3630 *Organometallics* **2007,** *26,* 3630−3632

Templated Rearrangement of Silylated Benzoxazolin-2-ones: A Novel Tridentate (ONO)$^{2-}$ Chelating Ligand System

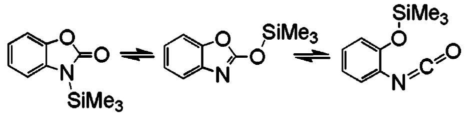
Jörg Wagler*[†,‡] and Anthony F. Hill[†]

Research School of Chemistry, Institute of Advanced Studies, The Australian National University, Canberra, ACT 0200, Australia, and Institut für Anorganische Chemie, Technische Universität Bergakademie Freiberg, D-09596 Freiberg, Germany

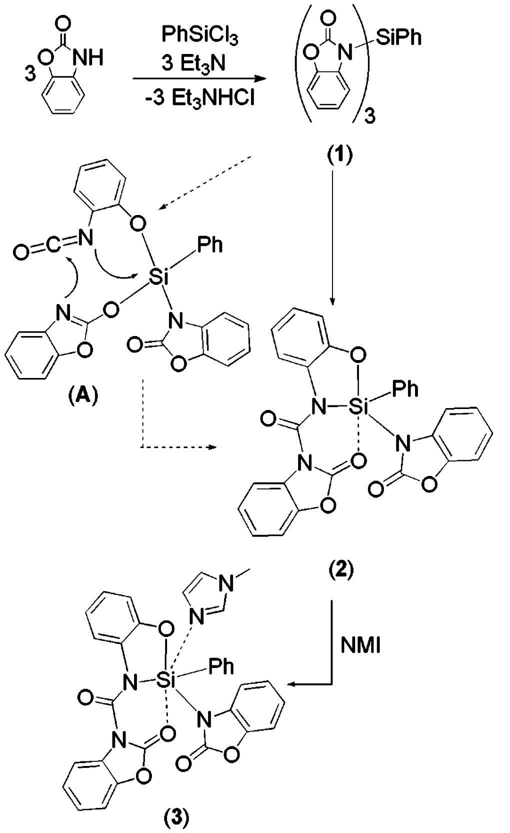
Received April 30, 2007

Summary: The reaction of phenyltrichlorosilane with benzoxazolin-2-one gives rise to phenyltris(benzoxazolin-2-on-1-yl)silane, which thermally rearranges to a pentacoordinate silicon compound bearing a novel (ONO) tridentate chelating ligand with interesting coordination properties.

Scheme 1



Scheme 2



Kricheldorf has previously shown that N-silylated benzoxazolin-2-one may be thermally isomerized to 2-(siloxy)phenylisocyanate (Scheme 1).[1] Isomerization reactions of 2-(siloxy)phenylisocyanates back to *N*-silylated benzoxazolinones (in both catalyzed and noncatalyzed processes) have also been reported.[2] The further chemistry of this 2-(siloxy)phenylisocyanate-*N*-silylbenzoxazolinone system has, however, not been explored in the interim.

Our investigations have now shown that the reaction of benzoxazolin-2-one with phenyltrichlorosilane and triethylamine yields phenyltris(benzoxazolin-2-on-1-yl)silane (**1**),[3] which may be isolated in good yield (Scheme 2). Thermal treatment of **1** (toluene, reflux), however, leads to the rearrangement of two of the benzoxazolinyl moieties to provide a novel tridentate chelating ligand system with the formation of a hypercoordinate silicon complex, **2** (Scheme 2).[4]

The intermediate formation of a 2-(siloxy)phenylisocyanate as well as a 2-siloxybenzoxazoline moiety provides an explanation for this rearrangement reaction (Scheme 2, **A**). On the basis of the results of Kricheldorf[1] (Scheme 1), the thermal treatment of **1** might lead to the stepwise transformation of the N-silylated benzoxazolinone groups via siloxybenzoxazolines to 2-(siloxy)phenylisocyanate moieties. If there are both isomeric forms coincident on the same Si atom, the lone pair of the N atom in the siloxybenzoxazoline moiety may attack the electrophilic isocyanate carbon atom and give rise to the formation of **2**. Other mechanisms, however, may also be involved and cannot be unambiguously excluded, at this stage.

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* Corresponding author. E-mail: joerg.wagler@chemie.tu-freiberg.de.

[†] Australian National University.

[‡] Technische Universität Bergakademie Freiberg.

(1) Kricheldorf, H. R. *Liebigs Ann. Chem.* **1973**, *771−772*, 772.

(2) (a) Kozyukov, V. P.; Mironov, V. F. *Zh. Obsh. Khim.* **1974**, *44*, 553. (b) Kuznetsova, M. G.; Mironova, N. V.; Kisin, A. V.; Kozyukov, V. P.; Nikitin, V. S.; Alekseev, N. V. *Zh. Obsh. Khim.* **1981**, *51*, 1196. (c) Chikina, N. L.; Kolodyazhnyi, Y. V.; Kozyukov, V. P.; Mironova, N. V.; Osipov, O. A. *Zh. Obsh. Khim.* **1984**, *54*, 139. (d) Chikina, N. L.; Kozyukov, V. P.; Mironova, N. V.; Garnovskii, A. D. *Zh. Obsh. Khim.* **1986**, *56*, 1107.

(3) **1**: Benzoxazolin-2-one (1.50 g, 11.1 mmol) and triethylamine (1.40 g, 13.7 mmol) in 20 mL of THF were stirred at ambient temperature, and phenyltrichlorosilane (0.80 g, 3.8 mmol) was added via syringe. The mixture was then stirred at 50 °C for 30 min and stored at 20 °C for 1 h. The Et_3NHCl precipitate was filtered and washed with 8 mL of THF. From the filtrate the solvent was removed under reduced pressure. The residue was dissolved in 10 mL of toluene (without heating) and stored at ambient temperature for 10 days to yield **1** as a white crystalline solid. The solution was decanted and the crystals dried in vacuum. Yield: 1.45 g (2.86 mmol, 77%). Anal. Found: C, 63.68; H, 3.68; N, 8.28. $C_{27}H_{17}N_3O_6Si$ requires: C, 63.90; H, 3.38; N, 8.28. δ_C (125.7 MHz, $CDCl_3$, Me_4Si): 110.5, 112.6, 122.8, 124.1, 124.3, 129.2, 131.0, 134.1, 136.4, 145.0, 156.6. δ_{Si} (59.6 MHz, $CDCl_3$, Me_4Si): −36.7. NB: For **1** and derived compounds, the ^1H NMR spectra were complex in the aromatic region of the spectra (6−8.5 ppm) and generally uninformative. Accordingly, only ^{13}C and ^{29}Si NMR data are reported.

(4) **2**: Procedure as for the preparation of **1**, but after dissolving the crude product in toluene (5 mL) the mixture was heated to reflux (for ca. 2 min.), whereupon a white precipitate formed. The mixture was then stored at room temperature, and after 2 weeks the solid was filtered, washed with 2 mL of toluene, and dried in vacuum. Yield: 1.28 g (2.52 mmol, 68%). Anal. Found: C, 63.58; H, 3.53; N, 8.02. $C_{27}H_{17}N_3O_6Si$ requires: C, 63.90; H, 3.38; N, 8.28). δ_C (125.7 MHz, $CDCl_3$, Me_4Si): δ 109.2, 111.4, 112.9, 113.8, 116.9, 119.5, 120.3, 122.3, 123.5, 125.5, 126.5, 126.8, 127.1, 128.0, 130.9, 131.0, 132.9, 135.9, 136.3, 142.5, 144.4, 147.4, 150.1, 156.8, 158.1. δ_{Si} (99.3 MHz, $CDCl_3$, Me_4Si): δ −96.0.

10.1021/om700416b CCC: $37.00

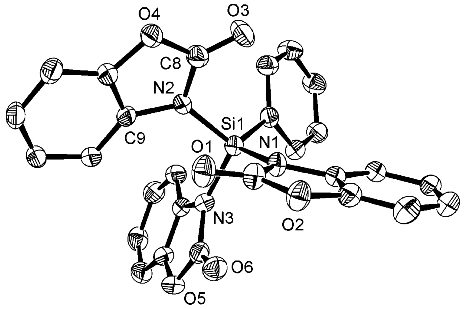


Figure 1. Molecular structure of **1** in the crystal (ORTEP plot with 50% probability ellipsoids, hydrogen atoms omitted, selected atoms labeled).

The molecular structure of **1**[5a] already suggests a tendency of this molecule to rearrange into another isomer (Figure 1). The bonds Si1−N1 (1.752(2) Å), Si1−N2 (1.752(2) Å), and Si1−N3 (1.746(2) Å) are in the normal range of Si−N bonds. Atom O3, however, exhibits the shortest Si−O separation of the three carbonyl moieties (3.02 Å), and the silicon atom is noticebly out of plane (0.516(3) Å) with respect to the five-membered ring of this benzoxazolinone moiety. Furthermore, the difference of 13.3° between the bond angles Si1−N2−C8 (117.8(1)°) and Si1−N2−C14 (131.1(1)°) indicates a pronounced orientation of O3 toward Si1, whereas the difference between the analogous angles is smaller at N1 (12.0°) and N3 (1.1°) and, therefore, the distances Si1−O1 (3.08 Å) and Si1−O5 (3.21 Å) are somewhat longer. In the ^{29}Si NMR spectrum of a $CDCl_3$ solution of **1** a signal at −36.7 ppm represents the $SiCN_3$ environment of **1**; however a minor peak at −40.7 ppm indicates the formation of an isomer with a $SiCN_2O$ environment in solution.

Recrystallization of the rearrangement product **2** from dichloromethane/diethyl ether afforded crystals of two monoclinic modifications. As there are no striking differences in the molecular conformation of **2**, only one of them is described here (Figure 2). The silicon atom Si1 is situated in an almost trigonal bipyramidal coordination sphere with the tridentate ligand in an $O_{ax}N_{eq}O_{ax}$ arrangement. In accordance with Scheme 2, the bond Si1−O1 (1.884(1) Å) is significantly longer than the distance Si1−O4 (1.704(1) Å). Even the bond Si1−N2 (1.844(1) Å) is still significantly shorter than the "dative" Si−O bond. The carbonyl groups C8═O3 and C15═O5 exhibit similar bond lengths (1.205(2) and 1.211(2) Å, respectively), whereas the C1═O1 separation (1.239(2) Å) is noticebly elongated as a result of the O1−Si1 coordination. The pentacoordination of the Si atom in **2** is retained in chloroform solution, as indicated by ^{29}Si NMR spectroscopy (−96.0 ppm).

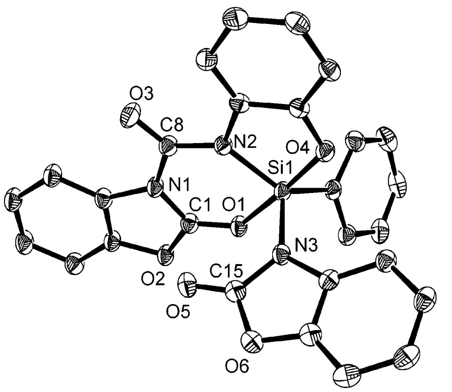
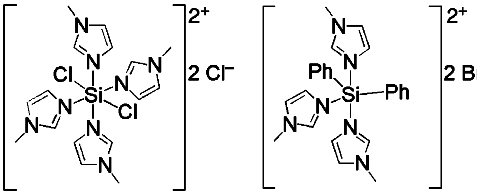


Figure 2. Molecular structure of **2** in the crystal (ORTEP plot with 50% probability ellipsoids, hydrogen atoms omitted, selected atoms labeled).

Chart 1



Although other pentacoordinate silicon complexes bearing tridentate (ONO) chelating ligands have been very recently reported,[6] our novel tridentate ligand system furnishes a silicon complex with notably different coordination behavior. This feature becomes obvious in the reaction of **2** with *N*-methylimidazole (NMI) to yield the hexacoordinate Si complex **3**[7] (Scheme 2). Hypercoordinate silicon complexes bearing the NMI ligand have been reported in the literature, and their molecular structures have been discussed.[8] A common feature of all crystallographically characterized hypercoordinate Si−NMI adducts is their cationic character (Chart 1).

The NMI ligand is a potent donor, as it may delocalize formal positive charges via two nitrogen atoms (imidazolium canonical form). In the Si−NMI complexes, which have been reported so far, the silicon atom diminishes the formal negative charge upon complex formation by Si−X (X = halide) bond ionization. Compound **3** provides the first crystallographic evidence of a neutral hypercoordinate silicon complex bearing the NMI ligand (Figure 3).[9−12]

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[5] Crystal structure analyses: (a) **1**: $C_{27}H_{17}N_3O_6Si$, CCDC-639925, *T* 100(2) K; monoclinic, $P2_1/n$ (No. 14); *a* 10.0718(6) Å, *b* 14.1564(9) Å, *c* 16.4521(9) Å, β 99.678(2)°; *V* 2312.4(2) Å^{-3}; *Z* 4; μ(Mo Kα) 0.153 mm^{-1}; θ_{max} 25°; 21 028 reflections (4059 unique, R_{int} 0.0699), 334 parameters, GoF 1.040, R_1/wR_2 [$I > 2\sigma(I)$] 0.0435/0.1006, R_1/wR_2 (all data) 0.0688/0.1099, residual electron density (highest peak, deepest hole) 0.285, −0.341 e Å^{-3}. (b) **2**: first modification $C_{27}H_{17}N_3O_6Si$, CCDC-639922, *T* 90(2) K; monoclinic, $P2_1/n$ (No. 14); *a* 10.1478(3) Å, *b* 13.9645(4) Å, *c* 16.6750(5) Å, β 106.381(1)°; *V* 2267.08(12) Å^{-3}; *Z* 4; μ(Mo Kα) 0.156 mm^{-1}; θ_{max} 30°; 42 960 reflections (6613 unique, R_{int} 0.0469), 334 parameters, GoF 1.051, R_1/wR_2 [$I > 2\sigma(I)$] 0.0403/0.0972, R_1/wR_2 (all data) 0.0585/0.1040, residual electron density (highest peak, deepest hole) 0.361, −0.359 e Å^{-3}. **2**: second modification $C_{27}H_{17}N_3O_6Si$, CCDC-639924, *T* 110(2) K; monoclinic, $P2_1/c$ (No. 14); *a* 6.8969(2) Å, *b* 34.1668(11) Å, *c* 10.0771(3) Å, β 104.992(1)°; *V* 2293.79(12) Å^{-3}; *Z* 4; μ(Mo Kα) 0.154 mm^{-1}; θ_{max} 30°; 37 204 reflections (6664 unique, R_{int} 0.0583), 334 parameters, GoF 1.064, R_1/wR_2 [$I > 2\sigma(I)$] 0.0419/0.0982, R_1/wR_2 (all data) 0.0655/0.1055, residual electron density (highest peak, deepest hole) 0.361, −0.318 e Å^{-3}. (c) **3**: $C_{31}H_{23}N_5O_6Si$, CCDC-639923, *T* 100(2) K; triclinic, $P\bar{1}$ (No. 2); *a* 9.8488(2) Å, *b* 12.2068(4) Å, *c* 12.6570(3) Å, α 65.848(1)°, β 80.353(2)°, γ 74.744(1)°; *V* 1336.42(6) Å^{-3}; *Z* 2; μ(Mo Kα) 0.146 mm^{-1}; θ_{max} 32°; 46 764 reflections (9249 unique, R_{int} 0.0436), 389 parameters, GoF 1.025, R_1/wR_2 [$I > 2\sigma(I)$] 0.0423/0.1090, R_1/wR_2 (all data) 0.0555/0.1146, residual electron density (highest peak, deepest hole) 0.583, −0.399 e Å^{-3}.

[6] (a) Wagler, J. *Organometallics* **2007**, *26*, 155. (b) Wagler, J.; Brendler, E. *Z. Naturforsch. B* **2007**, *62*, 225. (c) Böhme, U.; Wiesner, S.; Günther, B. *Inorg. Chem. Commun.* **2006**, *9*, 806. (d) Böhme, U.; Günther, B. *Inorg. Chem. Commun.* **2007**, *10*, 482.

[7] **3**: **2** (0.55 g, 1.1 mmol) was stirred in 1.5 mL of dichloromethane and NMI (0.19 g, 2.3 mmol) was added. The mixture was then stirred for 1 min to obtain a clear solution. The flask bearing this solution was then connected to a second flask with 2 mL of diethyl ether for gas-phase diffusion of the solvents. Within 2 days colorless crystals of **3** had formed, the solution was decanted, and the crystals were dried in vacuum. Yield: 0.52 g (0.88 mmol, 81%). Anal. Found: C, 63.01; H, 4.29; N, 11.90. $C_{31}H_{23}N_5O_6Si$ requires: C, 63.15; H, 3.93; N, 11.88. The crystals are poorly soluble in chloroform and dichloromethane. The ^{29}Si NMR shift has been determined by adding NMI to a solution of **2** in $CDCl_3$. δ_{Si} (59.6 MHz, $CDCl_3$, Me_4Si): −166.3 ppm.

[8] (a) Hensen, K.; Mayr-Stein, R.; Stumpf, T.; Pickel, P.; Bolte, M.; Fleischer, H. *J. Chem. Soc., Dalton Trans.* **2000**, 473. (b) Hensen, K.; Spangenberg, B.; Bolte, M. *Acta Crystallogr. C* **2000**, *56*, 1245. (c) Hensen, K.; Kettner, M.; Pickel, P.; Bolte, M. *Z. Naturforsch. B* **1999**, *54*, 2000. (d) Hensen, K.; Gebhardt, F.; Bolte, M. *Acta Crystallogr. C* **1998**, *54*, 1462. (e) Hensen, K.; Gebhardt, F.; Bolte, M. *Z. Anorg. Allg. Chem.* **1997**, *623*, 633. (f) Hensen, K.; Zengerly, T.; Müller, T.; Pickel, P. *Z. Anorg. Allg. Chem.* **1988**, *558*, 21.

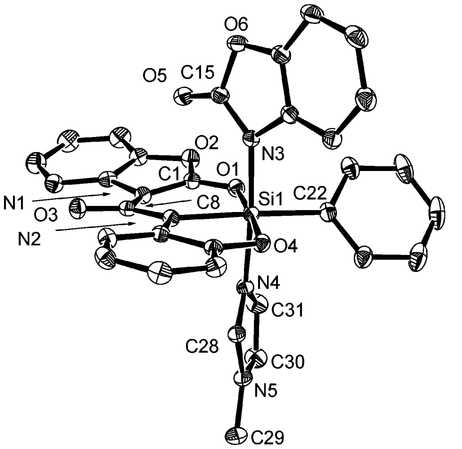


Figure 3. Molecular structure of **3** in the crystal (ORTEP plot with 50% probability ellipsoids, hydrogen atoms omitted, selected atoms labeled).

The Si atom of **3** is octahedrally coordinated, with the NMI nitrogen atom N4 occupying the position *trans* to the benzoxazolinone nitrogen N3. The bond Si1−C22 is located in the plane of the *mer*-coordinating (ONO) chelate. Like compound **2** there is a striking difference in the bond lengths Si1−O1 (1.849(1) Å) and Si1−O4 (1.721(1) Å). Whereas the "dative" bond Si1−O1 has been slightly shortened upon NMI coordination (ca 0.035 Å), the "covalent" bond Si1−N2 (1.947(1) Å) is significantly elongated (ca 0.103 Å), being only slightly shorter than the bond Si1−N4 (1.962(1) Å) to the NMI moiety and much longer than the Si1−N3 bond (1.896(1) Å) to the benzoxazolinone nitrogen atom. Simultaneously, the bond N2−C8 (**2**, 1.368(2) Å; **3**, 1.337(1) Å) has been shortened and the bond C8═O3 (**2**, 1.205(2) Å; **3**, 1.221(1) Å) has been lengthened.

These changes in bond lengths are consistent with a shift of formal negative charge to the carbonyl oxygen atom O3, providing a rationale for why this novel $(ONO)^{2-}$ tridentate chelating ligand system supports the formation of a formally neutral hexacoordinate Si−NMI adduct (Chart 2). The C−Si−N−C bonding features of the tridentate ligand in **3** (Si−N 1.947(1), C−N 1.337(1), Si−C 1.914(1) Å) are similar to those in a hexacoordinate silicon complex bearing an imine moiety *trans* to the silicon phenyl substituent (Si−N 1.959(1), C═N 1.302(1), Si−C 1.927(1) Å).[13]

It useful to note parallels between our ligand system and that described by Arduengo (Chart 3), e.g., in the stabilization of the hypervalent tin(II) complex **4**.[14] Formally the trianion derived from a 3-aza-1,5-dione, as a ligand, is best considered as an oxidized monoanion forming two coplanar five-membered chelates. In contrast, our system is based on a dianionic ligand forming five- and six-membered chelates, the most notable distinction being the electronic delocalization afforded by the exocyclic carbonyl group. Concluding from our results, the hitherto unknown dianionic (ONO) ligand *N*-(*o*-oxyphenyl)-benzoxazolin-2-one-1-carboxamide might be expected to display similar charge-dissipating properties in transition metal complexes. Therefore, it may well be a suitable supporting ligand for catalytically active metal centers to coordinate and activate substrates. Furthermore, given that silylated derivatives are often the reagent of choice for delivering N- and O-based ligands to transition metals, the compounds **2** and **3** are in some respects "ready-made" for such purposes. While the presence of a third benzoxazolinonyl group on silicon might appear redundant for the purposes of the ligand templation sequence, it does appear to be essential. We note that that diphenylbis(benzoxazolin-2-on-1-yl)silane and dimethylbis(benzoxazolin-2-on-1-yl)silane do not undergo such rearrangments in refluxing toluene. Investigations of the formation of this tridentate system without the third equivalent of benzoxazolinone as well as experiments to obtain the free ligand are currently in progress.

Chart 2

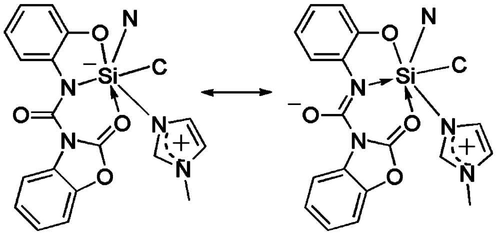
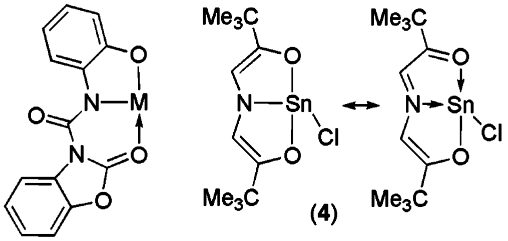


Chart 3



Acknowledgment. This work was supported by a fellowship within the Post-Doctoral Programme of the German Academic Exchange Service (DAAD) and by the Australian Research Council (DP0342701).

Supporting Information Available: X-ray crystallographic files in CIF format, for structure detereminations of compounds **1** (CCDC-639925), **2** (CCDC-639922, CCDC-639924), and **3** (CCDC-639923). This information is available free of charge via the Internet at http://pubs.acs.org.

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(9) Hypercoordinate nonionic silicon complexes bearing NMI-related ligands (e.g., vinylimidazole, vinylbenzimidazole) have been reported for some fluorosilanes. Crystal structure data are, however, not available. (a) Baikalova, L. V.; Domnina, E. S.; Chipanina, N. N.; Danovich, D. K.; Voronkov, M. G.; Albanov, A. I.; Shulunova, A. I. *Koord. Khim.* **1991**, *17*, 1629. (b) Ennan, A. A.; Dzerzhko, E. K.; Nikitin, V. I.; Garnovskii, A. D. *Zh. Neorg. Khim.* **1980**, *25*, 729. (c) Ennan, A. A.; Dzerzhko, E. K.; Garnovskii, A. D. *Koord. Khim.* **1979**, *5*, 947. (d) Dzerzhko, E. K.; Garnovskii, A. D.; Ennan, A. A. *Zh. Neorg. Khim.* **1979**, *24*, 357.

(10) Neutral hypercoordinate chloro-, bromo-, and iodosilanes bearing imidazole-type ligands have been claimed,[11] but without supporting structural data. The observation that even the Si−Cl bond of Me_3SiCl dissociates in the presence of NMI under formation of a tetracoordinate siliconium−cationic complex[12] would appear to suggest that the complexes by Voronkov et al. might also have been siliconium complexes.

(11) Voronkov, M. G.; Skvortsova, G. G.; Domnina, E. S.; Ivlev, Y. N.; Chernov, N. F.; Chipanina, N. N.; Voronov, V. K.; Taryashinova, D. D. *Zh. Obsh. Khim.* **1976**, *46*, 311.

(12) Hensen, K.; Zengerly, T.; Müller, T.; Pickel, P. *Z. Anorg. Allg. Chem.* **1988**, *558*, 21.

(13) Wagler, J.; Gerlach, D.; Roewer, G. *Inorg. Chim. Acta* **2007**, *360*, 1935.

(14) Bettermann, G.; Arduengo, A. J., III. *J. Am. Chem. Soc.* **1988**, *110*, 877.