Organometallics **2001,** *20,* 575−577

The Sodium Cuprate (tBu$_3$Si)$_2$CuNa: Formation and X-ray Crystal Structure Analysis

Hans-Wolfram Lerner,*,[†] Stefan Scholz,[†] and Michael Bolte[‡]

Institut für Anorganische Chemie and Institut für Organische Chemie,
Johann Wolfgang Goethe-Universität Frankfurt am Main, Marie-Curie-Strasse 11,
60439 Frankfurt am Main, Germany

Received May 31, 2000

*Summary: $(t\text{Bu}_3\text{Si})_2\text{CuNa(THF)}_n$ (**1**; $n = 2, 4$) is the first structurally characterized sodium cuprate and represents a heavier homologue of the well-known lithium cuprates. Yellow crystals of $(t\text{Bu}_3\text{Si})_2\text{CuNa(THF)}_2$ (**1a**) were obtained from heptane (space group $P2_1/n$); the ion-separated form $(t\text{Bu}_3\text{Si})_2\text{Cu}\underline{\text{N}}\text{a(THF)}_4$ (**1b**) crystallized from toluene (space group $R\bar{3}$).*

Introduction

Lithium alkyl cuprates are important and versatile organometallic reagents in organic synthesis.[1] Various details of their reaction mechanisms and molecular structures, however, have still not been fully elucidated and are therefore subject to current investigations.[2] NMR spectroscopy and ebullioscopic measurements on cuprates with small organic ligands showed that in many cases oligonuclear aggregates are formed, their structures depending on the solvent and on the stoichiometry of the reaction mixture.[3] Monomeric cuprates can be obtained (i) by complexation of their alkali-metal counterions with appropriate crown ethers[4] and (ii) by employing sterically demanding ligands which kinetically stabilize these reactive species.[5]

In contrast to the well-established cuprates with organic ligands, only a few compounds with a Si−Cu bond are known. Information regarding the structure and reactivity of these molcules is thus still rather limited.[6]

Results and Discussion

Up to now, only lithium cuprates have been structurally characterized by X-ray crystallography. We report here the synthesis and the X-ray crystal structure analysis of the sodium cuprate **1,** which was obtained from sodium tri-*tert*-butylsilanide, $t\text{Bu}_3\text{SiNa}$ (supersilylsodium),[7] and copper(I) chloride, CuCl, in tetrahydrofuran at −78 °C (Scheme 1). Removal of the solvent in vacuo gave a solid residue, which was first extracted with heptane and then with toluene. The hepane extract yielded bright yellow crystals of the cuprate **1a**, while **1b** crystallized from the toluene filtrate.

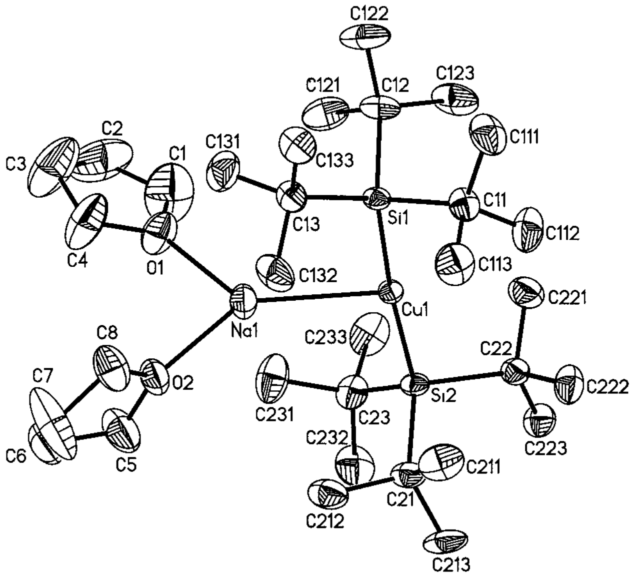

Figure 1. ORTEP drawing of **1a** showing the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

Scheme 1

$$2t\text{Bu}_3\text{SiNa(THF)}_n + \text{CuCl} \xrightarrow[-\text{NaCl}]{} (t\text{Bu}_3\text{Si})_2\text{CuNa(THF)}_n \quad n = 2\ (\mathbf{1a}),\ 4\ (\mathbf{1b})$$

The crystal structure of **1a** is shown in Figure 1. Crystal data and structure refinement details, bond distances and angles are given in Tables 1 and 2,

---

* To whom correspondence should be addressed. Fax: +49-69/798-29260. E-mail: lerner@chemie.uni-frankfurt.de.

[†] Institut für Anorganische Chemie.

[‡] Institut für Organische Chemie.

(1) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*; Plenum Press: New York, 1990; Part B, p 401.

(2) (a) Canisius, J.; Gerold, A.; Krause, N. *Angew. Chem.* **1999**, *111*, 1727; *Angew. Chem., Int. Ed.* **1999**, *38*, 1644. (b) Krause, N. *Angew. Chem.* **1999**, *111*, 83; *Angew. Chem., Int. Ed.* **1999**, *38*, 79. (c) Boche, G.; Bosold, F.; Marsch, M.; Harms, K. *Angew. Chem.* **1998**, *110*, 1779; *Angew. Chem., Int. Ed.* **1998**, *37*, 1684.

(3) (a) Ashby, E. C.; Watkins, J. J. *J. Am. Chem. Soc.* **1977**, *99*, 5312. (b) Hope, H.; Oram, D.; Power, P. P. *J. Am. Chem. Soc.* **1984**, *106*, 1149. (c) Bertz, S. H.; Nilsson, K.; Davidsson, Ö.; Snyder, J. P. *Angew. Chem.* **1998**, *110*, 327; *Angew. Chem., Int. Ed.* **1998**, *37*, 314. (d) Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Sullivan, A. C. *J. Organomet. Chem.* **1984**, *263*, C23. (e) Huang, H.; Liang, C. H.; Penner-Hahn, J. E. *Angew. Chem.* **1998**, *110*, 1628; *Angew. Chem., Int. Ed.* **1998**, *37*, 1564.

(4) Hope, H.; Olmstead, M. M.; Power, P. P.; Sandell, J.; Xu, X. *J. Am. Chem. Soc.* **1985**, *107*, 433.

(5) (a) Heine, A.; Stalke, D. *Angew. Chem.* **1993**, *105*, 90; *Angew. Chem., Int. Ed.* **1993**, *32*, 121. (b) Heine, A.; Herbst-Irmer, R.; Stalke, D. *J. Chem. Soc., Chem. Commun.* **1993**, 1731.

(6) (a) Lipshutz, B. H.; Scalfani, J. A.; Takanami, T. *J. Am. Chem. Soc.* **1998**, *120*, 4021. (b) Lipshutz, B. H. *Acc. Chem. Res.* **1997**, *30*, 277. (c) Fleming, I.; Newton, T. W.; Roessler, F. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2527. (d) Chen, H.-M.; Oliver, J. P. *J. Organomet. Chem.* **1986**, *316*, 255. (e) Klett, J.; Klinkhammer, K. W.; Niemeyer, M. *Chem. Eur. J.* **1999**, *5*, 2531. (f) Klinkhammer, K. W. *Z. Anorg. Allg. Chem.* **2000**, *626*, 1217.

(7) Wiberg, N.; Amelunxen, K.; Lerner, H.-W.; Schuster, H.; Nöth, H.; Krossing, I.; Schmidt-Amelunxen, M.; Seifert, T. *J. Organomet. Chem.* **1997**, *542*, 1 and references cited therein.

10.1021/om000458+ CCC: $20.00
Publication on Web 01/03/2001

Table 1. Crystal Data and Structure Refinement Details for 1a and 1b

	1a	**1b**
empirical formula	$C_{32}H_{70}CuNaO_2Si_2$	$C_{40}H_{86}CuNaO_4Si_2$
color	light yellow	light yellow
shape	plate	needle
fw	629.59	773.80
cryst syst	monoclinic	trigonal
space group	$P2_1/n$	$R\bar{3}$
a, Å	8.6800(2)	12.4260(6)
b, Å	19.9004(5)	12.4260(6)
c, Å	22.5662(5)	27.272(2)
α, deg	90	90
β, deg	96.248(2)	90
γ, deg	90	120
V, Å^3; Z	3874.8(2); 4	3646.8(4); 3
calcd density, Mg/m^3	1.079	1.057
abs coeff μ(Mo Kα), mm^{-1}	0.660	0.540
F(000)	1384	1278
cryst size, mm	0.7 × 0.35 × 0.1	0.28 × 0.12 × 0.12
θ-range, deg	1.37–25.03	2.03–27.23
index ranges	$-10 \leq h \leq 10$ $-23 \leq k \leq 23$ $-26 \leq l \leq 26$	$-15 \leq h \leq 12$ $-14 \leq k \leq 13$ $-34 \leq l \leq 32$
no. of rflns collected	43 791	9319
no of indep rflns	6845	1658
R(int)	0.0757	0.0817
abs cor	empirical	empirical
T_{min}, T_{max}	0.655, 0.937	0.864, 0.938
no. of data/restraints/ params	6845/0/343	1658/2/74
goodness of fit on F^2	1.166	1.084
final R indices ($I > 2\sigma(I)$): R1, wR2	0.075, 0.130	0.082, 0.213
R indices (all data): R1, wR2	0.113, 0.144	0.145, 0.244
largest diff peak and hole, e Å^3	0.48, −0.47	0.50, −0.36

Table 2. Seleceted Bond Lengths (Å) and Angles (deg) for 1a

Cu(1)–Si(2)	2.3581(13)	Si(2)–C(21)	1.978(5)
Cu(1)–Si(1)	2.3638(13)	Si(2)–C(22)	1.978(5)
Cu(1)–Na(1)	2.7393(18)	Si(2)–C(23)	1.985(5)
Si(1)–C(11)	1.970(5)	Na(1)–O(2)	2.273(4)
Si(1)–C(13)	1.982(5)	Na(1)–O(1)	2.300(4)
Si(1)–C(12)	1.984(5)		
Si(2)–Cu(1)–Si(1)	175.26(5)	C(21)–Si(2)–C(22)	109.4(2)
Si(2)–Cu(1)–Na(1)	95.15(5)	C(21)–Si(2)–C(23)	108.9(2)
Si(1)–Cu(1)–Na(1)	89.52(5)	C(22)–Si(2)–C(23)	106.9(2)
C(11)–Si(1)–C(13)	107.6(2)	C(21)–Si(2)–Cu(1)	105.49(15)
C(11)–Si(1)–C(12)	109.2(2)	C(22)–Si(2)–Cu(1)	107.69(14)
C(13)–Si(1)–C(12)	109.4(2)	C(23)–Si(2)–Cu(1)	118.32(15)
C(11)–Si(1)–Cu(1)	104.95(15)	O(2)–Na(1)–O(1)	90.57(15)
C(13)–Si(1)–Cu(1)	120.47(15)	O(2)–Na(1)–Cu(1)	137.14(12)
C(12)–Si(1)–Cu(1)	104.75(15)	O(1)–Na(1)–Cu(1)	132.25(13)

respectively. Its Si–Cu–Si unit deviates somewhat from linearity (bond angle Si(1)–Cu–Si(2) = 175.26(5)°), due to weak interactions between Cu and Na. The distance between the Cu and Na atoms is 2.7393(18) Å. **1a** features three short CH_3–Na contacts with an average H–Na distance of 2.576 Å. Apart from these three methyl groups, the Na atom is coordinated by one Cu atom and two molecules of tetrahydrofuran. Figure 2 shows the molecular structure of **1b** in the crystal lattice. Crystal data and structure refinement details, bond distances and angles are given in Tables 1 and 3, respectively. Similar to the isoelectronic compound $(tBu_3Si)_2Zn$,[9] the Si–Cu–Si unit is perfectly linear (Figure 3). The Cu–Na distance of 7.06 Å in the solvent-separated ion pair **1b** is significantly longer than the sum of the atomic radii.[8] The Na atom is coordinated by four O atoms, forming a slightly distorted tetrahedron.

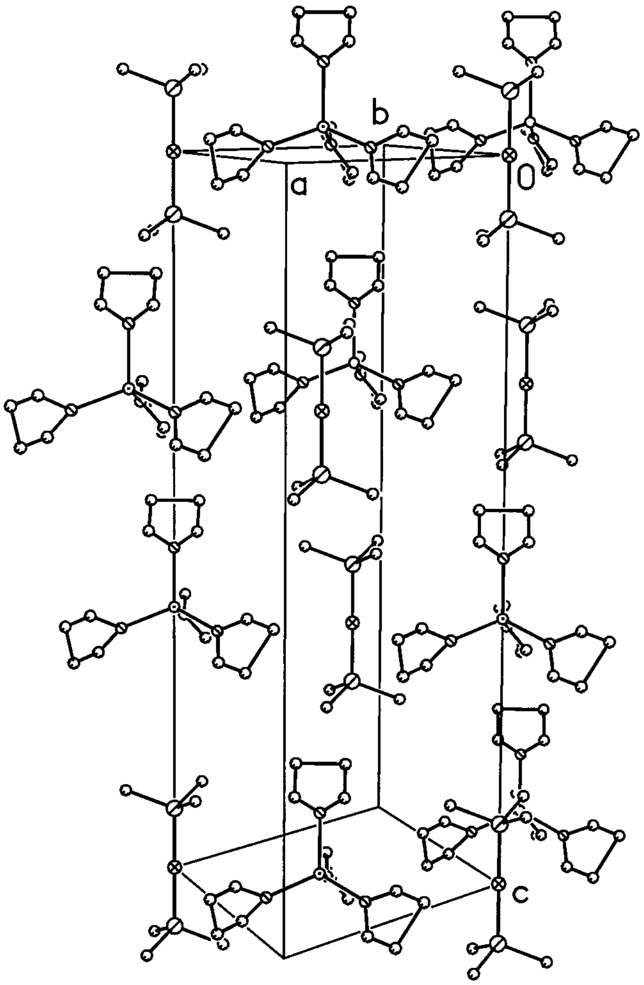

Figure 2. Packing diagram of **1b**. H atoms, the terminal methyl groups of the *tert*-butyl residues, and one of the disordered Na atoms have been omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 1b[a]

Cu(1)–Si(1)	2.307(2)	Na(1)–O(1)	2.207(16)
Si(1)–C(1)	1.972(6)	Na(1)–O(2)	2.29(3)
Si(1)–Cu(1)–Si(1)#1	180.0	O(1)–Na(1)–O(1)#3	111.0(6)
C(1)–Si(1)–C(1)#2	108.46(19)	O(1)–Na(1)–O(2)	107.9(6)
C(1)–Si(1)–Cu(1)	110.46(18)	C(2)–O(1)–Na(1)	131.8(17)
C(12)–C(1)–Si(1)	109.0(4)	C(3)#4-O(1)–Na(1)	136.8(15)
C(11)–C(1)–Si(1)	116.9(4)	C(21)–O(2)–Na(1)	124.0(15)
C(13)–C(1)–Si(1)	107.4(4)		

[a] Symmetry operators: (#1) $-x + {}^4/_3$, $-y + {}^2/_3$, $-z + {}^2/_3$; (#2) $-y + 1$, $x - y$, z; (#3) $-x + y + 1$, $-x + 1$, z; (#4) $-x + {}^5/_3$, $-y + {}^4/_3$, $-z + {}^4/_3$.

Both supersilyl copper compounds show a C–Si–C angle smaller than 110° (**1a**, 108.10°; **1b**, 108.46°), indicating a negatively polarized Si atom.[7]

Reaction with trimethylchlorosilane, Me_3SiCl, leads to the unsymmetrically substituted disilane tBu_3Si–$SiMe_3$. Oxidation of **1** with $AgNO_3$ or O_2 proceeds with the formation of the superdisilane tBu_3Si–$SitBu_3$.

---

(8) Hollemann, A. F.; Wiberg, N. *Lehrbuch der Anorganischen Chemie*; de Gruyter: Berlin, 1995; p XXXVI.

(9) (a) Wiberg, N.; Amelunxen, K.; Lerner, H.-W.; Nöth, H.; Appel, A.; Knizek, J.; Polborn, K. *Z. Anorg. Allg. Chem.* **1997**, *623*, 1861. (b) Wiberg, N. *Coord. Chem. Rev.* **1997**, *163*, 217.

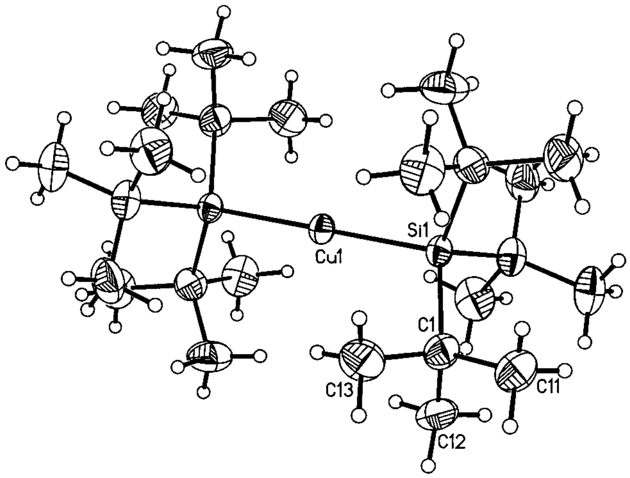

Figure 3. ORTEP drawing of the anion of **1b** showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

Experimental Section

General Procedures. All experiments were carried out under dry argon with strict exclusion of air and moisture using standard Schlenk techniques. *t*Bu$_3$SiNa in THF was prepared according to literature procedures.[7] The solvents (heptane, toluene, and tetrahydrofuran) were distilled from sodium/benzophenone prior to use.

The NMR spectra were recorded on a Bruker AM 250 (^{1}H/^{13}C, 250.133/62.896 MHz) and a Bruker AMX 400 (^{29}Si, 79.495 MHz) spectrometer. The ^{29}Si NMR spectra were recorded using the INEPT pulse sequence with empirically optimized parameters for polarization transfer from the *t*Bu substituents.

Synthesis of (*t*Bu$_3$Si)$_2$CuNa(THF)$_n$ (1). A slurry of dry CuCl (Riedel-de-Haën, Seelze, 0.455 g, 4.5 mmol) in tetrahydrofuran was cooled to −78 °C, and a solution of *t*Bu$_3$SiNa in tetrahydrofuran (10 mL, 0.5 M, 5.0 mmol) was added dropwise with stirring. The reaction mixture changes its color immediately to dark green. After the mixture was heated to room temperature, the solvent was removed in vacuo. The solid reaction product was extracted into heptane (yellow solution), and the remaining insoluble material was extracted into toluene. After filtration **1a** was crystallized from the heptane filtrate and **1b** from the toluene extract. Yield: **1a**, 31.5%; **1b**, 15.2%. Selected data for **1a**: decomposition at 75 °C; ^{1}H NMR (C$_6$D$_6$, internal TMS) δ 1.428 (s; 6 *t*Bu), δ 1.359 (m; 4 CH$_2$), δ 3.296 (m; 4 OCH$_2$); ^{13}C{^{1}H} NMR (C$_6$D$_6$, internal TMS) δ 25.3 (s; *C*Me$_3$), 34.6 (s; C*Me*$_3$), 25.6 (s; 4 CH$_2$), 68.1 (m; 4 OCH$_2$); ^{29}Si{^{1}H} NMR (C$_6$D$_6$, external TMS) 23.2 (s; 2 Si*t*Bu$_3$). Selected data for **1b**: decomposition at 95 °C; ^{1}H NMR (C$_6$D$_6$, internal TMS) δ 1.454 (s; 6 *t*Bu), 1.312 (m; 4 CH$_2$), 3.400 (m; 4 OCH$_2$); ^{13}C{^{1}H} NMR (C$_6$D$_6$, internal TMS) δ 25.1 (s; *C*Me$_3$), 34.1 (s; C*Me*$_3$), 25.5 (s; 4 CH$_2$), 68.1 (m; 4 OCH$_2$); ^{29}Si{^{1}H} NMR (C$_6$D$_6$, external TMS) δ 23.2 (s; 2 Si*t*Bu$_3$).

Reaction of 1 with Electrophiles. To a solution (0.2 mmol/mL) of **1a** in 1 mL of C$_6$D$_6$ was added 1 drop of water. The NMR (^{1}H, ^{13}C, ^{29}Si) spectra showed only the signals of the supersilane *t*Bu$_3$SiH[10] and thus indicated the formation of supersilane in quantitative yield. *t*Bu$_3$SiH: ^{1}H NMR (C$_6$D$_6$, internal TMS) δ 1.118 (s; 3 *t*Bu), 3.504 (s; 1 SiH); ^{13}C{^{1}H} NMR (C$_6$D$_6$, internal TMS): δ 21.0 (s; *C*Me$_3$), 30.8 (s; C*Me*$_3$); ^{29}Si{^{1}H} NMR (C$_6$D$_6$, external TMS) δ 17.8 (s; Si*t*Bu$_3$).

Excess of trimethylsilyl chloride, Me$_3$SiCl (0.1 mL, 0.8 mmol), was added slowly to a solution of **1a** (0.025 g, 0.04 mmol) in 1 mL of heptane. All volatile components were removed in vacuo, and the remaining solid residue was extracted into 1 mL of C$_6$D$_6$. The disilane *t*Bu$_3$SiSiMe$_3$[10] was formed as the reaction product in quantitative yield. *t*Bu$_3$SiSiMe$_3$: ^{1}H NMR (C$_6$D$_6$, internal TMS) δ 0.294 (s; 3Me), 1.162 (s; 3 *t*Bu); ^{13}C{^{1}H} NMR (C$_6$D$_6$, internal TMS) δ 3.3 (s; SiMe$_3$), 23.7 (s; *C*Me$_3$), 31.5 (s; C*Me*$_3$); ^{29}Si{^{1}H} NMR (C$_6$D$_6$, external TMS) δ −19.2 (s; SiMe$_3$), 2.3 (s; Si*t*Bu$_3$).

Oxidation of 1. 1 (0.017 g, 0.027 mmol) and AgNO$_3$ (0.104 g, 0.61 mmol) in 1 mL of benzene were mixed in an NMR tube. After 2 h the superdisilane *t*Bu$_3$SiSi*t*Bu$_3$[10] was formed in quantitative yield, as confirmed by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy. With dry air, compound **1a** (0.2 mmol in 1 mL of C$_6$D$_6$) reacts with formation of the superdisilane tBu$_3$SiSi*t*Bu$_3$.[10] *t*Bu$_3$SiSi*t*Bu$_3$: ^{1}H NMR (C$_6$D$_6$, internal TMS) δ 1.363 (s; 6 *t*Bu); ^{13}C{^{1}H} NMR (C$_6$D$_6$, internal TMS) δ 27.3 (s; *C*Me$_3$), 34.6 (s; C*Me*$_3$); ^{29}Si{^{1}H} NMR (C$_6$D$_6$, external TMS) δ 35.4 (s; 2 Si*t*Bu$_3$).

X-ray Structure Determination. Data collection was performed on a Siemens CCD three-circle diffractometer, with graphite-monochromated Mo Kα radiation. $T = 173$ K. Empirical absorption correction used SADABS,[11] and structure solution was by direct methods.[12] Structure refinement was carried out with full-matrix least-squares on F^2 with SHELXL-97.[13] Hydrogen atoms were placed on ideal positions and refined with fixed isotropic displacement parameters using a riding model. The H atoms of the disordered tetrahydrofuran molecules in **1b** could not be located and were not included in the refinement. The crystal structure of **1b** consists of ordered (*t*Bu$_3$Si$_2$)Cu anions and disordered Na(THF)$_4$ cations. Although the structure was refined well, the solution implies that there are unusual cavities in the ionic lattice. The Na atoms are located on a 3-fold rotation axis. Two different THF sites can be distinguished: one (O1, C2, C3) is found on a general position, and the second one (O2, C21) is located on the same 3-fold rotation axis as the Na atom. Both THF molecules are located on inversion centers, implying a 2-fold disorder of the O atoms; as a consequence of that, the Na atoms are also disordered, and they are only half-occupied. The carbon atoms C2 and C3 are fully occupied because the C atoms of two disordered THF molecules overlap exactly. Carbon atom C21, on the other hand, has to be refined with a site occupation factor of $^{2}/_{3}$, because the 3-fold rotation axis in combination with the inversion center generates five further postions of C21, and some of these are mutually exclusive.

Supporting Information Available: Tables of X-ray parameters, atomic coordinates and thermal parameters, and bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000458+

---

[10] Identified by comparison with the NMR data of an authentic sample, which was prepared according to a literature procedure.[7]

[11] Sheldrick, G. M. SADABS, A Program for Empirical Absorption Correction of Area Detector Data; University of Göttingen, Göttingen, Germany, 1996.

[12] Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467−473.

[13] Sheldrick, G. M. SHELXL-97, A Program for the Refinement of Crystal Structures; University of Göttingen, Göttingen, Germany, 1997.