A Novel Rhombohedral Grid Based on Tetraorganodistannoxane as Corner Unit

Ren-Gen Xiong,* Jing-Lin Zuo, and Xiao-Zeng You

Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, 210093, People's Republic of China

Hoong-Kun Fun and S.Shanmuga Sundara Raj

X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 Penang

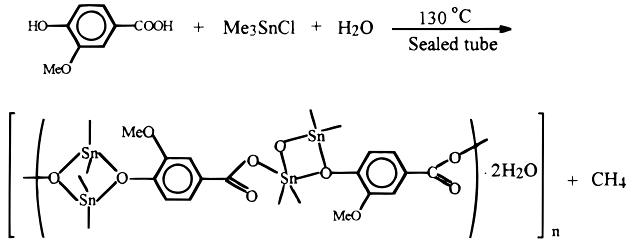
Received March 22, 2000

Summary: Under hydrothermal conditions, the reaction of vanillic acid with trimethyltin chloride gives rise to a novel 2D rhombohedral grid, {([Me$_2$Sn(VA)$_{0.5}$]$_2$O)$_2$·2H$_2$O}$_n$ (**1**), *with a tetraorganodistannoxane as corner unit.*

Introduction

The search for molecular constructs, such as squares, rhomboids, or metal-macrocycles is driven largely by the desire to perform catalysis,[1] host−guest chemistry,[2] enantioselective separation,[3] nonlinear material inclusions,[4] and fluorescent molecular structures or sensors.[5] Most of such structures are based on mononuclear metal ions, which are corner units.[5] Squares containing multinuclear or cluster units, as far as we are aware, are relatively rare.[6,7] Inspired by the pioneering work on one-dimensional organotin polymers containing tetraorganodistannoxane units, explored by Lockhart et al.,[8] we have used a tridentate dianion, VA^{2-} (4-hydroxy-3-methoxybenzoic acid or vanillic acid, HVAH) as the bridging ligand in a reaction with trimethyltin chloride under hydrothermal conditions to construct a novel two-dimensional, rhombohedral neutral grid, {([Me$_2$Sn(VA)$_{0.5}$]$_2$O)$_2$·2H$_2$O}$_n$ (**1**), with tetraorganodistannoxane corner unit. Here, we present its synthesis, crystal structure, and fluorescence. For comparison, a tetraorganodistannoxane unit analogue, ([Me$_2$Sn(BA)]$_2$O)$_2$ (**2**), (HBA = 4-quinolinecarboxylic acid), is also reported.

Scheme 1



1

Results and Discussion

Compounds **1** and **2** were synthesized under hydrothermal conditions by reactions of Me$_3$SnCl with HVAH and HBA, respectively (Schemes 1 and 2).

The presence of the carboxylate group was confirmed by the presence of very strong peaks in their IR spectra at 1737 (m), 1592, 1506, 1369 cm^{-1} for **1** and 1717 (m), 1565, 1376 cm^{-1} for **2**, respectively. Moreover, in the IR spectrum, complex **1** displayed a broad absorption

---

[1] (a) Fujita, M.; Kwon, Y. I.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 1151. (b) Fujita, M. *Chem. Soc. Rev.* **1998**, *27*, 417.

[2] (a) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460. (b) Yaghi, O. M.; Li, H.; Davis, C.; Richardson, D.; Groy, T. L. *Acc. Chem. Res.* **1998**, *31*, 474. (c) Janiak, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1431. (d) Zaworotko, M. J. *Chem. Soc. Rev.* **1994**, *23*, 283. (e) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1895. (f) Müller, A.; Reuter, H.; Dillinger, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311. (g) Hirsch, K. A.; Wilson, S. R.; Moore, J. S. *Chem. Commun.* **1998**, 13.

[3] (a) Olenyuk, B.; Whiteford, J. A.; Stang, P. J. *J. Am. Chem. Soc.* **1996**, *118*, 8221. (b) Stang, P. J.; Olenyuk, B. *Angew Chem., Int. Ed. Engl.* **1996**, *35*, 732. (c) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853. (d) Pu, L. *Chem. Rev.* **1998**, *98*, 2405. (e) Lu, J.; Yu, C.; Niu, T.; Paliwala, T.; Grisci, G.; Somosa, F.; Jacobson, A. J. *Inorg. Chem.* **1998**, *37*, 4637.

[4] (a) Huang, S. D.; Xiong, R.-G. *Polyhedron* **1997**, *16*, 3929. (b) Liu, C.-M.; Xiong, R.-G.; You, X.-Z.; Chen, W. *Acta Chem. Scand.* **1998**, *52*, 1353.

[5] (a) Slone, R. V.; Yoon, D. I.; Calhoun, R. M.; Hupp, J. T. *J. Am. Chem. Soc.* **1995**, *117*, 11813. (b) Fun, H.-K.; Raj, S. S. S.; Xiong, R.-G.; Zuo, J.-L.; Yu, Z.; Zhu, X.-L.; You, X.-Z. *J. Chem. Soc., Dalton Trans.* **1999**, 1711. (c) Benkstein, K. D.; Hupp, J. T.; Stern, C. L. *J. Am. Chem. Soc.*, **1998**, *120*, 12982.

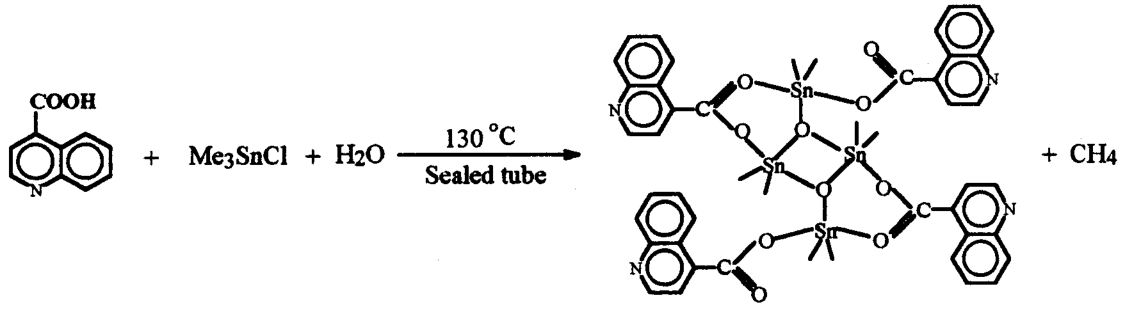
[6] (a) Drain, C. M.; Lehn, J. M. *J. Chem. Soc., Chem. Commun.* **1994**, 2313. (b) Drain, C. M.; Lehn, J. M. *J. Chem. Soc., Chem. Commun.* **1995**, 503. (c) Wang, Z.; Xiong, R.-G.; Foxman, B. M.; Wilson, S. R.; Lin, W. *Inorg. Chem.* **1999**, *38*, 1523. (d) AlQaisi, S. M.; Galat, K. J.; Chai, M.; Ray, D. J., III; Rinaldi, P. L.; Tessier, C. A.; Youngs, W. J. *J. Am. Chem. Soc.* **1998**, *120*, 12149. (e) Lin, W.; Evans, O. R.; Xiong, R.-G.; Wang, Z. *J. Am. Chem. Soc.* **1998**, *120*, 13272. (f) MacGillivray, L. R.; Groeneman, R. H.; Atwood, J. L. *J. Am. Chem. Soc.* **1998**, *120*, 2676. (g) Onitsuka, K.; Yamamoto, S.; Takahashi, S. *Angew. Chem., Int. Ed.* **1999**, *38*, 174. (h) Jones, C. J. *Chem. Soc. Rev.* **1998**, *27*, 289. (i) Hagrman, P. J.; Hagrman, D.; Zubieta, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2638. (j) Cotton, F. A.; Daniels, L. M.; Lin, C.; Morillo, C. A. *J. Am. Chem. Soc.* **1999**, *121*, 4538.

[7] (a) Bhandari, S.; Mahon, M. F.; McGinley, J. G.; Molloy, K. C.; Roper, C. E. E. *J. Chem. Soc., Dalton Trans.* **1998**, 3425. (b) Hill, M.; Malhon, M. F.; McGinley, J. G.; Molloy, K. C. *J. Chem. Soc., Dalton Trans.* **1996**, 835. (c) Goodger, A.; Hill, M.; Mahon, M. F.; McGinley, J. G.; Molloy, K. C. *J. Chem. Soc., Dalton Trans.* **1996**, 847. (d) Hill, M.; Mahon, M. F.; Molloy, K. C. *J. Chem. Soc., Dalton Trans.* **1996**, 1857. (e) Siebel, E.; Ibrahim, A. M. A.; Fischer, R. D. *Inorg. Chem.* **1999**, *38*, 2530.

[8] (a) Lockhard, P. T.; Manders, W. F.; Holt, E. M. *J. Am. Chem. Soc.* **1986**, *108*, 6611. (b) Valle, G.; Peruzzo, V.; Tagliavini, G.; Ganis, P. *J. Organomet. Chem.* **1984**, *276*, 325. (c) Faggiani, R.; Johnson, J. P.; Brown, I. D.; Birchall, T. *Acta Crystallogr.* **1978**, *B34*, 3743. (d) Garner, C. D.; Hughes, B.; King, T. J. *Inorg. Nucl. Chem. Lett.* **1976**, *12*, 859 (e) Graziani, R.; Bombieri, G.; Forsellini, E.; Furlan, P.; Peruzzo, V.; Tagliavini, G. *J. Organomet. Chem.* **1977**, *125*, 43. (f) Vollano, J. F.; Day, R. O.; Holmes, R. R. *Organometallics* **1984**, *3*, 750. (g) Schulte, M.; Schurmann, M.; Dakternieks, D.; Jurkschat, K. *Chem. Commun.* **1999**, 1291. (h) Mercier, F. A. G.; Meddour, A.; Gielen, M.; Biesemans, M.; Willem. R.; Tiekink, E. R. T. *Organometallics* **1998**, *17*, 5933.

10.1021/om0002531 CCC: $19.00
Publication on Web 08/30/2000

Scheme 2



2

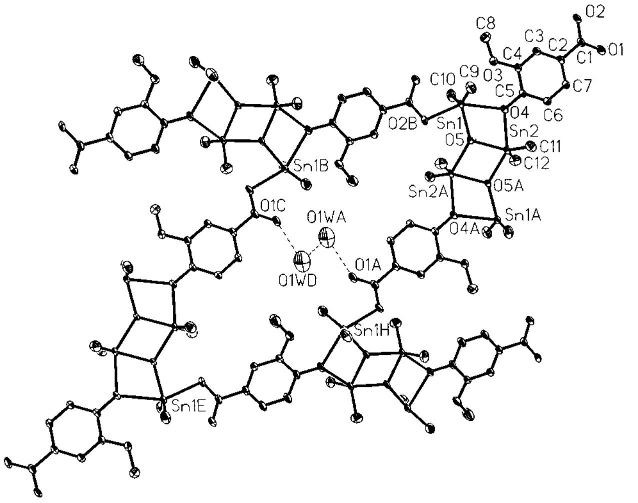


Figure 1. Rhombohedral grid unit representation of {-([$Me_2Sn(VA)_{0.5}]_2O)_2 \cdot 2H_2O$}$_n$ (**1**). The thermal ellipsoids are drawn at 30% probability level. Selected bond lengths (Å) and angles (deg): Sn(1)−O(5) 2.018(2), Sn(2)−O(5) 2.027-(2), Sn(1)−O(4) 2.381(2), Sn(2)−O(4) 2.252(2); O(5)−Sn(1)−O(4) 69.53(8), Sn(1)−O(4)−Sn(2) 97.98(8), Sn(1)−O(5)−Sn(2) 119.65(10), O(5)−Sn(2)−O(4) 72.13(8).

band at ca. 3575−3488 cm^{-1}, indicating the presence of uncoordinated water, which also was confirmed by thermogravimetric analysis (TGA) of a polycrystalline sample. The results indicate that a weight loss of 3.89% occurred at ca. 118 °C, which corresponds to the removal of two water molecules per ([$Me_2Sn(VA)_{0.5}]_2O)_2 \cdot 2H_2O$ unit (3.61% calculated). Most important is the fact that no weight loss was observed in the temperature range of ca. 120−220 °C, which suggested the formation of a stable molecular rhombohedral grid formulated as ([$Me_2Sn(VA)_{0.5}]_2O)_2$. It is noteworthy that coordination polymer **1** is insoluble in common solvents, such as ethanol, acetone, acetonitrile, and water.

The molecular structure of **1**, as shown in Figure 1, exhibits a 2D molecular rhomboid in which the corner of the rhombic grid is composed of a typical ladder-type tetraorganodistannoxane unit. The ladder core can be viewed as four-rung ladders, with Sn(1)−O(4), Sn(2)−O(5), and their symmetry equivalents representing the rungs. Similar ladder frameworks have been documented in those arrangements found in [(n-BuSn(O)-$O_2CR)_2$-n-BuSn($O_2CR)_3]_2$ (R═Ph and Me),[9] [(n-BuSn(O)$O_2CC_6H_{11})_2$(n-BuSn($O_2CC_6H_{11})_3]_2$,[9] and [(n-BuSn(O)$O_2CPh)_2$(n-BuSn(Cl)($O_2CPh)_2]_2$.[9] The central Sn(2)O(5)Sn(2A)O(5A) ring is strictly planar, with the terminal tins being 0.0522 Å out of the ladder plane. Similarly, the terminal oxygen atoms deviate by 0.0167 Å from this plane (with a dihedral angles of 5° between the central and outer rings). In this case, the ladder does not have linear sides but is bent, with the angles Sn-(1)−O(5)−Sn(2A) and O(4)−Sn(2)−O(5A) being 133.9° and 146.5°, respectively. Each tin atom has a distorted trigonal bipyramidal geometry. Both Sn(1) and Sn(2) are each coordinated by two Me groups and by O(5) in equatorial positions. The axial positions at Sn(1) and Sn(2) are occupied by O(4) of a phenolato group and O(2B) of a carboxylate from different VA^{2-} groups and by O(4) and O(5A), respectively. Thus, each VA^{2-} ligand affords one μ_2 oxygen atom of phenolato and one oxygen atom of carboxylate as a tridentate ligand connecting two ladders to give rise to a 2D rhombic grid with an approximate dimension of 10.06 × 13.63 Å, as defined Sn1F−Sn1C−Sn1−Sn1O (Figure 2). The structural feature of **1** is quite different from that of {([$Me_2Sn(OAc)]_2O)_2$}$_n$, the only known 1D polymeric organotin compound in which a tetraorganodistannoxane core is composed of four distorted octahedral Me_2Sn moieties and further connected by two tetradentate acetate groups, resulting in the formation of a 1D chain

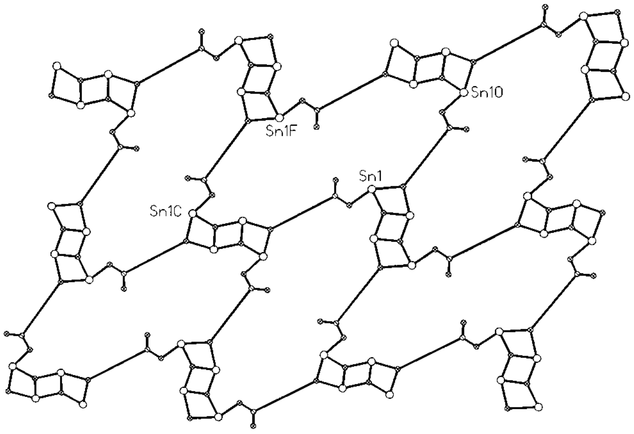


Figure 2. 2D rhombic grid diagram of {([$Me_2Sn(VA)_{0.5}]_2O)_2 \cdot 2H_2O$}$_n$ (**1**) illustrating the connectivity between different ladder corners bridged by the carboxylate and phenolate ends of the VA^{2-} group. For clarity, the 3-methoxybenzene ring of the VA^{2-} group is represented with a straight line, and two Me groups on the Sn atom and clathrated waters are omitted. The open, cross-hatched and hatched circles are Sn, C, and O, respectively.

---

[9] (a) Holmes, R. R. *Acc. Chem. Res.* **1989**, *22*, 190, and references therein. (b) Holmes, R. R. *Phosphorus, Sulfur Silicon* **1999**, *150–151*, 1.

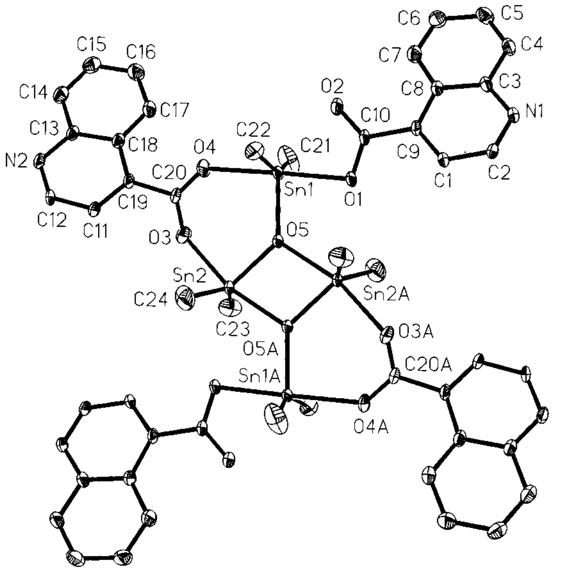


Figure 3. ORTEP view of tetraorganodistannoxane of ($[Me_2Sn(BA)]_2O)_2$ (**2**). The thermal ellipsoids are drawn at 30% probability level. Selected bond lengths (Å) and angles (deg): Sn(1)−O(1) 2.191(3), Sn(1)−O(4) 2.290(3), Sn(1)−O(5) 2.035(3), Sn(2)−O(5) 2.033(3), Sn(2)−O(3) 2.230(4); O(5)−Sn(1)−O(4) 94.57(12), O(3)−Sn(2)−O(5) 90.16(12), Sn(1)−O(5)−Sn(2) 133.10(13).

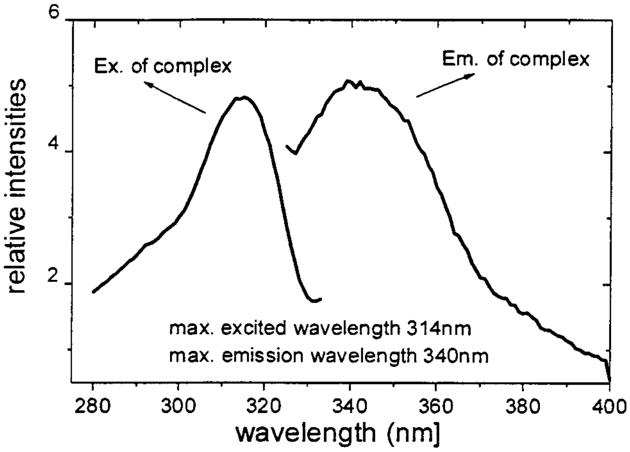


Figure 4. Fluorescent emission spectrum of $\{([Me_2Sn(VA)_{0.5}]_2O)_2{\cdot}2H_2O\}_n$ (**1**) in the solid state.

structure.[8] Interestingly, two guest water molecules are strongly held in the rhombic cavity of **1** by strong hydrogen bondings between water and carboxylate/water (O(1C)···O(1WD) (2.836 Å), O(1WA)···O(1B) (2.836 Å), and O(1WD)···O(1WA) (2.804 Å)) (Figure 1). Also, it can be seen from the packing diagram (see the Supporting Information) that the methyl group acts as a pillar supporting the different 2D grid (clay mimics) layers, similar to those found in 4,4′-bpy-Cd[1,4] and organic clay.[10]

Unlike **1**, the molecular structure of **2**, as depicted in Figure 3, is a tetranuclear centrosymmetric dimeric structure with one four-membered planar Sn(2)−O(5)−Sn(2A)−O(5A) ring and two six-membered planar Sn(1)−O(4)−C(20)−O(3)−Sn(2)−O(5) and Sn(1A)−O(4A)−C(20A)−O(3A)−Sn(2A)−O(5A) rings. The four Me_2Sn moieties are linked by two bridging carboxylate groups, while the remaining two carboxylate groups are attached to each of the exocyclic Me_2Sn moieties. Similar tretraorganodistannoxane units have been documented in the arrangements of $[(n\text{-}Bu_2SnO_2CC_6H_4\text{-}o\text{-}CH_3)_2O]_2$[11] and $[(n\text{-}Bu_2SnO_2CC_6H_4\text{-}o\text{-}Cl)_2O]_2$.[11] Thus, there are two distinct types of BA^- groups in **2**; two are bidentate, bridging two Me_2Sn moieties, and two BA^- are monodentate to a single Me_2Sn moiety. The remaining N atom of the pyridine ring in the BA^- group failed to coordinate to the Me_2Sn moiety, reulting in the formation of a tetranuclear centrosymmetric dimer.

Finally, both Sn−O and Sn−C bonds in **1** and **2** are unexceptional (see notes of Figure 1 and Figure 3). Although the Sn−Sn distance (3.302 and 3.301 Å for **1** and **2**) is indicative of some M−M interaction, it does not represent an actual bond.[12]

As expected, a strong yellow fluorescent emission (at ca. 520 nm with an exciting wavelength of 254 nm) for **2** was observed since a similar peak was observed for the free ligand. Very important is the fact that the fluorescent emission (Figure 4) of **1** makes it a candidate for sensing applications on the basis of recognition and inclusion of appropriate guest molecules.[5]

Experimental Section

$\{([Me_2Sn(VA)_{0.5}]_2O)_2{\cdot}2H_2O\}_n$ (1). Samples of 1.2 mmol of Me_3SnCl and 1 mmol of HAVH were placed in a thick-walled Pyrex tube (ca. 20 cm long). After addition of 0.2 mL of pyridine and 1.75 mL of water, the tube contents were frozen with liquid N_2, and the tube was evacuated under vacuum and flame-sealed. The tube was heated at 130 °C for 2 days. A pale-yellow, crystalline product was formed (only one pure phase). The yield of **1** was 35.5% (0.106 g) based on Me_3SnCl. Anal. Calcd for $C_{12}H_{20}O_6Sn_2$: C, 28.96; H, 4.05. Found: C, 29.10; H, 4.10. IR (KBr, cm^{-1}): 3575(m), 3488(m), 3002(w), 1737(s), 1592(s), 1559(m), 1506(m), 1369(vs), 1282(s), 1225(s), 1114(m), 1028(w),775(s), 634(m), 597(s), and 556(m).

($[Me_2Sn(BA)]_2O)_2$ (2). Samples of 1.2 mmol of Me_3SnCl and 1 mmol of HBA were placed in a thick-walled Pyrex tube (ca. 20 cm long). Addition of 0.2 mL of pyridine and 1.75 mL of water was followed by the procedures described above. A yellow crystalline product was formed (only one pure phase). The yield of **2** was 45.5% (0.180 g) based on Me_3SnCl. Anal. Calcd for $C_{24}H_{24}N_2O_5Sn_2$: C, 43.82; H, 3.68; N, 4.26. Found: C, 43.65; H, 3.90; N, 4.42. IR (KBr, cm^{-1}): 3441(m), 3002(w), 2362(m), 1717(s), 1565(s), 1418(m), 1376(vs), 1338(sh,m), 1202(s), 1225(s), 1149(w), 1076(w),777(s), 635(m), and 492(m).

X-ray Crystallographic Determinations of 1 and 2. Crystal data for **1**: $C_{12}H_{20}O_6Sn_2$, monoclinic, $P2_1/c$, $a = 8.4156(1)$, $b = 14.9765(1)$, $c = 13.4185(2)$ Å, $\beta = 98.3130(10)°$, $V = 1673.45(3)$ Å^3, $Z = 4$, $M = 497.66$, $D_c = 1.975$ Mg m^{-3}, $R_1 = 2.88\%$, $wR_2 = 7.07\%$ (3616 reflections). $T = 293$ K, $\mu = 3.003$ mm^{-1}. Crystal data for **2**: $C_{24}H_{24}N_2O_5Sn_2$, triclinic, $P\bar{1}$ (No. 2), $a = 9.4860(1)$, $b = 10.6219(1)$, $c = 13.6199(2)$ Å, $\alpha = 73.975(1)$, $\beta = 83.405(1)$, $\gamma = 67.590(1)°$, $V = 1219.32(2)$ Å^3, $Z = 2$, $M = 657.83$, $D_c = 1.792$ Mg m^{-3}, $R_1 = 3.89\%$, $wR_2 = 10.36\%$ (4632 reflections). $T = 293$K, $\mu = 2.085$ mm^{-1}. The data were collected on a Siemens SMART CCD area detector diffractometer equipped with Mo Kα radiation ($\lambda = 0.71073$ Å) using ω-scan mode. The data collection covered over a hemisphere of reciprocal space by a combination of three sets of exposures;

---

[10] (a) Biradha, K.; Dennis, D.; MacKinnon, V. A.; Sharma, C. V. K.; Zaworotko, M. J. *J. Am. Chem. Soc.* **1998**, *120*, 11894. (b) Russell, V. A.; Evans, C. C.; Li, W.; Ward, M. D. *Science* **1997**, *276*, 575.

[11] (a) Narula, S. P.; Kaur, S.; Shankar, R.; Bharadwaj, S. K.; Chadha, R. K. *J. Organomet. Chem*. **1996**, *506*, 181. (b) Beckmann, J.; Biesemans, M.; Hassler, K.; Jurkschat, K.; Martins, J. C.; Schurmann, M.; Willem, R. *Inorg. Chem.* **1998**, *37*, 4891.

[12] Wells, A. F. *Structure Inorganic Chemistry*, 5th ed.; Clarendon Press: Oxford, U.K., 1984, p 1157.

each set had a different ϕ angle (0°, 88°, and 180°) for the crystal, and each exposure of 30 s covered 0.3° in ω. The crystal-to-detector distance was 4 cm, and the detector swing angle was −35°. Coverage of the unique set is over 99% complete. Crystal decay was monitored by repeating 30 initial frames at the end of data collection and analyzing the duplicate reflections and was found to be negligible. The unit cell parameters were determined using SMART (Siemens, 1996a).[13] The three sets of data collected were reduced using the program SAINT (Siemens, 1996b).[14] The structure was solved with Direct methods using the program SHELXTL (Sheldrick, 1997).[15] All the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using full-matrix least-squares procedure. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent carbon atoms. The final difference Fourier map was found to be featureless.

Acknowledgment. This work was supported by The Major State Basic Research Development Program (Grant No. G2000077500) and the National Natural Science Foundation of China. The authors would like to thank the Malaysian Government and University Sains Malaysia for the research grant R & D No. 190-9609-2801. S.S.S.R. thanks the Univeristy Sains Malaysia for a Visiting Postdoctoral Fellowship.

Supporting Information Available: Crystallographic data (CIF and PDF) (excluding structure factors) and tables of atomic coordinates, thermal parameters, and bond distances and angles for complexes **1** and **2** and a figure giving an additional view of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0002531

---

[13] Siemens (1996a). *SMART Software Reference Manual*; Siemens Analytical X-ray Systems, Inc.: Madison, WI, 1996.

[14] Siemens (1996b). *SAINT v4 Software Reference Manual*; Siemens Analytical X-ray Systems, Inc.: Madison, WI, 1996.

[15] Sheldrick, G. M. *SHELXTL V5.1 Software Reference Manual*; Bruker AXS, Inc.: Madison, WI, 1997.

Additions and Corrections

2000, Volume 19

Thomas Koch, Steffen Blaurock, Fernando B. Somoza, Jr., Andreas Voigt, Reinhard Kirmse, and Evamarie Hey-Hawkins*: Unexpected P−Si or P−C Bond Cleavage in the Reaction of $Li_2[(C_5Me_4)SiMe_2PR]$ (R = Cyclohexyl, 2,4,6-$Me_3C_6H_2$) and $Li[(C_5H_4)CMe_2PHR]$ (R = Ph, ^{t}Bu) with $ZrCl_4$ or $[TiCl_3(thf)_3]$: Formation and Molecular Structure of the *ansa*-Metallocenes $[\{(\eta\text{-}C_5Me_4)_2SiMe_2\}ZrCl_2]$ and $[\{(\eta\text{-}C_5H_4)_2CMe_2\}MCl_2]$ (M = Ti, Zr).

Pages 2559−2560. Full details of the crystallographic study of $[\{(\eta\text{-}C_5H_4)_2CMe_2\}MCl_2]$ (M = Ti, Zr) were previously reported: Shaltout, R. M.; Corey, J. Y.; Rath, N. P. *J. Organomet. Chem.* **1995**, *503*, 205.

OM000690F

10.1021/om000690f
Published on Web 08/31/2000