DOI: 10.1002/ejic.200801061

Persistent Alkylgallium Peroxides – Synthesis of the Cage Compound $Na_4[(Ga\text{-}R)_3(O_2)_3(O)]_2(Et_2O)(DABCO)$ [R = $CH(SiMe_3)_2$]

Werner Uhl,*[a] Mohammad R. Halvagar,[a] Friedhelm Rogel,[a] and Werner Massa[b]

Keywords: Gallium / Peroxides / Cage compounds

Reaction of $Na[H_3Ga\text{-}CH(SiMe_3)_2]$ (**1**) with the adduct $(H_2O_2)_2$·DABCO affords the alkylgallium peroxide $Na_4[(Ga\text{-}R)_3(O_2)_3(O)]_2(Et_2O)(DABCO)$ (**2**) [R = $CH(SiMe_3)_2$] by hydrogen release. Compound **2** possesses oxidizing peroxo groups in close proximity to reducing Ga–C bonds and a higher thermal stability than the analogous lithium peroxo complex. In the solid state a cage compound is formed in which two $Ga_3(O_2)_3$ heterocycles are bridged by four sodium atoms.

Introduction

Organoelement peroxides of the Group 13 elements are of interest owing to their potential applicability as oxygen transfer reagents. Furthermore, they may exhibit singular coordination behaviour by the bidentate character of the peroxo groups. However, the synthesis of organoaluminum or -gallium peroxides is great experimental challenge because they have strongly reducing Al–C or Ga–C bonds in close proximity to oxidative peroxo groups. Such compounds were often postulated as transient species in the reactions of oxygen with alkylaluminum or -gallium derivatives, but their conflicting functionalities are usually quenched in fast secondary processes by the insertion of an oxygen atom of a peroxo group into remaining E–C bonds.[1] Nevertheless, these compounds were reported to be applicable in secondary reactions.[2] Owing to their inherent reactivity persistent and well characterized organoelement peroxides of aluminium and gallium are extremely rare. Tri(*tert*-butyl)gallium and -indium gave the insertion of an oxygen molecule into one E–C bond.[3] These products are highly explosive in the solid state. A digallium peroxide possessing terminal Ga–C bonds was isolated only in trace quantities.[4] Furthermore, peroxo groups were found in two aluminum compounds which do not contain intact Al–C bonds.[5] Recently the crystal structures of two relatively inert alkylaluminum and -gallium peroxides were reported, which were stabilized by bis(trimethylsilyl)methyl groups.[6,7] Both compounds were obtained by the simple reactions of alkylelement hydrides with hydrogen peroxide or *tert*-butyl hydrogen peroxide and the release of hydrogen. Slow decomposition occurred in the solid state or in solution at room temperature. In one compound the highly polarizing lithium cation was employed as a counterion. We hoped that the softer sodium ion could enhance the stability of such peroxides for an easier handling and a broader applicability.

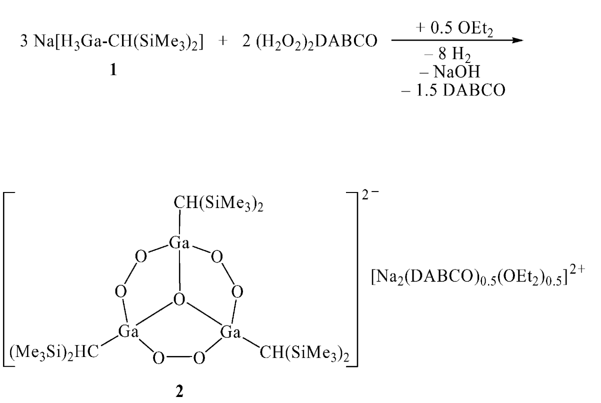
Results and Discussion

Treatment of $Na[GaH_4]$[8] with the alkyllithium compound $LiCH(SiMe_3)_2$ in diethyl ether afforded the suitable starting compound $Na[H_3Ga\text{-}CH(SiMe_3)_2]$ (**1**). Owing to the relatively weak sodium–ether interaction diethyl ether was completely removed upon evacuation at room temperature. Compound **1** was directly obtained in high purity and could by used in secondary reactions without further purification. A cooled (–60 °C) ethereal solution of **1** was subsequently treated with an excess of the adduct $(H_2O_2)_2$-DABCO (diazabicyclooctane, DABCO)[9] which is easily available from the addition of DABCO to aqueous solutions of hydrogen peroxide. Elemental hydrogen evolved, which was identified by absorption with a palladium wire and formation of molybdenum blue in a secondary reaction.[10] Filtration of the reaction mixture afforded a colorless solution from which upon cooling colorless crystals of **2** precipitated in 52% yield. An idealized reaction course is shown in Equation (1).

The molecular structure of **2** strongly resembles that of the corresponding lithium compound (see Figures 1 and 2).[7] A cage is formed in which two puckered $Ga_3(O_2)_3$ rings are bridged by four sodium ions. Each heterocycle is centered by a single oxygen atom and has the gallium atoms bridged by three peroxo groups. The O–O distances (151.8 pm) are longer than in hydrogen peroxide,[11] but correspond well to values observed for cyclic organoperoxides such as dioxetanes or dioxiranes[12] or for dianionic

---

[a] Institut für Anorganische und Analytische Chemie der Westfälischen Wilhelms-Universität Münster,
Corrensstraße 30, 48149 Münster, Germany
Fax: +49-251-833660
E-mail: uhlw@uni-muenster.de
[b] Fachbereich Chemie der Philipps-Universität Marburg,
Hans-Meerwein-Straße, 35032 Marburg, Germany



(1)

peroxo groups.[13] Slightly longer O–O bond lengths (152.9 pm) were detected for the corresponding lithium compound.[7] The Ga–O–O–Ga moieties in **2** reveal a torsion angle of 53° on average which is considerably smaller than in the *gauche* arrangement characteristic of acyclic peroxo compounds (> 90°).[11,14] The Ga–O distances are in a narrow range at about 189 pm. One sodium ion (Na1) is located in the center of the cage and bridges both $Ga_3(O_2)_3$ heterocycles by an interaction to one oxygen atom of each peroxo group and possesses a distorted octahedral coordination sphere (Na–O 238.3 pm on average). The remaining three sodium atoms are coordinated in a side-on mode by two peroxo groups (Na–O 230.4 pm), one from each molecular moiety. Coordination numbers of five result for these metal atoms by the terminal bonding of a diethyl ether molecule (Na3) or by an interaction with nitrogen atoms of DABCO ligands (Na1, Na4). These bifunctional ligands bridge two sodium atoms of different cages. Hence, in contrast to the lithium compound one-dimensional coordination polymers result (Figure 3). Both anionic building blocks of the cages are twisted by 11° relative to the Ga–O bonds to the μ_3-oxygen atoms to yield a helical structure.

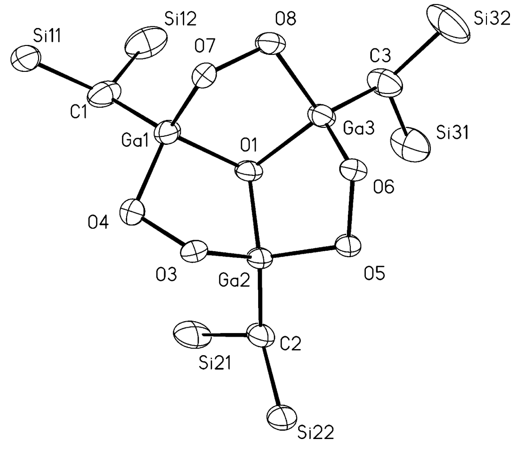


Figure 1. Structure of the $[(RGa)_3O_7]^{2-}$ ion of **2**. Methyl groups and hydrogen atoms are omitted. Selected bond lengths [pm], bond angles and torsion angles [°]: Ga1–O1 188.3(5), Ga1–O4 180.0(5), Ga1–O7 189.0(4), Ga2–O1 189.1(4), Ga2–O3 189.6(4), Ga2–O5 188.7(5), Ga3–O1 189.4(4), Ga3–O6 188.6(5), Ga3–O8 188.2(4), Ga4–O2 190.4(4), Ga4–O12 188.8(5), Ga4–O14 189.2(5), Ga5–O2 187.7(5), Ga5–O10 188.4(4), Ga5–O13 189.4(4), Ga6–O2 188.0(5), Ga6–O9 190.2(4), Ga6–O11 186.9(5), O–O 151.9 (av.), Ga–O(1/2)–Ga 107.1 (av.), Ga–O–O 106.1 (av.), Ga–O–O–Ga 53.3 (av.).

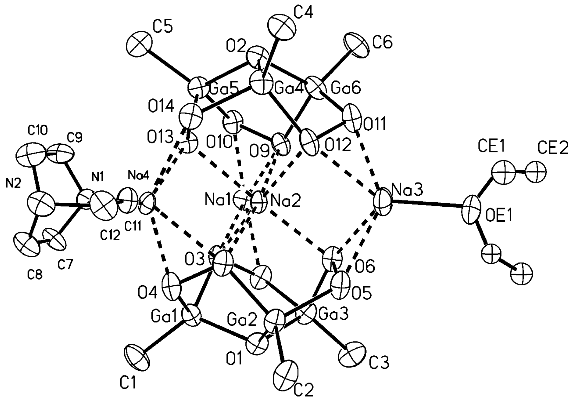


Figure 2. Structure of the dimeric formula unit of **2** including sodium atoms. $SiMe_3$ groups are omitted. Selected bond lengths [pm] and angles [°]: Na2–O 238.3 (av.), Na(1/3/4)–O 230.4 (av.), Na3–OE1 234.0(7), Na4–N1 240.8(5), O–Na2–O 84.5(2) to 98.9(2) and 172.9(2) to 174.5(2).

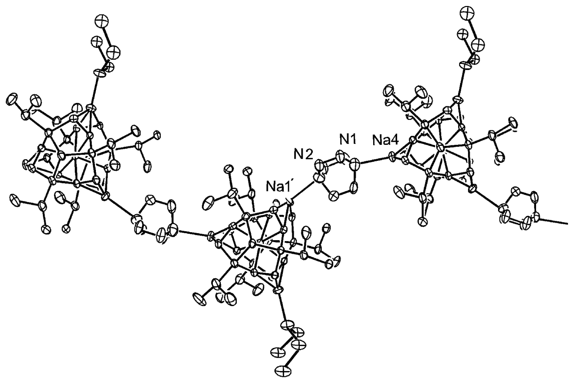


Figure 3. Chain structure of **2** in the solid state. $SiMe_3$ groups are omitted. Selected bond lengths [pm] and angles [°]: Na4–N1 240.8(5), Na1′–N2 246.0(6); Na1′ generated by $-x + 3/2$, $y + 1/2$, $-z + 3/2$.

Based on experimental and quantum-chemical studies on alkali metal and transition metal peroxides,[15] the stretching frequencies of dianionic O_2 moieties having O–O bond lengths of 140 to 150 pm are to be expected between 800 to 1000 cm^{-1}. Two intense absorptions at 945 and 988 cm^{-1} in the IR spectrum of **2** may be interpreted in terms of such O–O stretching vibrations. Solid samples of **2** are stable at room temperature over weeks. Decomposition by gas evolution started slowly upon warming and was completed at 96 °C. Solutions of **2** in benzene or THF could be stored at room temperature for several days without decomposition. **2** proved to be more stable than the corresponding lithium compound which makes it a promising candidate for a broader application in secondary reactions. The particular inertness of the Ga–C bonds in bis(trimethylsilyl)methylaluminium or -gallium peroxides may depend on a diminution of the negative charge in α-position to the Group 13-elements by hyperconjugation with σ*-orbitals of the Si–C bonds and, hence, a significantly lowered reducing power of the respective carbon atoms.[16]

Experimental Section

General: All procedures were carried out under purified argon. Cyclopentane was dried with $LiAlH_4$, diethyl ether and THF over Na/benzophenone. $NaGaH_4$, $LiCH(SiMe_3)_2$ and the adduct $(H_2O_2)_2{\cdot}DABCO$ were prepared according to literature procedures.[8,9,17]

Synthesis of 1: Freshly sublimed $LiCH(SiMe_3)_2$ (0.834 g, 5.02 mmol) was dissolved in 15 mL of diethyl ether. The solution was added dropwise to a suspension of freshly prepared $NaGaH_4$ (0.60 g, 6.20 mmol, excess) in the same solvent (15 mL) at room temperature. The mixture was stirred for 12 h and filtered. The solvent of the filtrate was completely removed in vacuo. A highly viscous residue remained which crystallized upon thorough evacuation over several hours. Owing to the NMR spectroscopic characterization the product **1** was formed directly in a high purity and can be applied in secondary reactions without further purification. In contrast to the corresponding lithium compound, $[(Me_3Si)_2CHGaH_3Li]$,[7] the ether content of **1** was removed easily by evacuation over a few minutes. Recrystallization of **1** from cyclopentane (20/–30 °C) afforded colorless crystals; yield 1.00 g (78 %), m.p. (argon, sealed capillary) 106 to 110 °C. ^1H NMR (C_6D_6, 400 MHz): δ = 2.36 (s, 3 H, br., GaH), 0.33 (s, 18 H, $SiMe_3$), –1.03 (s, 1 H, GaCH) ppm. ^{13}C NMR (C_6D_6, 100 MHz): δ = 3.17 ($SiMe_3$), –5.11 (GaC) ppm. ^{29}Si NMR (C_6D_6, 79.5 MHz): δ = 0.5 ppm; no resonance in the ^7Li NMR spectrum. IR (paraffin, CsBr): $\tilde{\nu}$ = 1763 (s, br.), 1580 [s, br., ν(GaH)], 1452 (s), 1377 (s, paraffin), 1298 (w), 1248 [s, $\delta(CH_3)$], 1165 (w), 1155 (w), 1020 [s, $\delta(CHSi_2)$], 934 (m), 843 (s), 756 [m, $\rho(CH_3Si)$], 720 (w, paraffin), 673 (m), 660 [m, $\nu_{as}(SiC)$], 611 [m, $\nu_s(SiC)$], 563 [m, br., ν(GaC)] cm^{-1}. $C_7H_{22}GaNaSi_2$ (255.13): calcd. C 33.0, H 8.7, Na 9.0; found C 32.6, H 8.6, Na 8.8.

Synthesis of 2: The solid and freshly prepared adduct $(H_2O_2)_2{\cdot}DABCO$ (0.72 g, 4.00 mmol, excess) was suspended in 15 mL of diethyl ether and intensively stirred at 0 °C for 10 min. The suspension was cooled to –60 °C and treated with a solution of the gallium hydride, $[(Me_3Si)_2CHGaH_3]Na$ (**1**), (0.50 g, 1.96 mmol) in 5 mL of diethyl ether. The mixture was warmed to room temperature over a period of 20 min. Gas evolution occurred. Hydrogen was detected by absorption with a palladium wire and subsequent reduction of molybdate to give a deep blue aqueous solution of molybdenum blue. Filtration and cooling of the filtrate to –20 °C afforded colorless crystals of the peroxide **2**; yield 0.34 g (52 %), m.p. (argon, sealed capillary). The crystals slowly decomposed at temperatures above room temperature with evolution of gas; this reaction was completed by heating at 96 °C and gave a yellow material. Repeated fractional crystallization was required in order to completely remove the excess of DABCO; the analytical and spectroscopic data were recorded with thoroughly evacuated, ether-free samples. The peroxide content was determined by hydrolysis of the crystalline product **2** in dilute HNO_3. Addition of iodide produces iodine, which was determined by titration with thiosulfate. More than 95 % of the calculated peroxide content was reproducibly obtained. ^1H NMR ([D_8]THF, 400 MHz, 220 K): δ = 2.63 (s, 24 H, DABCO), 0.1 (s, 108 H, $SiMe_3$), –0.86 (s, 6 H, GaCH) ppm. ^{13}C NMR ([D_8]THF, 100 MHz, 220 K): δ = 48.7 (DABCO), 3.89 ($SiMe_3$), –1.5 (GaC) ppm. ^{29}Si NMR ([D_8]THF, 79.5 MHz, 220 K): δ = –1.95 ppm. IR (paraffin, CsBr): $\tilde{\nu}$ = 1460 (vs), 1377 (s, paraffin), 1315 (m), 1298 (w), 1247 [s, $\delta(CH_3)$], 1157 (w), 1061 [s, ν(CC), ν(CN)], 1018 [m, $\delta(CHSi_2)$], 988 (m), 945 [m, ν(OO)(?)], 889 (m), 845 (vs), 756 [m, $\rho(CH_3Si)$], 723 (w, paraffin), 677 [w, $\nu_{as}(SiC)$], 629 [w, $\nu_s(SiC)$], 611 (w), 549 (m, br.), 511 [w, ν(GaC), ν(GaO), ν(LiO)] cm^{-1}.

Crystal Structure Determination: Single crystals of **2** were obtained from the reaction mixture upon cooling to –20 °C. The crystallographic data were collected with a Bruker APEX diffractometer with graphite-monochromated Mo-K_α radiation. The crystals were coated with a perfluoropolyether, picked up with a glass fiber and immediately mounted in the cooled nitrogen stream of the diffractometer. Twinned crystals were obtained with a *pseudo*-orthorhombic cell. Refinement was conducted in the monoclinic space group $P2_1/c$ by application of the twin matrix [–1,0,0,0,–1,0,0,0,1]. The ratio of the twin components was 0.52 to 0.48. Crystallographic data and details of the final R values are provided in Table 1.[20] All non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms attached to carbon were calculated on ideal positions and allowed to ride on the bonded atom with $U = 1.2U_{eq}(C)$. The DABCO and ether molecules were disordered; their methylene and methyl groups were refined on split positions (0.71 to 0.29 and 0.65 to 0.35, respectively). One trimethylsilyl group showed a rotational disorder; the positions of the methyl groups were refined with occupancy factors of 0.33. Residual electron density indicated the presence of disordered solvent molecules. Their atomic positions could not clearly be resolved and refined. Therefore the SQUEEZE program was applied which gave an electron density corresponding to four DABCO or six ether molecules.

Table 1. Crystal data and structure refinement for compound **2**.[a,b]

	2
Formula	$C_{52}H_{136}Ga_6N_2Na_4O_{15}Si_{12}$
Temperature /K	153(2)
Crystal system	monoclinic
Space group[18]	$P2_1/c$ (no. 14)
a /pm	2258.4(1)
b /pm	2376.2(1)
c /pm	2043.7(1)
α /°	90
β /°	90
γ /°	90
V /10^{-30} m^3	10967.3(9)
Z	4
$D_{calcd.}$ /$g\,cm^{-3}$	1.137
μ /mm^{-1}	1.641
Crystal size /mm	0.22 × 0.09 × 0.07
Theta range for data collection /°	$0.86 \le \theta \le 24.55$
Index ranges	$-26 \le h \le 26$ $-27 \le k \le 27$ $-23 \le l \le 23$
Independent reflections	18310 [R_{int} = 0.0594]
Parameters	906
$R = \Sigma\lVert F_o\rvert - \lvert F_c\rVert/\Sigma\lvert F_o\rvert$ [$I > 2\sigma(I)$]	0.0558 (14824)
$wR_2 = [\Sigma w(\lvert F_o\rvert^2 - \lvert F_c\rvert^2)^2/\Sigma\lvert F_o\rvert^2]^{1/2}$ (all data)	0.1747
Max./min. residual electron density /10^{30} $e\,m^{-3}$	1.811/–0.490

[a] Program SHELXL-97;[19] solutions by direct methods, full-matrix refinement with all independent structure factors. [b] See ref.[20] for CCDC reference number.

Acknowledgments

We are grateful to the Deutsche Forschungsgemeinschaft (DFG) (SFB 424) and the Fonds der Chemischen Industrie for generous financial support.

---

[1] a) J. J. Eisch, *Comprehensive Organometallic Chemistry* (Ed.: G. Wilkinson, F. G. A. Stone, W. W. Abel), Pergamon, Oxford, **1982**, vol. 1, p. 557–622; b) P. B. Brindley, *The Chemistry of Peroxides* (Ed.: S. Patai), Wiley, London, **1983**, p. 807–828.

[2] Y. A. Aleksandrov, N. V. Chikinova, *J. Organomet. Chem.* **1991**, *418*, 1–59.

[3] a) W. M. Cleaver, A. R. Barron, *J. Am. Chem. Soc.* **1989**, *111*, 8966–8967; b) M. B. Power, W. M. Cleaver, A. W. Apblett, A. R. Barron, J. W. Ziller, *Polyhedron* **1992**, *11*, 477–486; c) M. B. Power, J. W. Ziller, A. R. Barron, *Organometallics* **1993**, *12*, 4908–4916; d) A. R. Barron, *Chem. Soc. Rev.* **1993**, *22*, 93–99.

[4] W. Uhl, S. Melle, M. Prött, *Z. Anorg. Allg. Chem.* **2005**, *631*, 1377–1382.

[5] a) J. Lewinski, J. Zachara, E. Grabska, *J. Am. Chem. Soc.* **1996**, *118*, 6794–6795; b) J. Lewinski, J. Zachara, P. Gos, E. Grabska, T. Kopec, I. Madura, W. Marciniak, I. Prowotorow, *Chem. Eur. J.* **2000**, *6*, 3215–3227; c) S. S. Kumar, S. Singh, H. W. Roesky, J. Magull, *Inorg. Chem.* **2005**, *44*, 1199–1201.

[6] a) W. Uhl, B. Jana, *Chem. Eur. J.* **2008**, *14*, 3067–3071; b) W. Uhl, B. Jana, *J. Organomet. Chem.*, in print.

[7] W. Uhl, M. R. Halvagar, *Angew. Chem.* **2008**, *120*, 1981–1983; *Angew. Chem. Int. Ed.* **2008**, *47*, 1955–1957.

[8] L. I. Zakharkin, V. V. Gavrilenko, Yu. N. Karaksin, *Synth. Inorg. Met.-Org. Chem.* **1971**, *1*, 37–43.

[9] P. Dembech, A. Ricci, G. Seconi, M. Taddei, C. S. Brook, M. Guzman, A. B. Smith, *Org. Synth.* **1997**, *74*, 84–90.

[10] C. Zenghelis, *Z. Anal. Chem.* **1911**, *49*, 729–732.

[11] a) J.-M. Savariault, M. S. Lehmann, *J. Am. Chem. Soc.* **1980**, *102*, 1298–1303; b) S. Samdal, V. S. Mastryukov, J. E. Boggs, *J. Mol. Struct.* **1995**, *346*, 35–40; see also cited literature.

[12] a) W. Sandera, K. Schroeder, S. Muthusamy, A. Kirschfeld, W. Kappert, R. Boese, E. Kraka, C. Sosa, D. Cremer, *J. Am. Chem. Soc.* **1997**, *119*, 7265–7270; b) W. Adam, E. M. Peters, K. Peters, H. G. von Schnering, *Angew. Chem.* **1983**, *95*, 566–567; *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 546–547.

[13] a) G. C. Forbes, A. R. Kennedy, R. E. Mulvey, R. B. Rowlings, W. Clegg, S. T. Liddle, C. C. Wilson, *Chem. Commun.* **2000**, 1759–1760; b) A. R. Kennedy, R. E. Mulvey, R. B. Rowlings, *J. Am. Chem. Soc.* **1998**, *120*, 7816–7824; c) C. Drost, C. Jäger, S. Freitag, U. Klingebiel, M. Noltemeyer, G. M. Sheldrick, *Chem. Ber.* **1994**, *127*, 845–847; d) H. Föppl, *Z. Anorg. Allg. Chem.* **1957**, *291*, 12–50; e) J. H. Yates, R. M. Pitzer, *J. Chem. Phys.* **1977**, *66*, 3592–3597.

[14] S. Wolfe, *Acc. Chem. Res.* **1972**, *5*, 102–111.

[15] a) P. Fantucci, G. Pacchioni, *J. Chem. Soc., Dalton Trans.* **1987**, 355–360; b) H. Yates, R. M. Pitzer, *J. Chem. Phys.* **1977**, *66*, 3592–3597; c) C. J. Cramer, W. B. Tolman, K. H. Theopold, A. L. Rheingold, *Proc. Natl. Acad. Sci. USA* **2003**, *100*, 3635–3640.

[16] E. A. Brinkman, S. Berger, J. I. Brauman, *J. Am. Chem. Soc.* **1994**, *116*, 8304–8310.

[17] P. J. Davidson, D. H. Harris, M. F. Lappert, *J. Chem. Soc., Dalton Trans.* **1976**, 2268–2274.

[18] T. Hahn (Ed.) *International Tables for Crystallography, Space-Group Symmetry*, vol. A, Kluwer Academic Publishers, Dordrecht, Boston, London, **1989**.

[19] *SHELXTL-Plus*, rel. 4.1, Siemens Analytical X-RAY Instruments Inc., Madison, WI, **1990**. G. M. Sheldrick, *SHELXL-97, Program for the Refinement of Structures*, University of Göttingen, **1997**.

[20] CCDC-692178 (for **2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Received: November 30, 2008