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# Synthesis and Structure of the First Alkyl-Bridged Double Ladder: $\{[R(Cl)Sn(CH_2)_3Sn(Cl)R]O\}_4$ (R = $Me_3SiCH_2$)

Dainis Dakternieks,*,† Klaus Jurkschat,*,† Dieter Schollmeyer,‡ and Hong Wu†

*School of Biological and Chemical Sciences, Deakin University, Geelong 3217, Australia, and Institut für Organische Chemie der Johannes Gutenberg-Universität, Johann Joachim Becher-Weg, D-6500 Mainz, Germany*

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*Summary: Reaction of* $(^tBu_2SnO)_3$ *with* $R(Cl_2)Sn(CH_2)_3Sn(Cl_2)R$ *(R =* $Me_3SiCH_2$*) gives an alkyl-bridged double ladder* $\{[R(Cl)Sn(CH_2)_3Sn(Cl)R]O\}_4$ *which has been characterized in the solid state by X-ray crystallography and in solution by multinuclear NMR spectroscopy. The compound consists of two ladder-type layers which are bridged by four propyl chains. The structure observed in the solid state is retained in solution.*

Controlled hydrolysis of diorganotin dihalides commonly proceeds via formation of dimeric tetraorganodistannoxanes $[R_2(X)SnOSn(X)R_2]_2$ and $[R_2(X)SnOSn(OH)R_2]_2$. An alternative route for preparation of these compounds is reaction between diorganotin oxides and diorganotin dihalides. Dimeric tetraorganodistannoxanes feature a planar central $Sn_2O_2$ ring and adopt the so called ladder-type structure both in solution and in the solid state.[1–5] Furthermore, these compounds are active catalysts for a variety of organic reactions.[6,7]

There is no report on the extension of this framework to more than four tin atoms by linking two ladder units together via a spacer. We have found that di-*tert*-butyltin oxide, $(^tBu_2SnO)_3$, acts as an efficient source of anhydrous $O^{2-}$ and consequently have used the reaction of di-*tert*-butyltin oxide with 1,3-bis(((trimethylsilyl)methyl)dichlorostannyl)propane, **1**, to form the alkyl-bridged double ladder **2** and di-*tert*-butyldichlorostannane almost quantitatively (eq 1).

$$\underset{\mathbf{1}}{R(Cl_2)Sn(CH_2)_3Sn(Cl_2)R} + 1/3\,(^tBu_2SnO)_3 \quad (1)$$

R=$Me_3SiCH_2$ $\quad \big\downarrow$ toluene or $CH_2Cl_2$

$$\underset{\mathbf{2}}{\{[R(Cl)Sn(CH_2)_3Sn(Cl)R]O\}_4} + {}^tBu_2SnCl_2$$

The corresponding monohydroxide, **3**, is obtained by the treatment of **1** with potassium hydroxide (eq 2). The

$$\mathbf{1} \xrightarrow[\text{- KCl}]{KOH/H_2O/CH_2Cl_2} \underset{\mathbf{3}}{\{[R(Cl)Sn(CH_2)_3Sn(OH)R]O\}_4} \quad (2)$$

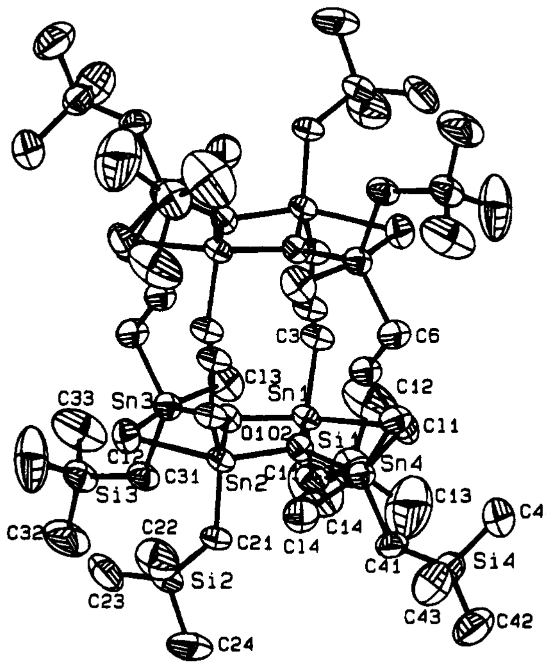

**Figure 1.** ORTEP diagram of **2**.

molecular structure of **2** is shown in Figure 1, and selected bond lengths and bond angles are given in Table 1. The SCHAKAL diagram in Figure 2 is clearer and shows compound **2**, which contains a center of symmetry, consists of two ladder-type layers which are bridged by four propyl chains. Each layer contains four Sn, four Cl, and two O atoms in a nearly planar arrangement. All tin atoms have a distorted trigonal bipyramidal geometry but with different environments. At Sn(1) the axial positions are occupied by Cl(1) and O(1) and the equatorial ones by C(3), C(11), and O(2). At Sn(2), the atoms O(2) and Cl(2) occupy axial positions whereas the equatorial positions are occupied by C(1), C(21), and O(1). Atoms Sn(3) and Sn(4) each have two axial chlorine atoms (Cl(2), Cl(3) and Cl(1), Cl(4), respectively). The equatorial sites about these two tin atoms are again occupied by two carbons and one oxygen (C(6), C(31), O(1) and C(4), C(41), O(2) respectively). In general the bond lengths resemble those found in $\{[Me_3SiCH_2(Cl)Sn]_2O\}_2$[8] with the difference that the bridging

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† Deakin University.

‡ Johannes Gutenberg-Universität.

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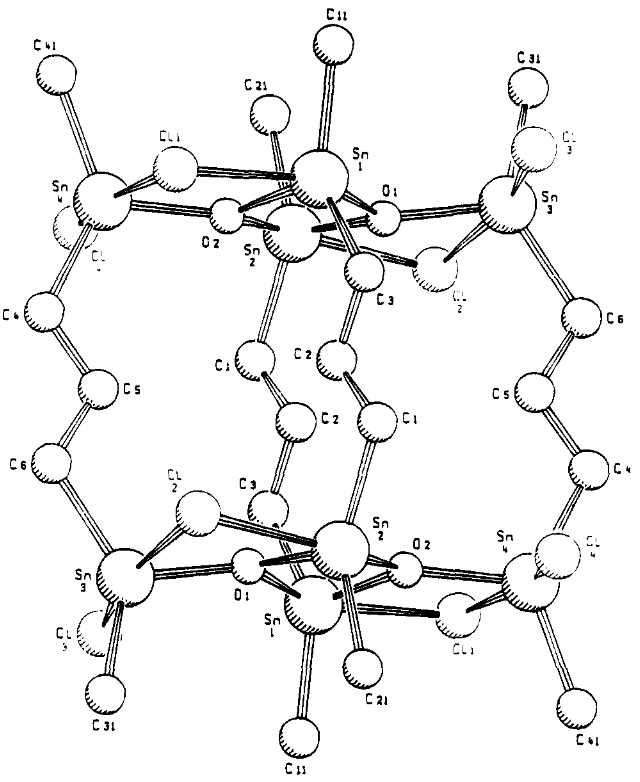


**Figure 2.** SCHAKAL diagram of **2** with the $Me_3Si$ groups omitted for clarity.

**Table 1. Selected Bond Distances (Å) and Angles (deg) in 2**

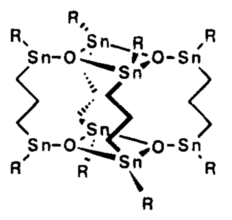
| | | | |
|---|---|---|---|
| Sn(1)—Cl(1) | 2.706(3) | Sn(4)—Cl(1) | 2.728(3) |
| Sn(2)—Cl(2) | 2.678(3) | Sn(4)—Cl(4) | 2.453(3) |
| Sn(3)—Cl(2) | 2.717(3) | Sn(3)—Cl(3) | 2.457(3) |
| Sn(1)—O(1) | 2.118(5) | Sn(1)—O(2) | 2.063(5) |
| Sn(2)—O(1) | 2.060(5) | Sn(2)—O(2) | 2.135(5) |
| Sn(3)—O(1) | 2.039(5) | Sn(4)—O(2) | 2.031(5) |
| Sn(1)—C(3) | 2.126(7) | Sn(1)—C(11) | 2.136(10) |
| Sn(2)—C(1) | 2.157(8) | Sn(2)—C(21) | 2.114(8) |
| Sn(3)—C(6) | 2.151(9) | Sn(3)—C(31) | 2.137(9) |
| Sn(4)—C(4) | 2.166(9) | Sn(4)—C(41) | 2.126(9) |
| | | | |
| O(1)—Sn(1)—Cl(1) | 150.05(15) | O(2)—Sn(1)—Cl(1) | 76.86(15) |
| O(2)—Sn(1)—O(1) | 73.77(20) | C(3)—Sn(1)—Cl(1) | 89.02(22) |
| C(3)—Sn(1)—O(1) | 99.33(25) | C(3)—Cn(1)—O(2) | 117.54(24) |
| C(11)—Sn(1)—Cl(1) | 93.04(27) | C(11)—Cn(1)—O(1) | 101.83(29) |
| C(11)—Sn(1)—O(2) | 108.99(30) | C(11)—Sn(1)—C(3) | 132.58(32) |
| O(1)—Sn(2)—Cl(2) | 77.33(15) | O(2)—Sn(2)—Cl(2) | 149.74(14) |
| O(2)—Sn(2)—O(1) | 73.47(19) | C(1)—Sn(2)—Cl(2) | 86.42(22) |
| C(1)—Sn(2)—O(1) | 116.12(25) | C(1)—Sn(2)—O(2) | 99.30(25) |
| C(21)—Sn(2)—Cl(2) | 96.69(25) | C(21)—Sn(2)—O(1) | 108.41(26) |
| C(12)—Sn(2)—O(2) | 99.84(26) | C(12)—Sn(2)—C(1) | 134.88(30) |
| Sn(4)—O(2)—Sn(2) | 130.44(19) | Cl(3)—Sn(3)—Cl(2) | 164.48(8) |
| O(1)—Sn(3)—Cl(2) | 76.73(15) | O(1)—Sn(3)—Cl(3) | 87.75(16) |
| C(6)—Sn(3)—Cl(2) | 88.38(24) | C(6)—Sn(3)—Cl(3) | 98.28(25) |
| C(6)—Sn(3)—O(1) | 114.79(27) | C(31)—Sn(3)—Cl(2) | 89.79(25) |
| C(31)—Sn(3)—Cl(3) | 95.88(25) | C(31)—Sn(3)—O(1) | 110.95(28) |
| C(31)—Sn(3)—C(6) | 132.41(33) | Cl(4)—Sn(4)—Cl(1) | 164.76(8) |
| O(2)—Sn(4)—Cl(1) | 76.83(15) | O(2)—Sn(4)—Cl(4) | 88.22(16) |
| C(4)—Sn(4)—Cl(1) | 90.11(25) | C(4)—Sn(4)—Cl(4) | 98.81(25) |
| C(4)—Sn(4)—O(2) | 114.02(28) | C(41)—Sn(4)—Cl(1) | 88.20(25) |
| C(41)—Sn(4)—Cl(4) | 95.67(25) | C(41)—Sn(4)—O(2) | 115.39(30) |
| C(41)—Sn(4)—C(4) | 128.10(35) | Sn(4)—Cl(1)—Sn(1) | 82.64(8) |
| Sn(3)—Cl(2)—Sn(2) | 82.46(8) | Sn(2)—O(1)—Sn(1) | 105.98(20) |
| Sn(3)—O(1)—Sn(1) | 130.52(20) | Sn(3)—O(1)—Sn(2) | 120.29(19) |
| Sn(2)—O(2)—Sn(1) | 105.28(19) | Sn(4)—O(2)—Sn(1) | 122.47(20) |

Cl(1) and Cl(2) in **2** are more symmetrically bonded to Sn(1), Sn(4) and Sn(2), Sn(3), respectively, than the corresponding chlorine atoms in $\{[Me_3SiCH_2(Cl)Sn]_2O\}_2$.

The $^{119}Sn$ NMR spectrum of **2** (in $CH_2Cl_2$) shows two resonances of equal intensity (−96.1 ppm, $^2J(^{119}Sn-O-^{117/119}Sn)$ 67 Hz, and −132.9 ppm, $^2J(^{119}Sn-O-^{117/119}Sn)$ 69 Hz). The $^{13}C$ NMR spectrum displays two signals of equal intensity for each carbon (35.8 ppm, $^1J(^{119}Sn-^{13}C)$ 623 Hz, $^3J(^{119}Sn-^{13}C)$ 143 Hz; 38.8 ppm, $^1J(^{119}Sn-^{13}C)$ 687 Hz, $^3J(^{119}Sn-^{13}C)$ 159 Hz ($SnCH_2$); 20.4, 20.9 ppm ($CH_2$); 16.8 ppm, $^1J(^{119}Sn-^{13}C)$ 378 Hz; 20.2 ppm, $^1J(^{119}Sn-^{13}C)$ 397 Hz ($SiCH_2$); 0.9, 1.5 ppm ($SiCH_3$)).

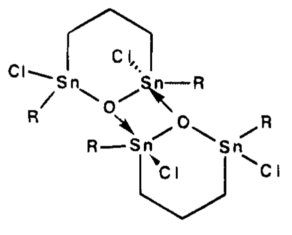
The $^1H$ NMR spectrum shows two singlets of equal intensity for the $SiCH_3$ protons (0.81 and 0.92 ppm), two equal intensity singlets for the $SiCH_2$ protons (0.75 ppm, $^2J(^{119}Sn-^1H)$ 118 Hz; 0.86 ppm, $^2J(^{119}Sn-^1H)$ 122 Hz), and complex patterns for the propylene protons (1.88 and 2.48 ppm).

The NMR data, especially the $^{13}C$ spectrum, reveal that the structure **A** found in the solid state is retained in solution. The alternative structure **B** can be excluded since no splitting of the $^{13}C$ resonance of $CH_2$ would be expected for this arrangement. The reason for the adoption of **A** over **B** is very likely the high tendency of all tin atoms in **2** to become pentacoordinate. In **B** only two of the four tins can achieve pentacoordination. The NMR results obtained for **3** are very similar to **2** indicating the same type of structure.



chloride atoms are omitted for clarity

**A**



**B**

## Experimental Section

**Synthesis. $[(Me_3SiCH_2)Cl_2SnCH_2]_2CH_2$, 1.** Mercuric dichloride (9.23 g, 26.96 mmol) was added in small portions to a magnetically stirred solution of $(Ph_3SnCH_2)_2CH_2$ (10 g, 13.48 mmol) (prepared from $Ph_3SnNa$ and $ClCH_2CH_2CH_2Cl$) in 70 mL of acetone at 0 °C. The reaction mixture was allowed to warm to room temperature and stirring continued for a further 2 h. The PhHgCl formed was filtered off and the solvent removed in vacuo. Ether (50 mL) was added to the residue, and the mixture was stirred for 5 min and then filtered to remove residual PhHgCl. The filtrate was evaporated to give crude $(Ph_2ClSnCH_2)_2CH_2$ ($\delta(^{119}Sn)$ 6.6 ppm in $CH_2Cl_2$), which was subsequently redissolved in ether (50 mL). This solution was added dropwise to a magnetically stirred solution of $Me_3SiCH_2MgCl$ (40 mmol in 50 mL of ether). The reaction mixture was refluxed for 2 h and hydrolyzed with aqueous ammonium chloride; the ether layer was separated and dried over $MgSO_4$. Evaporation of the solvent gave $[Ph_2(Me_3SiCH_2)SnCH_2]_2CH_2$ as an oil ($\delta(^{119}Sn)$ −62.4 ppm in $CH_2Cl_2$). Mercuric dichloride (11.41 g, 42 mmol) was added in small portions to a magnetically stirred solution of $[Ph_2(Me_3SiCH_2)SnCH_2]_2CH_2$ (8.0 g, 10.5 mmol) in 80 mL of acetone. The reaction mixture was stirred overnight and then filtered to remove the PhHgCl formed. The solvent was evaporated and the residue stirred for 5 min in 40 mL of ether followed by filtration to remove residual PhHgCl. The filtrate was evaporated and the residue recrystallized from $CH_2Cl_2$/hexane (1:1) to give 5.3 g of $[Me_3SiCH_2(Cl_2)SnCH_2]_2CH_2$, **1** (85%), as

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(8) Table 7 in ref 2.

**Table 2. Summary of Crystallographic Data for Compound 2**

| | |
|---|---|
| mol formula | $C_{44}H_{64}Cl_8Si_8O_4Sn_8$ |
| mol wt | 2163.2 |
| cryst system, space group | triclinic, $P\bar{1}$ (No. 2) |
| radiation (λ (Å)) | Mo Kα radiation (0.710 69) |
| *a* (Å), α (deg) | 12.176(3), 103.28(4) |
| *b* (Å), β (deg) | 12.660(5), 105.70(2) |
| *c* (Å), γ (deg) | 17.281(5), 105.04(3) |
| *V* (Å³) | 2340(2) |
| *Z* | 1 |
| $D_{calcd}$ (g cm$^{-3}$) | 1.544 |
| *F*(000) | 1008 |
| cryst dimens, mm | 0.30 × 0.30 × 0.90 |
| range of *hkl* | ±15,±15,+20 |
| ref reflns | 3, every 4000 s |
| loss of intensity (%) | 30 |
| corr | linear fit |
| no. of reflns: measd, indep (int *R*) | 14 001, 11 863 (0.007) |
| no. of reflns used, limit | 9873, $I > 2\sigma(I)$ |
| μ, cm$^{-1}$ | 22.76 (no abs corr) |

**Table 3. Fractional Atomic Coordinates with Esd's in Parentheses**

| | *x* | *y* | *z* |
|---|---|---|---|
| Sn(1) | 0.5952(4) | 0.43229(4) | 0.18837(3) |
| Sn(2) | 0.29336(4) | 0.56023(4) | 0.13738(3) |
| Sn(3) | 0.19144(5) | 0.25321(4) | 0.05871(4) |
| Sn(4) | −0.16940(5) | 0.25799(5) | −0.27277(4) |
| Cl(1) | −0.0233(2) | 0.5787(2) | 0.2774(2) |
| Cl(2) | 0.3507(2) | 0.4175(2) | 0.0272(2) |
| Cl(3) | 0.0351(2) | 0.1499(2) | 0.1058(2) |
| Cl(4) | 0.3534(2) | 0.8435(2) | 0.2505(2) |
| O(1) | 0.1659(4) | 0.4017(4) | 0.1128(3) |
| O(2) | 0.1671(6) | 0.5928(4) | 0.1962(3) |
| C(1) | 0.2576(6) | 0.6444(6) | 0.0427(5) |
| C(2) | 0.1375(6) | 0.5804(6) | −0.0272(5) |
| C(3) | 0.1161(6) | 0.6429(6) | −0.0921(5) |
| C(4) | −0.0472(8) | 0.1815(7) | −0.2095(5) |
| C(5) | 0.0088(8) | 0.2356(7) | −0.1144(5) |
| C(6) | 0.0960(8) | 0.1765(6) | −0.0762(5) |
| Si(1) | 0.0419(3) | 0.2998(3) | 0.3396(2) |
| C(11) | 0.1433(8) | 0.3893(8) | 0.2968(5) |
| C(12) | −0.116(1) | 0.238(1) | 0.270(1) |
| C(13) | 0.054(2) | 0.389(2) | 0.443(1) |
| C(14) | 0.094(2) | 0.179(1) | 0.357(1) |
| Si(2) | 0.6016(2) | 0.6423(3) | 0.2453(2) |
| C(21) | 0.4437(6) | 0.5900(7) | 0.2463(5) |
| C(22) | 0.613(1) | 0.747(1) | 0.1841(9) |
| C(23) | 0.6463(10) | 0.524(1) | 0.1932(9) |
| C(24) | 0.7058(10) | 0.719(1) | 0.3573(8) |
| Si(3) | 0.4010(2) | 0.1197(2) | 0.0984(2) |
| C(31) | 0.3405(7) | 0.2301(7) | 0.1440(6) |
| C(32) | 0.525(1) | 0.111(1) | 0.1803(9) |
| C(33) | 0.283(1) | −0.0204(10) | 0.054(1) |
| C(34) | 0.453(2) | 0.155(1) | 0.014(1) |
| Si(4) | 0.2486(3) | 0.9068(2) | 0.4758(2) |
| C(41) | 0.2549(8) | 0.7766(7) | 0.4053(5) |
| C(42) | 0.320(1) | 0.922(1) | 0.5886(7) |
| C(43) | 0.337(1) | 1.0342(9) | 0.4567(8) |
| C(44) | 0.087(1) | 0.895(1) | 0.4538(8) |

colorless crystals, mp 88−90 °C. Anal. Found: C, 21.97; H, 4.63; Cl, 23.51. Calcd for $C_{11}H_{28}Cl_4Si_2Sn_2$ (595.73): C, 22.18; H, 4.74; Cl, 23.80. $^1H$ NMR ($CDCl_3$): δ 0.20 (s, 18H, $Me_3Si$), 0.90 (s, 4H, $SiCH_2$, $^2J(^{119}Sn-^1H)$ 90 Hz), 1.84 (t, 4H, $SnCH_2$, $^2J(^{119}Sn-^1H)$ 49 Hz), 2.3 (q, 2H, $CH_2$). $\delta(^{119}Sn(CH_2Cl_2))$ 132.8 ppm.

**{[$Me_3SiCH_2(Cl)Sn(CH_2)_3Sn(Cl)CH_2SiMe_3]O\}_4$, 2.** Compound **1** (1.25 g, 2.1 mmol) and $(^tBu_2SnO)_3$ (0.52 g, 0.7 mmol) were mixed in 30 mL of toluene, and the mixture was refluxed for 5 min. The reaction mixture was filtered and the solvent slowly evaporated at room temperature to a volume of about 5 mL to give 1.03 g (91%) of **2** as colorless crystals, mp 304−305 °C. Anal. Found: C, 24.36; H, 5.95; Cl, 13.06. Calcd for $C_{44}H_{112}Cl_8O_4Si_8Sn_8$ (2163.2): C, 24.43; H, 5.22; Cl, 13.11. Molecular weight (0.199 g in 29.122 g of $CHCl_3$ at 40 °C using a Knauer AO 280 osmometer): 1920.

**{[$Me_3SiCH_2(Cl)Sn(CH_2)_3Sn(OH)CH_2SiMe_3]O\}_4$, 3.** Compound **1** (0.50 g, 0.84 mmol) in 20 mL of $CH_2Cl_2$ was added dropwise to a magnetically stirred solution of KOH (0.14 g, 2.5 mmol) in 15 mL of ethanol and 5 mL of water. The reaction mixture was stirred for 3 h and the solvent removed in vacuo. The residue was then stirred with 40 mL of $CH_2Cl_2$ and filtered to remove KCl. The filtrate was slowly evaporated to give 0.394 g (90%) of **3** as colorless crystals, mp 261−264 °C. Anal. Found: C, 25.96; H, 5.69; Cl, 6.91. Calcd for $C_{44}H_{116}Cl_4O_8Si_8Sn_8$ (2089.64): C, 25.29; H, 5.59; Cl, 6.79. $^1H$ NMR ($CDCl_3$): δ 0.14 (s, 36H, $Me_3Si$), 0.20 (s, 36H, $Me_3Si$), 0.81 (s, 8H, $CH_2Si$), 0.92 (s, 8H, $CH_2Si$), 1.60 (m, 16H, $CH_2Sn$), 2.40 (m, 8H, $CH_2$). $^{13}C$ NMR ($CDCl_3$): δ 1.2, 1.7 ($Me_3Si$), 11.5 ($^1J(^{119}Sn-^{13}C)$ 424 Hz), 14.9 ($^1J(^{119}Sn-^{13}C)$ 424 Hz) ($CH_2Si$), 21.3, 21.7 ($CH_2$), 31.4 ($^1J(^{119}Sn-^{13}C)$ 632 Hz, $^3J(^{119}Sn-^{13}C)$ 143 Hz), 33.7 ($^1J(^{119}Sn-^{13}C)$ 647 Hz, $^3J(^{119}Sn-^{13}C)$ 131 Hz) ($CH_2Sn$). $^{119}Sn$ NMR ($CH_2Cl_2$): δ −160.5 ($^2J(^{119}Sn-O-^{117/119}Sn)$ 94 Hz), −162.9 ($^2J(^{119}Sn-O-^{117/119}Sn)$ 94 Hz. NMR measurements were recorded on a Jeol GX 270 MHz spectrometer.

**Crystal Structure Determination**. Compound **2** crystallized as colorless rectangular blocks (from dichloromethane solution). Data were collected at 298 K on a CAD4 diffractometer using the θ/2θ scan type (θ range 1.5−30°) giving 11 863 unique reflections. Relevant crystallographic data are given in Table 2. The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares (using 325 variables) first with isotropic thermal parameters and then with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were localized in the difference Fourier map. Calculations were carried on an IBM RISC-6000 computer using the SHELX-76 and SHELX-86 programs, yielding final $R = 0.0497$ and $R_w = 0.0497$. Fractional atomic coordinates are given in Table 3.

**Acknowledgment.** We are grateful to the Australian Research Council (ARC) and to the Stifterverband für die Deutsche Wissenschaft for financial assistance.

**Supplementary Material Available:** Tables of complete bond distances and angles, anisotropic displacement factors, and complete atom coordinates and displacement factors (6 pages). Ordering information is given on any current masthead page.

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