Inorg. Chem. **2005**, *44*, 3537–3540

Inorganic Chemistry

Article

OH Functionality of Germanium(II) Compounds for the Formation of Heterobimetallic Oxides

Leslie W. Pineda, Vojtech Jancik, Herbert W. Roesky,* and Regine Herbst-Irmer

Institut für Anorganische Chemie der Georg-August-Universität Göttingen, Tammannstrasse 4,
37077 Göttingen, Germany

Received November 17, 2004

Two novel germanium(II) μ-oxo heterobimetallic oxides with different oxidation states at the metal centers have been reported. The reaction of LGeOH [L = N(Ar)C(Me)CHC(Me)N(Ar) (Ar = 2,6-i-$Pr_2C_6H_3$)] with Cp_2MMe_2 (M = Zr, Hf) in Et_2O afforded LGeOM(Me)Cp_2 [M = Zr (**2**), Hf (**3**)] in moderate yield. Compounds **2** and **3** were characterized by elemental analysis, IR, NMR, EI-MS, and single X-ray structural analysis. Compounds **2** and **3** crystallized in the space group $P\bar{1}$, and the geometry at the metal centers is tetrahedral. The Ge–O bond lengths of **2** and **3** are very similar (1.797(2) and 1.799(3) Å, respectively), and a bent M–O–M′ angle in **2** (143.8(1)°) and **3** (141.9(2)°) features both oxide systems. Different orientations of the Cp and Me groups of the metal centers were observed, and deviations of the Cp groups were exhibited.

Introduction

The interest in metal and organometallic oxides stems from the application of these compounds in industry as catalysts, as cocatalysts, and as a model for the fixation of catalysts on oxide surfaces.[1] Moreover, steady and increasingly attention has been focused on the synthesis and characterization of heterobimetallic oxides, which are used as polyfunctional catalysts and precursors for the preparation of bi- and polymetallic heterogeneous catalysts.[2]

Regarding the chemistry of the germanium(II) compounds bearing a Ge–O linkages was limited to alkoxy- and arylalkoxygermylenes,[3,4] and the isolation of μ-oxo linkages with two different metals was elusive so far. We have recently described the preparation and structural characterization of a terminal hydroxide based on germanium(II) LGeOH (**1**), where L is the β-diketiminato ligand N(Ar)C(Me)CHC(Me)N(Ar) (Ar = 2,6-i-$Pr_2C_6H_3$).[5] Compound **1** has a free lone pair of electrons at the metal center which reacts with elemental sulfur to yield LGe(S)OH, as a stable germa acid.[6] Herein we report on the reactions of **1** with methylated metallocene derivatives of group 4 (M = Zr, Hf) that lead to the isolation and characterization of discrete new μ-oxo heterobimetallic oxide systems.

Experimental Section

General Comments. All experimental manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. The samples for spectral measurements were prepared in a drybox. The solvents were purified according to the conventional procedures and were freshly distilled prior to use. Zirconocene dichloride and hafnocene dichloride were purchased from Fluka. Cp_2ZrMe_2 and Cp_2HfMe_2 were prepared as described in the literature.[7] NMR spectra were recorded on a Bruker Avance 500 instrument, and the chemical shifts are reported with reference to tetramethylsilane (TMS). IR spectra were recorded on a Bio-Rad Digilab FTS-7 spectrometer. Mass spectra were obtained on a Finnigan MAT 8230 spectrometer by the EI technique. Melting

---

* Author to whom correspondence should be addressed. E-mail: hroesky@gwdg.de.

(1) Coperèt, C.; Chabanas, M.; Sait-Arroman, R. P.; Basset, J.-M. *Angew. Chem., Int. Ed.* **2003**, *42*, 156–181.

(2) Roesky, H. W.; Haiduc, I.; Hosmane, N. S. *Chem. Rev.* **2003**, *103*, 2579–2595. (b) Carofiglio, T.; Floriani, C.; Rosi, M.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1991**, *30*, 3245–3246. (c) Rau, M. S.; Kretz, C. M.; Geoffroy, G. L.; Rheingold, A. L.; Haggerty, B. S. *Organometallics* **1994**, *13*, 1624–1634. (d) Erker, G.; Albrecht, M.; Werner, S.; Krüger, C. *Z. Naturforsch.* **1990**, *45b*, 1205–1209. (e) Bansal, S.; Singh, Y. Singh, A. *Heteroat. Chem.* **2004**, 21–25. (f) Li, H.; Eddaoudi, M.; Plévert, J.; O′Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2000**, *122*, 12409–12410.

(3) Jutzi, P.; Keitemeyer, S.; Neumann, B.; Stammler, H.-G. *Organometallics* **1999**, *18*, 4778–4784.

(4) Cetinkaya, B.; Gümrükcü, I.; Lappert, M. F.; Atwood, J. L.; Rogers, R. D.; Zaworotko, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 2088–2089. (b) Fjeldberg, T.; Hitchcock, P. B.; Lappert, M. F.; Smith, S. J.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1985**, 939–941.

(5) Pineda, L. W.; Jancik, V.; Roesky, H. W.; Neculai, D.; Neculai, A. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 1419–1421.

(6) Pineda, L. W.; Jancik, V.; Roesky, H. W.; Herbst-Irmer, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 5534–5536.

(7) Samuel, E.; Rausch, M. D. *J. Am. Chem. Soc.* **1973**, *95*, 6263–6267.

10.1021/ic048383f CCC: $30.25

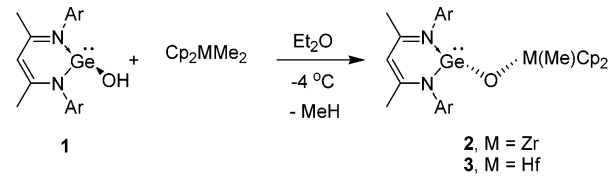
points were obtained in sealed capillaries on a Büchi B 540 instrument. CHN analyses were performed at the Analytical Laboratory of the Institute of Inorganic Chemistry at Göttingen, Germany.

Preparation of LGe(μ-O)Zr(Me)Cp$_2$ (2). A solution of freshly sublimed Cp_2ZrMe_2 (0.44 g, 1.77 mmol) in ether (10 mL) was added via cannula to a solution of **1** (0.90 g, 1.77 mmol) in diethyl ether (25 mL) at −4 °C. The reaction mixture was kept stirring at this temperature for 15 min and then was allowed to warm to room temperature under formation of a precipitate. Once the gas evolution ceased, the yellow-orange precipitate was filtered off and dried in vacuo: yield 0.65 g (50%); mp 292 °C dec; ^{1}H NMR (500.13 MHz, C_6D_6, 25 °C, TMS) δ 7.13−7.24 (m, 6H; *m*-, *p*-Ar-*H*), 5.39 (s, 10H; C_5H_5), 4.65 (s, 1H; γ-C*H*), 3.54 (sept, 2H, $^3J_{H-H} = 6.8$ Hz; C*H*(CH$_3$)$_2$), 3.35 (sept, 2H, $^3J_{H-H} = 6.8$ Hz; C*H*(CH$_3$)$_2$), 1.53 (d, 6H, $^3J_{H-H} = 6.8$ Hz; CH(C*H*$_3$)$_2$), 1.48 (d, 6H, $^3J_{H-H} = 6.8$ Hz; CH(C*H*$_3$)$_2$), 1.44 (s, 6H; C*H*$_3$), 1.16 (d, 6H, $^3J_{H-H} = 6.8$ Hz; CH(C*H*$_3$)$_2$), 1.13 (d, 6H, $^3J_{H-H} = 6.8$ Hz; CH(C*H*$_3$)$_2$), 0.14 (s, 3H; C*H*$_3$); ^{13}C NMR (125.75 MHz, C_6D_6, 25 °C, TMS) δ 163.53 (*C*N), 144.46, 144.26, 141.04, 126.85, 124.53, 124.15 (*i*-, *o*-, *m*-, *p*-*Ar*), 110.25 (*C*$_5$H$_5$), 95.48 (γ-*C*H), 28.54 (*C*H$_3$), 28.52 (*C*H(CH$_3$)$_2$), 26.38 (*C*H(CH$_3$)$_2$), 24.59 (CH(*C*H$_3$)$_2$), 24.29 (CH(*C*H$_3$)$_2$), 24.08 (CH(*C*H$_3$)$_2$), 22.58 (CH(*C*H$_3$)$_2$), 20.75 (*C*H$_3$); EI-MS (70 eV) [*m*/*e* (%)] 742 (15) [M$^+$], 491 (100) [M$^+$ − OZr(Me)Cp$_2$]. Anal. Calcd for $C_{40}H_{54}GeN_2OZr$ ($M_r = 742.69$): C, 64.69; H, 7.33; N, 3.77. Found: C, 64.51; H, 7.29; N, 3.90.

Preparation of LGe(μ-O)Hf(Me)Cp$_2$ (3). Freshly sublimed Cp_2HfMe_2 (0.59 g, 1.77 mmol) dissolved in ether (15 mL) was transferred using a cannula to a flask charged with **1** (0.90 g, 1.77 mmol) in diethyl ether (25 mL) at −4 °C. After 25 min the cooling bath was removed and stirring was continued until the methane evolution ceased. Finally, after removal of the solvent the remaining crude product was recrystallized from a toluene/hexane mixture resulting in a yellow-orange microcrystalline solid at −32 °C that was filtered off and dried in vacuo: yield 0.75 g (51%); mp 317 °C dec; ^{1}H NMR (500.13 MHz, C_6D_6, 25 °C, TMS) δ 7.14−7.23 (m, 6H; *m*-, *p*-Ar-*H*), 5.33 (s, 10H; C$_5$*H*$_5$), 4.65 (s, 1H; γ-C*H*), 3.56 (sept, 2H, $^3J_{H-H} = 6.8$ Hz; C*H*(CH$_3$)$_2$), 3.35 (sept, 2H, $^3J_{H-H} = 6.8$ Hz; C*H*(CH$_3$)$_2$), 1.54 (d, 6H, $^3J_{H-H} = 6.8$ Hz; CH(C*H*$_3$)$_2$), 1.48 (d, 6H, $^3J_{H-H} = 6.8$ Hz; CH(C*H*$_3$)$_2$), 1.44 (s, 6H; C*H*$_3$), 1.17 (d, 6H, $^3J_{H-H} = 6.8$ Hz; CH(C*H*$_3$)$_2$), 1.13 (d, 6H, $^3J_{H-H} = 6.8$ Hz; CH(C*H*$_3$)$_2$), 0.02 (s, 3H; C*H*$_3$); ^{13}C NMR (125.75 MHz, C_6D_6, 25 °C, TMS) δ 163.95 (*C*N), 144.85, 144.48, 141.50, 127.13, 124.88, 124.45 (*i*-, *o*-, *m*-, *p*-*Ar*), 110.01 (*C*$_5$H$_5$), 95.80 (γ-*C*H), 28.87 (*C*H$_3$), 28.84 (*C*H(CH$_3$)$_2$), 26.70 (*C*H(CH$_3$)$_2$), 24.86 (CH(*C*H$_3$)$_2$), 24.62 (CH(*C*H$_3$)$_2$), 24.41 (CH(*C*H$_3$)$_2$), 23.86 (CH(*C*H$_3$)$_2$), 22.94 (*C*H$_3$); EI-MS (70 eV) [*m*/*e* (%)] 830 (15) [M$^+$], 491 (100) [M$^+$ − OHf(Me)Cp$_2$]. Anal. Calcd for $C_{40}H_{54}GeHfN_2O$ ($M_r = 829.95$): C, 57.89; H, 6.56; N, 3.38. Found: C, 57.71; H, 6.77; N, 3.24.

X-ray Structure Determination of 2 and 3. Data for the structure were collected on a Bruker three-circle diffractometer equipped with a SMART 6000 CCD detector. Intensity measurements were performed on a rapidly cooled crystal. The structure was solved by direct methods (SHELXS-97)[8] and refined with all data by full-matrix least squares on F^2.[9] The hydrogen atoms of C−H bonds were placed in idealized positions and refined isotropically with riding model, whereas the non-hydrogen atoms were refined anisotropically.

Scheme 1



Results and Discussion

By taking advantage of the oxophilicity of group 4 metals, we accomplished the isolation of compounds **2** and **3** by treatment of equivalent amounts of **1** and Cp_2MMe_2 (M = Zr, Hf)[7] in diethyl ether at −4 °C under methane evolution (Scheme 1).

The low solubility of **2** in the ethereal solution facilitates its separation as an air-sensitive yellow-orange microcrystalline solid. Conversely, **3** after removal of the solvent and recrystallization from a toluene/hexane mixture resulted in an air-sensitive yellow-orange microcrystalline product. Compounds **2** and **3** were characterized by analytical, spectroscopic, and single-crystal X-ray diffraction studies. The IR spectra of **2** and **3** are devoid of any OH absorption in the range 3000−3500 cm^{-1}. ^{1}H NMR spectra of **2** and **3** exhibit the characteristic Cp resonances as singlets (δ 5.39 and 5.33 ppm, respectively). In addition, a set of resonances assignable to the isopropyl and methyl protons associated with the β-diketiminato ligand in the range between δ 1.54 and 1.12 ppm and the absence of the hydroxyl proton resonance features both **2** and **3**. At higher field appears the resonance of the methyl protons coordinated to the metal (δ 0.14 ppm in **2** and δ 0.02 ppm in **3**). Electron impact (EI) spectrometry shows the parent ion [M$^+$] with the isotopic pattern for **2** and **3** (*m*/*e* = 742 and *m*/*e* = 830). Particularly interesting is the same fragmentation pattern of both compounds featuring the cleavage of [M$^+$ − OM(Me)Cp$_2$] (*m*/*e* = 491).

Structural Description. The compositions of **2** and **3** were unambiguously assigned by X-ray analysis. Yellow-orange crystals of **2** and **3** were obtained from a toluene/hexane mixture at −32 °C. Crystallographic data for the structural analyses of compounds **2** and **3** are given in Table 1, and important bond parameters are listed in Table 2.

Compounds **2** and **3** crystallize in the triclinic space group $P\bar{1}$ with one molecule in the asymmetric unit. **2** and **3** exhibit a germanium atom bonded through a bridging oxygen atom to a zirconium and hafnium atom, respectively. The coordination environment about the germanium atom is completed by a β-diketiminato ligand. Two Cp ligands and one methyl group complete the coordination sphere at the zirconium and hafnium atom, respectively. The geometry around the zirconium, as well as at the hafnium, is tetrahedral. The same geometry can be assigned for the germanium assuming that a lone pair of electrons occupies the fourth vacant site. The structures of **2** and **3** are shown in Figures 1 and 2. For **2** the Ge(1) and C(3) (γ-CH) deviate from the C_2N_2 ligand plane by 1.020 and 0.152 Å, respectively, resulting in a boat conformation. The Ge−N bond lengths (2.030 and 2.061 Å) and N−Ge−N angle (87.0°)

---

[8] Sheldrick, G. M. SHELXS-97, Program for Structure Solution. *Acta Crystallogr., Sect. A* **1990**, *46*, 467−473.

[9] Sheldrick, G. M. *SHELXL-97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

Table 1. Crystal Data and Structure Refinement for Compounds **2** and **3**

	2	3
formula	$C_{40}H_{54}GeN_2OZr$	$C_{40}H_{54}GeHfN_2O$
fw	742.66	829.93
cryst system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
temp, K	100(2)	100(2)
λ, Å	1.54178	1.54178
a, Å	9.444(1)	9.323(1)
b, Å	10.522(1)	10.474(1)
c, Å	19.750(1)	20.200(1)
α, deg	88.64(1)	89.13(1)
β, deg	89.60(1)	89.87(1)
γ, deg	67.44(1)	67.04(1)
V, Å^3	1812(1)	1816(1)
Z	2	2
ρ_{calcd}, g/cm^3	1.361	1.518
μ, mm^{-1}	3.617	6.440
F(000)	776	840
cryst size, mm^3	$0.10 \times 0.08 \times 0.03$	$0.10 \times 0.08 \times 0.04$
θ range for data collcn, deg	2.24–58.96	2.19–58.94
index ranges	$-10 \leq h \leq 10$	$-10 \leq h \leq 9$
	$-11 \leq k \leq 11$	$-11 \leq k \leq 11$
	$-21 \leq l \leq 21$	$-21 \leq l \leq 22$
no. of reflcns collcd	14 140	13 915
no. of indepnt reflcns (R_{int})	5044 (0.0265)	5077 (0.0221)
no. of data/restraints/params	5044/0/421	5077/0/422
GoF on F^2	1.063	1.265
R1,[a] wR2[b] ($I > 2\sigma(I)$)	0.0288, 0.0728	0.0287, 0.0782
R1,[a] wR2[b] (all data)	0.0297, 0.0735	0.0296, 0.0785
extinctn coeff	0.00037(9)	
largest diff peak/hole, e Å^{-3}	1.232/−0.553	1.551/−0.801

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o)^2]^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compounds **2** and **3**

	Compound **2**		
Zr(1)−O(1)	1.951(2)	O(1)−Ge(1)−N(1)	99.0(1)
Zr(1)−C(30)	2.285(3)	O(1)−Ge(1)−N(2)	99.3(1)
Ge(1)−O(1)	1.797(2)	N(1)−Ge(1)−N(2)	87.0(1)
Ge(1)−N(1)	2.030(2)	O(1)−Zr(1)−C(30)	98.5(1)
Ge(1)−N(2)	2.061(2)	Ge(1)−O(1)−Zr(1)	143.8(1)
X_{Cp1}−Zr(1)[a]	2.240	X_{Cp1}−Zr(1)−X_{Cp2}	129.2
X_{Cp2}−Zr(1)[a]	2.259		
	Compound **3**		
Hf(1)−O(1)	1.940(3)	O(1)−Ge(1)−N(1)	97.5(2)
Hf(1)−C(30)	2.276(6)	O(1)−Ge(1)−N(2)	100.7(2)
Ge(1)−O(1)	1.799(3)	N(1)−Ge(1)−N(2)	86.8(1)
Ge(1)−N(1)	2.038(4)	O(1)−Hf(1)−C(30)	96.3(2)
Ge(1)−N(2)	2.052(4)	Ge(1)−O(1)−Hf(1)	141.9(2)
X_{Cp1}−Hf(1)[a]	2.222	X_{Cp1}−Hf(1)−X_{Cp2}	128.0
X_{Cp2}−Hf(1)[a]	2.236		

[a] X_{Cp} = centroid distance of the Cp rings.

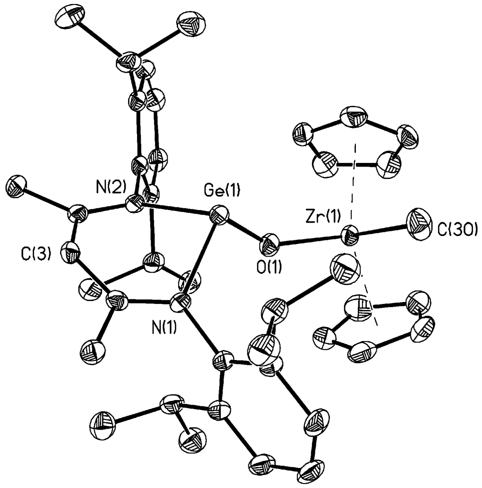


Figure 1. Molecular structure of **2**. Hydrogen atoms are omitted for clarity.

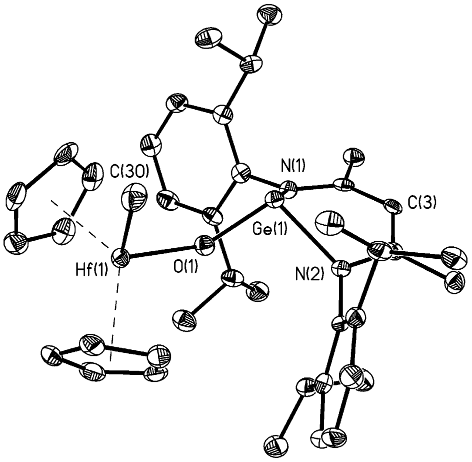


Figure 2. Molecular structure of **3**. Hydrogen atoms are omitted for clarity.

are comparable to those reported in **1** and further examples.[10] A bent Ge−O−Zr (143.8°) linkage with Ge−O (1.797 Å) and a Zr−O bond length (1.951 Å) show the characteristic features of compound **2**. The Zr−O bond length in $[(Cp)_2ZrCl]_2O$ (1.94 Å)[11] is in good agreement with that in **2**; nevertheless, a slightly shorter Zr−O bond length is observed in $Cp(CO)_3WOZr(Cl)Cp_2$ (1.871 Å)[12] and a longer distance in $[Cp_2Zr(Me)OAl(Me)_2]_2$ (2.044 Å).[2d] The Zr−C(Cp) bond lengths range from 2.517 to 2.568 Å. The X_{Cp1}−Zr−X_{Cp2} centroid distances are 2.240 and 2.259 Å with an angle of 129.2°. Both Cp ligands are twisted to each other by 21° from the eclipsed conformation.

Compound **3** shows similar structural parameters compared with that of **2** but with different orientation of the Cp and C(30) groups (torsion angle for C(30)−Zr(1)−O(1)−Ge(1) of −41.7° and C(30)−Hf(1)−O(1)−Ge(1) of −12.3°). A boat-like conformation is also observed due to the nonplanar Ge(1) and C(3) (γ-CH) atoms (1.038 and 0.154 Å) within the C_2N_2 framework. The Ge−N bond length and N−Ge−N angle is 2.045(av) Å and 86.8°, respectively. Aside from the Ge−O bond distance (1.799 Å) and the Hf−O bond length (1.940 Å), a bent Ge−O−Hf angle (141.9°) features the structure of **3**. The X_{Cp1}−Hf−X_{Cp2} centroid distances are 2.222 and 2.236 Å with an angle of 128.0°. A deviation (23°) from an ideally eclipsed Cp group is also observed in **3**. A comparison with earlier examples, even though they are based on Ge(IV) as in $Ph_3SiOGePh_3$ and $Ph_3GeOSnPh_3$,[13] shows that M−O−M′ angles (142.5 and 134.9°, respectively)

---

(10) Ding. Y.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Organometallics* **2001**, *20*, 1190−1194. (b) Ding. Y.; Hao, H.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Organometallics* **2001**, *20*, 4806−4811. (c) Ding. Y.; Ma, Q.; Roesky, H. W.; Herbst-Irmer, R.; Noltemeyer, M.; Schmidt, H.-G. *Organometallics* **2002**, *21*, 5216−5220.

(11) Clarke, J. F.; Drew, M. G. B. *Acta Crystallogr.* **1974**, *B30*, 2267−2269.

(12) Jacobsen, E. N.; Trost, M. K.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 8092−8094.

(13) Morosin, B.; Harrah, L. A. *Acta Crystallogr.* **1981**, *B37*, 579−586.

are quite similar to that occurring in compounds **2** and **3**.

It is worth mentioning that the slight shortening of the Ge−O bond length observed for both **2** and **3** compared with that in **1** (1.828 Å) is due to the tendency of both transition metals to form a strong bond toward hard donors with the consequence that the electron density shifts from the donor atom to the transition metal center and enhances the interaction between the germanium atom and the donor.

Conclusion

In summary, the synthesis and structural characterization of two novel heterobimetallic complexes based on germanium(II) and an oxygen bridge are reported. **2** and **3** contain two metal centers in high and low oxidation states. Presently, we are studying the ability of **2** and **3** to coordinate to metal carbonyl fragments. Moreover, we are investigating the possibility of using **2** and **3** as precursor for tailor-made Ge^{II}(μ-O)Zr and Ge^{II}(μ-O)Hf oxides, respectively.

Acknowledgment. This work is dedicated to Professor Konrad Seppelt on the occasion of his 60th birthday. We thank the Deutsche Forschungsgemeinschaft, the Göttinger Akademie der Wissenschaften, and the Fonds der Chemischen Industrie for funding. L.W.P. thanks the Deutscher Akademischer Austauschdienst (DAAD) for a predoctoral fellowship.

Supporting Information Available: X-ray data (CIF) for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC048383F