H. *Chem. Commun.* **1997**, 1183.

(8) Marek, I.; Normant, J.-F. *Chem. Rev.* **1996**, *96*, 3241−3267.

(9) Gais, H. J.; Vollhardt, J.; Günther, H.; Moskau, D.; Lindner, H. J.; Braun, S. J. *Am. Chem. Soc.* **1988**, *110*, 978. Uhl, W.; Layh, M.; Massa, W. *Chem. Ber.* **1991**, *124*, 1511. Hogenbirk, M.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *J. Am. Chem. Soc.* **1992**, *114*, 7302.

(10) Goedheijt, M. S.; Nijbacker, T.; Akkerman, O. S.; Bickelhaupt, F.; Veldman, N.; Spek, A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1550.

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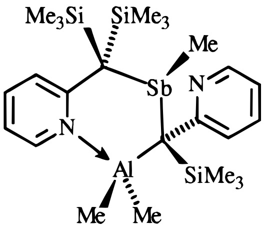

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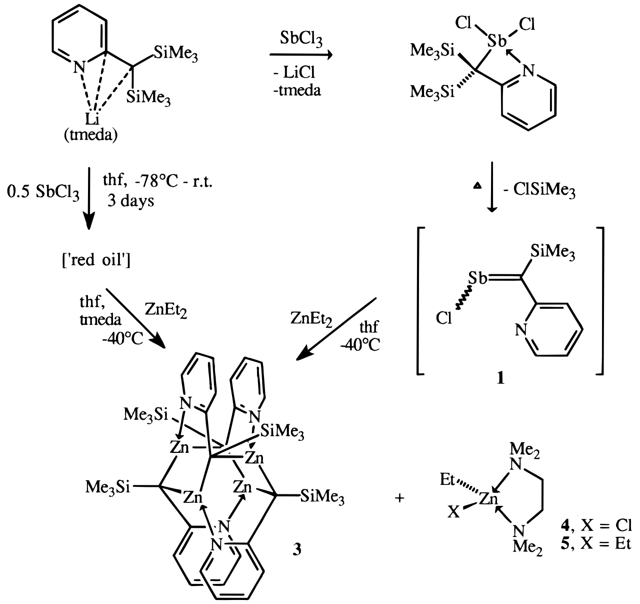
Figure 1. Structure of **2**.

Scheme 1



The specific 1:1 reaction of crystalline RLi(tmeda) and $SbCl_3$ in thf gives, after 3 days of stirring at room temperature and subsequent extraction into and crystallization from CH_2Cl_2, rodlike crystals of **2** derived from the elimination of $SiMe_3Cl$ and the [2 + 2] self-cycloaddition of the stibene (ClSb=C) intermediate.[6]

The addition to **1,** at −40 °C, of a slight excess of a thf/tmeda (*N*,*N*,*N*′,*N*′-tetramethylenediamine) solution of Et_2Zn resulted in three crystalline products,[11] which were isolated on the basis of their slightly differing solubilities in hexane/thf: first colorless rods of [(tmeda·Et(Cl)Zn], **4**, followed by colorless needles of [tmeda·Et_2Zn], **5**, and finally yellow rodlike crystals of the *geminal* diorganozinc tetramer [(2-pyridyl)($SiMe_3$)CZn]$_4$, **3**. However, complete separation of the crystals can only be guaranteed if separated manually.

Complex **3** arises from the metathetical exchange of two ethyl groups for the (2-pyridyl)($SiMe_3$)C^{2-} moiety. Formation of **4** accounts for the residual chloride on **1**, while crystals of **5** were obviously obtained as a result of the nonstoichiometric addition of Et_2Zn. Presumably, the residual antimony-containing species is volatile Et_3Sb. All three crystals are sensitive to atmospheric moisture with an important aspect of previously unreported **5** being that it is nonpyrophoric. Though difficult to maximize, the yield of **3** is low, ca. 20%, and this seems to be indicative of an inherent instability in solution over protracted periods of time. We found that if the solution is left at 4 °C or above for greater than 5 or 6 days, we could not isolate **3**.

As we have previously reported, the specific 2:1 reaction of crystalline RLi(tmeda) and $SbCl_3$ does not give the target monochloride species, $[R_2SbCl]_n$, but, due to the spontaneous elimination of Me_3SiCl, an implied stibene intermediate as the main component of an intractable red oil. Addition of Me_3Al to this red oil results in the dimetallic heterocycle, **2**.[7] However, addition, at low temperature, of a thf solution of Et_2Zn to a thf solution of the red oil results in crystals of **3** and **4**, at 4 °C.[12] Mechanistically this is difficult to explain. However, it suggests that polymeric or, indeed, oligomeric derivatives of $(RSbCl)_n$ also are present in the red oil as well as the implied stibene species, (2-pyridyl)($SiMe_3$)C=Sb−C($SiMe_3$)$_2$(2-pyridyl). As yet, we have found no evidence of the Zn analogue of **1** being formed. The fact that **4** is present indicates that all of the tmeda is not removed in vacuo with the thf.

Single crystals of **3** (Figure 2), **4** (Figure 3), and **5** (Figure 4) suitable for X-ray crystal structure determinations were obtained from a hexane/thf solution at 4 °C.[13,14] Complex **3** is comprised of tetrameric arrays of {(2-pyridyl)($SiMe_3$)C}Zn with crystallographically imposed S_4 symmetry, with Zn{C($SiMe_3$)(2-pyridyl)} as the asymmetric unit. In these cluster/caged molecules, each ligand bridges two metal centers through the *gem*-C centers and bridges a third metal center through the N-donor group such that each metal center is three coordinate. The metal and *gem*-C centers form an eight-membered ring. The trimethylsilyl groups are directed away from the center of the cage, at right angles to the unique axis, whereas the pyridyl groups shroud the two

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[11] Synthesis of $(RSbCl)_\infty$ (**1**):[6] $RSbCl_2$ was prepared as previously described.[3] The in vacuo removal of Et_2O from this reaction followed by the addition of toluene, subsequent filtration to remove LiCl, and heating to 50 °C for 4 h leads to the precipitation of a pale yellow powder. Removal of toluene and recrystallization at 4 °C from thf/toluene results in bright yellow rodlike crystals of **1**. (ii) Alternatively, the metathesis reaction of RLi and $SbCl_3$ can be carried out in thf at −78 °C, allowed to warm slowly to room temperature, and stirred for 3 days. The thf is removed in vacuo, and a CH_2Cl_2 extraction of the remaining solids allows for the crystallization of **1**, again at 4 °C. Yield: 63% (not maximised). Mp: 201−203 °C. Synthesis of [{(2-pyridyl)($SiMe_3$)C}Zn]$_4$ (**3**): Yellow crystals of $(RSbCl)_\infty$ (1.60 g, 5.0 mmol), prepared as previously described,[6] were dissolved in thf (10 mL) and cooled to −40 °C. To this was added a cooled thf/tmeda (10:1, 10 mL) solution of Et_2Zn (1.54 g, 12.5 mmol), and the reaction mixture was allowed to warm slowly to ambient temperature, at which point it was stirred for a further 2 h. Thf was removed in vacuo, and a hexane/thf (9:1) mixture was added; the resulting pale orange solution was cooled to 4 °C, initially yielding a large crop of yellow crystals of **3, 4**, and **5**. Characterization of [Zn{C($SiMe_3$)(2-pyridyl)}]$_4$: (**3**): yield 0.29 g (1.2 mmol, 24%); mp 189 °C (decomp); ^1H NMR (400 MHz, C_6D_6, 298 K) δ 7.35 (d, 1H), 7.17 (d, 1H), 6.69 (t, 1H), 5.96 (t, 1H), 0.41 (s, 9H); ^{13}C NMR (100.6 MHz, C_6D_6, 298 K) δ 179.2, 144.87, 135.7, 124.2, 112.4, 61.1 (Py−*C*−Si), 3.5 ($SiMe_3$). Elemental analysis correct for $C_{36}H_{52}N_4Si_4Zn_4$. Characterization of [(tmeda)ZnClEt] (**4**): yield 1.10 g (4.6 mmol); mp 115−116 °C; ^1H NMR (400 MHz, C_6D_6, 298 K) δ 1.98 (br s, 4H), 1.78 (br s, 12H), 1.64 (t, 3H), 0.38 (q, 2H); ^{13}C NMR (100.6 MHz, C_6D_6, 298 K) δ 56.5, 46.9, 13.8 (CH_3CH_2Zn), −1.55 (CH_2Zn). Elemental analysis correct for $C_8H_{21}ClN_2Zn$. Characterization of [(tmeda)Et_2Zn] (**5**): yield 0.4 g (1.7 mmol); mp 32−33 °C ^1H NMR (400 MHz, C_6D_6, 298 K) δ 1.89 (s, 6H), 1.75 (s, 2H), 1.72 (t, 3H, CH_3CH_2Zn, $J = 3$ Hz), 1.19 (q, 2H, CH_2Zn, $J = 3$ Hz); ^{13}C NMR (100.6 MHz, C_6D_6, 298 K) δ 56.7, 46.3, 14.7 (CH_3CH_2Zn), 1.4 (CH_2Zn). Elemental analysis correct for $C_{10}H_{26}N_2Zn$.

[12] A thf (10 mL) solution of Et_2Zn was added to a cooled, −40 °C, thf (10 mL) solution of the red oil (6 mmol, based on consumption of R), prepared as described.[7] This was allowed to warm to ambient temperature over 4 h giving an orange solution. The removal of one-half of the quantity of thf in vacuo and addition of hexane (3 mL) followed by cooling to 4 °C gave a small crop of both **3** (typical yield ca. 15%) and **4**.

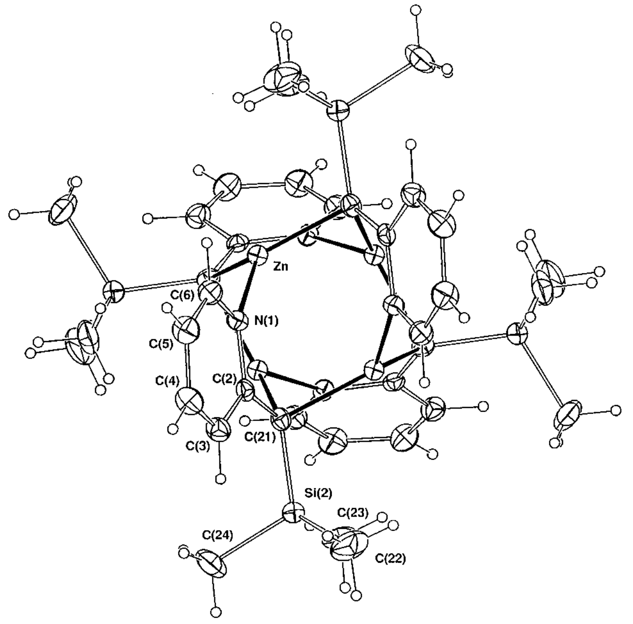

Figure 2. Projection of [{(2-pyridyl)(SiMe$_3$)C}Zn]$_4$, **3**. Important bond distances (Å) and angles (deg): Zn−N 2.031(5), Zn−C(21′, 21″) 2.040(7), 2.024(6), Zn···Zn 2.671(1), C(2)−C(21) 1.466(9), C(21)−Si 1.844(7); N(1)−Zn−C(21′,21″) 111.3(2), 114.6(2), C(21′)−Zn−C(21″) 128.8(3), Zn″−C(21)−Zn‴ 82.2(2), C(2)−C(21)−Si(2),Zn″,Zn‴ 119.1(5), 109.3(5), 112.9(5), Si(2)−C(21)−Zn″,Zn‴ 109.8(3), 117.1(3). Prime denotes $^3/_2 - x$, $^3/_2 - y$, z. Double prime denotes y, $^3/_2 - x$, $^1/_2 - z$. Triple prime denotes $^3/_2 - y$, x, $^1/_2 - z$.

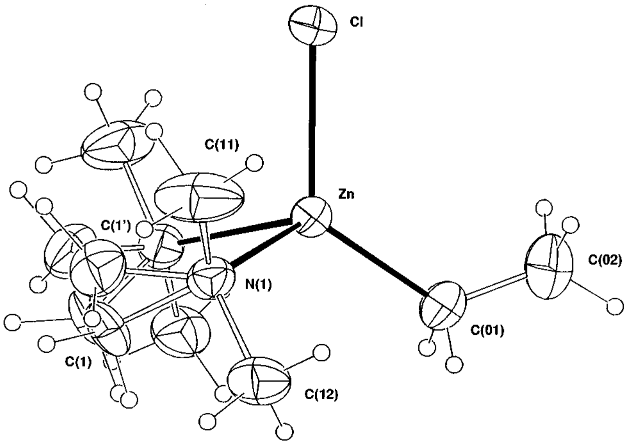

Figure 3. Molecular structure of [(tmeda)ZnClEt], **4**.[19]

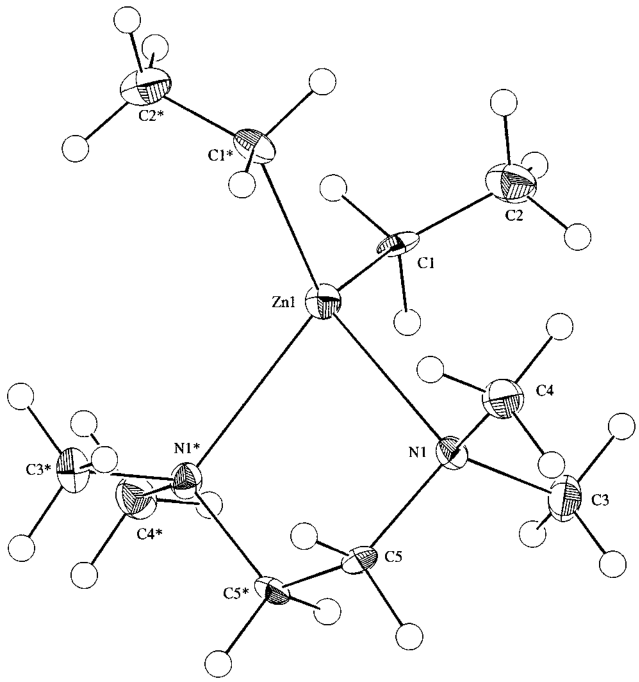

Figure 4. Molecular structure of [(tmeda)Et$_2$Zn], **5**.[19]

ends of the cage close to the principal axis. The dihedral angle between pairs of pyridyl planes is 51.4(3)°.

The *gem*-C centers are tetrahedrally distorted, most strikingly at the Zn−C−Zn angle, 82.2(2)°. The three-coordinate metal centers are distorted from a regular trigonal planar environment by (i) a departure of the metal center from the plane of its nearest neighbors by 0.269(2) Å, with the sum of the angles at the metal center being 354.7°, and (ii) variation of angles within the plane, 111.3(2)−128.8(3) Å. In this structure, the favored four coordination of zinc by additional donor groups is blocked by the pendant trimethylsilyl groups and geometrical constraints prohibit electron-deficient bonding, which is sporadically found in organozinc chemistry.[15] The noted instability of **3** may result from the exposed nature of the Zn centers and the fact that they are only three coordinate.

The Zn−C distances, mean 2.032 Å, are within the range for Zn−C-alkyl distances, with Zn−C in **4** and **5**, for example, at 1.94(1) and 2.17(2) Å respectively, for [R$_2$Zn] at 2.070 Å (mean),[5] and in the compound closely related to this [{CH$_2$(SiMe$_2$)$_2$C(H)}Zn(Cl)(tmeda)] at 1.873(6) Å.[16] The Zn−N distance of 2.138(7) Å is similar to that in [{(6-methyl-2-pyridyl)(SiMe$_3$)N}Zn]$_2$, 2.126 Å,[17] but is significantly shorter than that in [R$_2$Zn], 2.294 Å (mean), which might be expected due to the strained four-membered chelate rings.[5] The Zn···Zn

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(13) [Zn{C(SiMe$_3$)(2-pyridyl)}]$_4$ (**3**): C$_{36}$H$_{52}$N$_4$Si$_4$Zn$_4$, tetragonal, $P4_2/n$ (C^4_{4h}, No. 86), $a = b = 13.974(7)$ Å, $c = 10.938(2)$ Å, $V = 2136(2)$ Å^3, $F(000) = 944$, $\rho_{\text{calc}} = 1.422$ g cm^{-3}, μ(Mo Kα) = 23.6 cm^{-1}, A^* (min, max) 1.51, 2.14 (Gaussian), 0.36 × 0.18 × 0.65 mm^3, $Z = 2$, four-circle diffractometer, Mo Kα radiation ($\lambda = 0.7107_3$ Å), $T = 293$ K, 1743 unique reflections (1178 observed, $I > 3.0\sigma(I)$, $2\theta_{\max} = 50°$, $R = 0.052$, $R' = 0.056$ (statistical weights). [(tmeda)Et(Cl)Zn], **4**: C$_8$H$_{21}$ClN$_2$Zn, orthorhombic, *Pmna* ($D^{16}{}_{2h}$, No. 62), $a = 12.696(10)$ Å, $b = 8.852(3)$ Å, $c = 11.293(2)$ Å, $V = 1269(1)$ Å^3, $F(000) = 520$, $\rho_{\text{calc}} = 1.288$ g cm^{-3}, μ(Mo Kα) = 21.1 cm^{-1}, A^*(min, max) 1.68, 1.83 (Gaussian), 0.55 × 0.45 × 0.45 mm^3, $Z = 4$, Enraf-Nonius CAD4 diffractometer, Mo Kα radiation, $T = 293$ K, 1551 unique reflections (741 observed, $I > 3.0\sigma(I)$, $2\theta_{\max} = 50°$, $R = 0.061$, $R' = 0.063$ (statistical weights). Solutions solved were by direct methods.[14] Crystals of **3** were twinned and all 0*kl* reflections given a separate scale factor, which was refined separately. The ethyl group in **3** is disordered across a mirror plane. Hydrogen atoms were included as invariants. [(tmeda)Et$_2$Zn] (**5**): C$_{10}$H$_{26}$N$_2$Zn, monoclinic, *C*2/*c* (No. 15), $a = 12.729(5)$ Å, $b = 7.941(3)$ Å, $c = 13.398(5)$ Å, $\beta = 105.44(3)°$, $V = 1305.3(8)$ Å^3, $F(000) = 520$, $\rho_{\text{calc}} = 1.22$ g cm^{-3}, μ(Mo Kα) = 18.49 cm^{-1}, A^*(min, max) 0.84, 1.00 (Gaussian), 0.30 × 0.30 × 0.15 mm^3, $Z = 4$, Nicolet diffractometer, Mo Kα radiation, $T = 173$ K, 1860 unique reflections (382 observed, $I > 3.0\sigma(I)$, $2\theta_{\max} = 45°$, $R = 0.032$, $R' = 0.031$. All hydrogen atoms were calculated. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-100630. Copies of the data can be obtained from free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: Int. code +(1223) 336-336-033. E-mail: deposit@chemcrys.cam.ac.uk).

(14) *XTAL User's Manual*−*version 3.0*; Hall, S. R., Stewart, M., Eds.; The Universities of Western Australia and Maryland 1990.

(15) Markies, P. R.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *Organometallics* **1990**, *9*, 2243.

(16) Rademacher, B.; Schwarz, W.; Westerhausen, M. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1395.

distances are surprisingly short at 2.671(1) Å, which is significantly shorter than the corresponding distance in [{PhZn(μ-Ph)}$_2$], 2.685(1) Å,[15] and close to that of metallic zinc, 2.669(4) Å,[18] which is indicative of some intermetallic bonding.

Interestingly, the structure of **3** relates to that of [{-(2-pyridyl)(SiMe$_3$)C(H)}Cu]$_4$, crystallizing in the same space group with similar cell dimensions with the same overall S_4 symmetry of the cage.[4] The differences are the attachment of one carbon and an N center to each copper, the change in valency at carbon, and the formal oxidation state of the metal. These are offset by the H atom attached to the ligating carbon and the presence of only one metal-to-carbon interaction.

Molecules of **4** lie on mirror planes with distorted tetrahedral metal centers, as expected by the bidentate ligand. The bond distances and angles are similar to those in [(tmeda)ZnCl{C(H)(SiMe$_2$)$_2$CH$_2$}].[16] Molecules of **5** lie on a C_2 symmetry axis, the bond distances and angles being unexceptional (cf. [Me$_2$Zn·tmeda] and [^{t}-Bu$_2$Zn·tmeda]).[20]

Access to a novel cage cluster of a *gem*-organodizinc species now allows for deeper mechanistic and synthetic studies of such complexes. An interesting comparison will be with the zinc carbenoid, [ICH$_2$ZnI], utilized in Simmons−Smith cyclization reactions. The formation of a stibene intermediate (−Sb═C) or an oligomeric analogue also sets the ground rules for using the intermediate for generating *gem*-organodimetallic species of other elements, leading on to potential application in synthesis.

Acknowledgment. This work is supported by the Australian Research Council.

Supporting Information Available: Tables of positional and isotropic displacement parameters, anisotropic displacement parameters, bond lengths, and bond angles (16 pages). Ordering information is given on any current masthead page.

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[17] Engelhardt, L. M.; Jacobsen, G. E.; Patalinghug, W. C.; Skelton, B. W.; Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1991**, 2859.

[18] *CRC Handbook of Chemistry and Physics*, 60th ed.; CRC Press: Boca Raton, FL, 1980.

[19] Key distances (Å) and angles (deg) for **4**: Zn−C, Cl, −N 1.94(1), 2.269(3), 2.138(7); C−Zn−Cl, −N 124.9(4), 116.1(3); N−Zn−Cl, −N 103.8(2), 84.4(3). Key distances (Å) and angles (deg) for **5**: Zn−N(1) 2.294(5), Zn−C(1) 2.17(2); N(1)−Zn−N(1*) 80.7, N(1)−Zn−C(1) 111.1(6), N(1)−Zn−C(1*) 115.1(6).

[20] O'Brien, P.; Hursthouse, M. B.; Motavelli, M.; Walsh, J. R.; Jones, A. C. *J. Organomet. Chem.* **1993**, *449*, 1.