Inorg. Chem. **2005**, *44*, 5556–5558

Inorganic Chemistry
Communication

Unusual Anions $[LAl(SH)(S)]^-$ and $[LAl(S)_2]^{2-}$ Stabilized by Weakly Coordinating Imidazolium Cations. Synthesis of $LAl(SSiMe_2)_2O$ (L = $HC[C(Me)N(Ar)]_2$, Ar = 2,6-$i$$Pr_2C_6H_3$)

Vojtech Jancik and Herbert W. Roesky*

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

Received May 4, 2005

Deprotonation of an Al–SH moiety has been achieved easily by using N-heterocyclic carbene as the base. Monomeric mono- and bis-imidazolium salts $[C_tH^+][LAl(SH)(S)]^-$ ($[C_tH^+]$ = *N*,*N*′-bis-*tert*-butylimidazolium), $[C_mH^+][LAl(SH)(S)]^-$, and $[C_mH^+]_2[LAl(S)_2]^{2-}$ ($[C_mH^+]$ = *N*,*N*′-bismesitylimidazolium), containing unusual anions $[LAl(SH)(S)]^-$ and $[LAl(S)_2]^{2-}$, have been synthesized in nearly quantitative yields. Furthermore, $[C_mH^+]_2[LAl(S)_2]^{2-}$ has been successfully used for the preparation of $LAl(SSiMe_2)_2O$ containing the $[O(Me_2SiS)_2]^{2-}$ ligand.

The field of weakly coordinating ions has developed as an important area of chemistry over the last 2 decades.[1] These ionic species can be divided into two groups; the first one contains ion pairs featuring mostly unique cations,[1a−j] while the second one uses stable cations (e.g., R_4N^+,[1k−m] R_4P^+,[1n−p] or imidazolium(1+);[1q] R = alkyl, aryl) to stabilize unusual anions.[1k−q] A representation of the first group can be demonstrated by the nearly planar $[i\text{Pr}_3\text{Si}]^+$ cation stabilized by a bulky carborane anion $[CB_{11}H_6Br_6]^-$,[1a] whereas the second group can be demonstrated by numerous examples of polyoxometalates.[1k−q] Recently, we have reported the successful preparation of mono- and dilithium salts ($[\{LAl(SH)[SLi(thf)_2]\}_2]$ (**1**) and $[\{LAl[(SLi)_2(thf)_3]\}_2]\cdot 2THF$ (**2**)) containing relatively short S−Li bonds.[2] Easy access of these compounds prompted us to examine the stability of the corresponding anions $[LAl(SH)(S)]^-$ and $[LAl(S)_2]^{2-}$ by weakly coordinating cations. These species are of interest as precursors for further reactions because of the high nucleophilicity and weak Lewis basicity of the sulfur atom. N-Heterocyclic carbenes were used for deprotonation of the SH moieties due to their strong Lewis basicity.[3] Finally, it is well-known that imidazolium cations stabilize a wide range of anions (e.g., BPh_4^-, PF_6^-, $Cd(SCN)_3^-$).[1q,4] The equimolar reaction of $[LAl(SH)_2]$ (**3**) and *N*,*N*′-bis-*tert*-butylimidazol-2-ylidene[5] (N-heterocyclic carbene) in THF resulted in the formation of the expected monoimidazolium salt $[C_tH^+][LAl(SH)(S)]^-$ (**4**) ($[C_tH^+]$ = *N*,*N*′-bis-*tert*-butylimidazolium(1+)) in a quantitative yield (section S2 in the Supporting Information). Surprisingly, the reaction between **3** and *N*,*N*′-bis-*tert*-butylimidazol-2-ylidene in a 1:2 molar ratio did not give the expected $[C_tH^+]_2[LAl(S)_2]^{2-}$ but led to a mixture of **4** and free carbene. Double deprotonation was successfully achieved by using 2 equiv of *N*,*N*′-bismesitylimidazol-2-ylidene,[6] giving quantitatively $[C_mH^+]_2[LAl(S)_2]^{2-}$ ($[C_mH^+]$ = *N*,*N*′-bismesitylimidazolium(1+)) (**5**) (section S3 in the Supporting Information).

---

* To whom correspondence should be addressed. E-mail: hroesky@gwdg.de. Fax: (+49) 551-39-3373.

(1) For example, see: (a) Reed, C. A. *Acc. Chem. Res.* **1998**, *31*, 325−332. (b) Reed, C. A. *Acc. Chem. Res.* **1998**, *31*, 133−139. (c) Krossing, I.; Rabe, I. *J. Am. Chem. Soc.* **2004**, *126*, 7571−7577. (d) Krossing, I.; Rabe, I. *Angew. Chem.* **2004**, *116*, 2116−2142; *Angew. Chem., Int. Ed.* **2004**, *43*, 2066−2090. (e) Krossing, I.; Reisinger, A. *Angew. Chem.* **2003**, *115*, 5903−5906; *Angew. Chem., Int. Ed.* **2003**, *42*, 5725−5728. (f) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927−942. (g) Hurlburt, P. K.; Rack, J. J.; Luck, J. S.; Dec, S. F.; Webb, J. D.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1994**, *116*, 10004−10014. (h) Van Seggen, D. M.; Hurlburt, P. K.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1992**, *114*, 10995−10997. (i) Atwood, J. L.; Steed J. W. In *Supramolecular Chemistry of Anions*; Bianchi, A., Bowman-James, K., Garcia-Espana, E., Eds.; VCH: New York, 1997; pp 147−215. (j) Stasch, A.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Inorg. Chem.* **2005**, *44*, in press. (k) Long, D.-L.; Kögerler, P.; Cronin, L. *Angew. Chem.* **2004**, *116*, 1853−1856; *Angew. Chem., Int. Ed.* **2004**, *43*, 1817−1820. (l) Vasylyev, M.; Neumann, R. *J. Am. Chem. Soc.* **2004**, *126*, 884−890. (m) Xu, L.; Lu, M.; Xu, B.; Wei, Y.; Peng, Z.; Powell, D. R. *Angew. Chem.* **2002**, *114*, 4303−4306; *Angew. Chem., Int. Ed.* **2002**, *41*, 4129−4132. (n) Bhattacharyya, R.; Biswas, S.; Armstrong, J.; Holt, E. M. *Inorg. Chem.* **1989**, *28*, 4297−4300. (o) Kang, H.; Liu, S.; Shaikh, S. N.; Nicholson, T.; Zubieta, J. *Inorg. Chem.* **1989**, *28*, 920−933. (p) Day, V. W.; Klemperer, W. G.; Maltbie, D. J. *J. Am. Chem. Soc.* **1987**, *109*, 2991−3002. (q) Sun, H.; Harms, K.; Sundermeyer, J. *J. Am. Chem. Soc.* **2004**, *126*, 9550−9551.

(2) Jancik, V.; Roesky, H. W.; Neculai, D.; Neculai, A. M.; Herbst-Irmer, R. *Angew. Chem.* **2004**, *116*, 6318−6322; *Angew. Chem., Int. Ed.* **2004**, *43*, 6192−6196.

(3) Magill, A. M.; Cavell, K. J.; Yates, B. F. *J. Am. Chem. Soc.* **2004**, *126*, 8717−8724.

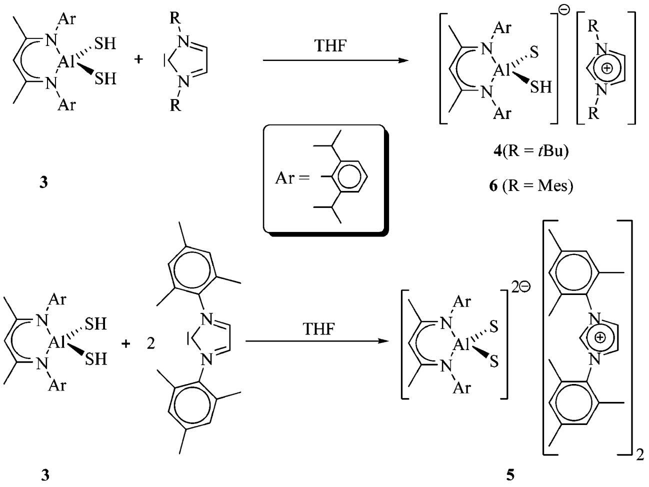
(4) (a) Chen, W.; Liu, F.; You, X. *J. Solid State Chem.* **2002**, *167*, 119−125. (b) Liu, F.; Chen, W.; You, X. *J. Chem. Crystallogr.* **2002**, *32*, 27−31. (c) Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361−363. (d) Niehues, M.; Kehr, G.; Erker, G.; Wibbeling, B.; Fröhlich, R.; Blacque, O.; Berke, H. *J. Organomet. Chem.* **2002**, *663*, 192−203.

(5) Arduengo, A. J., III; Bock, H.; Chen, H.; Denk, M.; Dixon, D. A.; Green, J. C.; Herrmann, W. A.; Jones, N. L.; Wagner, M.; West, R. *J. Am. Chem. Soc.* **1994**, *116*, 6641−6649.

(6) Arduengo, A. J., III; Dias, H. V. R.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530−5534.

10.1021/ic050693q CCC: $30.25

Scheme 1. Synthesis of Imidazolium Salts **4**−**6**



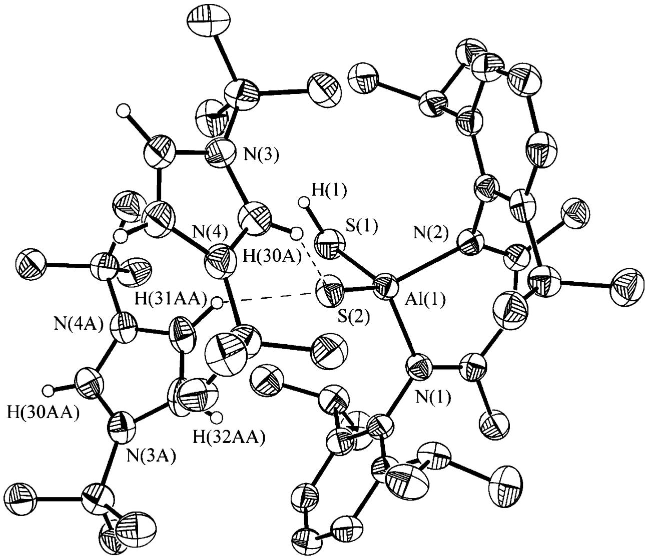


Figure 1. Molecular structure of **4**·THF (50% probability ellipsoids). Hydrogen atoms (except the S−H and imidazole ring protons), the second position of the disordered *t*Bu group, and the THF molecule are omitted for clarity. The cation containing N(3A) and N(4A) is stabilized by another [LAl(SH)(S$^-$)] anion, which is not depicted. Selected bond lengths [Å] and angles [deg]: Al(1)−N(1), 1.946(2); Al(1)−N(2), 1.921(2); Al(1)−S(1), 2.290(1); Al(1)−S(2), 2.116(1); S(1)−H(1), 1.17(3); S(2)···H(30A), 2.54; S(2)···H(31AA), 2.76; N(1)−Al(1)−N(2), 95.1(1); S(1)−Al(1)−S(2), 115.0(1); Al(1)−S(1)−H(1), 96(1).

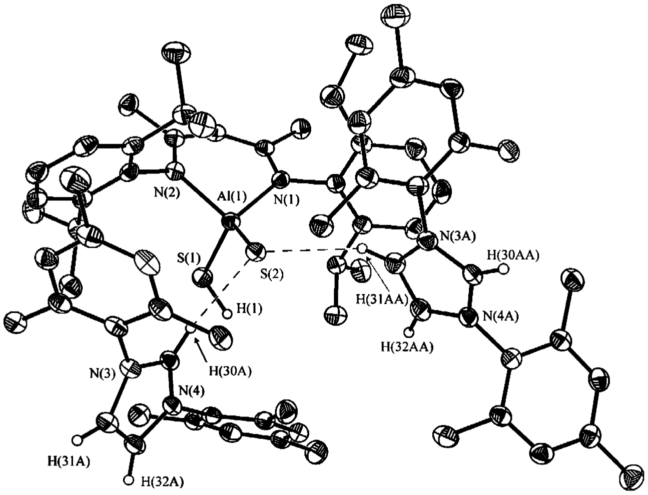
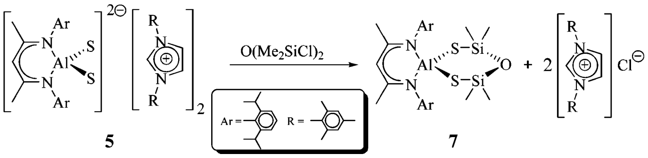


Figure 2. Molecular structure of **6**·THF (50% probability ellipsoids). Hydrogen atoms (except the S−H and imidazole ring protons) and the solvent molecule are omitted for clarity. The cation containing N(3A) and N(4A) is stabilized by another [LAl(SH)(S$^-$)] anion, which is not depicted. Selected bond lengths [Å] and angles [deg]: Al(1)−N(1), 1.938(2); Al(1)−N(2), 1.930(2); Al(1)−S(2), 2.115(1); Al(1)−S(1), 2.279(1); S(1)−H(1), 1.25(2); S(2)···H(30A), 2.46; S(2)···H(31AA), 2.63; N(1)−Al(1)−N(2), 95.7(1); S(1)−Al(1)−S(2), 117.8(1); Al(1)−S(2)−H(2), 93(1).

Compound **5** is labile and decomposes to [C$_m$H$^+$][LAl(SH)(S)]$^-$ (**6**) in the presence of trace amounts of moisture both in solution and in the solid state even at low temperature. The latter can be prepared by the direct reaction of **3** with 1 equiv of *N*,*N*′-bismesitylimidazol-2-ylidene (section S4 in the Supporting Information; Scheme 1). The ^{1}H NMR spectra of **5** and **6** are very similar and indicate substitution on the Al center with the absence of SH protons for both species, although this condition is not fulfilled for **6** (one Al−S moiety and one Al−SH moiety). This can be explained by fast proton migration. Further measurements revealed that this process is fast even at low temperature and starts immediately after mixing **3** with small amounts of the carbene. In the presence of air, the pale yellow solutions of these three salts turned to blue-green, indicating their decomposition. In the case of **4**, the intense blue-green color appeared even if degassed and dry solvents were used. We were not able to obtain any ^{1}H NMR data of satisfactory quality for **4**, even at low temperature and 500 MHz. In the salts **5** and **6**, the color remained for 3 days when the flasks were stored at −30 °C but disappeared within 1 h at ambient temperature. The high reactivity of the salts **4**−**6** did not allow their characterization by IR spectra and elemental analysis. Thus, the purities of compounds **5** and **6** were determined by ^{1}H NMR spectroscopy, whereas the purity of compound **4** was confirmed by mounting 10 different crystals from several preparations and measuring their cell parameters. For all of the crystals, the cell parameters were nearly identical. Pale yellow crystals of compounds **4** and **6** were obtained by slow crystallization of their saturated THF solutions at −32 °C. Compound **4** crystallizes in the orthorhombic space group $P2_12_12_1$ and **6** in the monoclinic space group $P2_1/c$ (section S6 in the Supporting Information). Both **4** and **6** contain an ion pair and one solvating THF molecule in the asymmetric unit (Figures 1 and 2). The deprotonation of the S−H moiety resulted in the formation of a "naked" Al−S center and shows a significant influence on the geometry of the N$_2$AlS$_2$ core. The Al−S$^-$ bond lengths are 2.116 Å for **4** and 2.115 Å for **6** and represent the shortest Al−S bonds described so far (compared with 2.159−2.483 Å for known covalent Al−S bonds).[7] The remaining Al−S(H) bond lengths are 2.290 (**4**) and 2.279 Å (**6**), respectively, and significantly longer than those in **3** (2.217 and 2.223 Å). The negative charge on the sulfur in both cases is reduced by two close contacts with hydrogen atoms of the two independent imidazolium cations. In the case of **6**, the first cation coordinates to the sulfur with the hydrogen atom on C(30) (MesN−C*H*−NMes; S···H = 2.46 Å) and the second cation with the hydrogen atom on C(31) (MesN−C*H*−CH−NMes; 2.63 Å). In compound **4**, the bonding mode is the

Scheme 2. Synthesis of Compound **7**



same like that of **6** (*t*BuN−C*H*−*Nt*Bu; S···H = 2.54 Å; *t*BuN−C*H*−*CH*−*Nt*Bu; 2.78 Å). The weak S···H interactions are depicted in Figures 1 and 2. The originally deformed tetrahedral core N_2AlS_2 in $LAl(SH)_2$[8] is further deformed in **4** and **6** with smaller N−Al−N angles (97.3° in **3**, 95.1° in **4**, and 95.7° in **6**) and wider S−Al−S angles (105.4° in **3**, 115.0° in **4**, and 117.8° in **6**).

To demonstrate the double deprotonation of **5**, it was reacted with $O(Me_2SiCl)_2$ in a 1:1 molar ratio. Nearly quantitative conversion of **5** to the Al−S−Si moiety containing $LAl(SSiMe_2)_2O$ (**7**) was observed (Scheme 2; section S5 in the Supporting Information). Furthermore, the *N,N′*-bismesitylimidazolium chloride can be easily separated from the products after extraction with THF. It should be mentioned that our earlier attempt to use the lithium salts **1** and **2**[2] failed and only a mixture of products was isolated from the reaction with $O(Me_2SiCl)_2$. Furthermore, only one example with the Al−S−Si framework ($Me_2Al(\mu\text{-}SSiPh_3)_2AlMe_2$) that contains the sulfur atom in coordination number three has been reported so far.[9] There are no reports on the preparation of such a moiety from Al−S precursors. Compound **7** was obtained as a white microcrystalline solid sensitive toward moisture, and its composition and molecular structure were determined by multinuclear NMR spectroscopy and mass spectrometry (MS) and unambiguously by X-ray structural analysis. The electron impact MS spectrum of **7** shows the molecular ion peak at *m*/*z* 640 (90%), demonstrating the high thermal stability of the $Al(SSi)_2O$ six-membered ring. Recrystallization of **7** from a toluene/hexane mixture at −32 °C resulted in X-ray quality monocrystals. Compound **7** crystallizes in the monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit (Figure 3; section S6 in the Supporting Information). The $Al(SSi)_2O$ ring possesses a deformed boat conformation, and the S(1)−Al−S(2) plane is almost perpendicular to the N(1)−Al(1)−N(2) one (89.2°). The Al−S bond lengths are 2.222 and 2.234 Å, slightly longer than those in **3** and significantly longer than the corresponding ones in $LAl(\mu\text{-}S)_2TiCp_2$ (2.197 and 2.208 Å)[2] but shorter than those in $LAl(\mu\text{-}S)_2AlL$ (2.237 and 2.245 Å).[10] The Si−S bond lengths (2.128 and 2.138 Å) are within the range published for other compounds (1.949−2.288 Å).[11] As expected, the formation of the stable $Al(SSi)_2O$ six-membered ring resulted in a more obtuse S−Al−S angle [113.1°, compared to those of **3** (105.4°)[3] and $LAl(\mu\text{-}S)_2TiCp_2$ (102.5°)],[2] which confirms lower ring strain than that in $LAl(\mu\text{-}S)_2TiCp_2$.

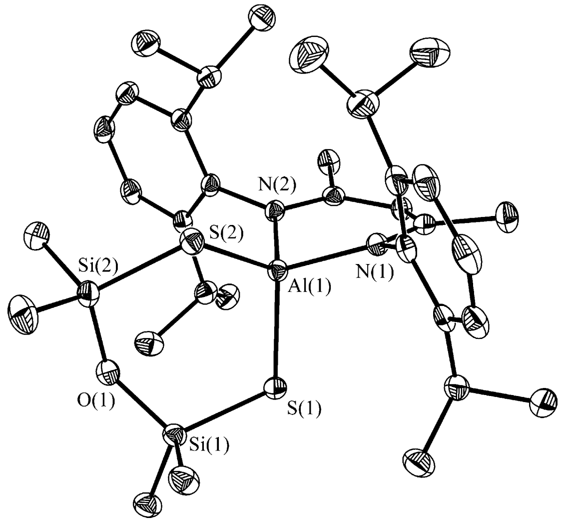


Figure 3. Molecular structure of **7** (50% probability ellipsoids). All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Al(1)−N(1), 1.908(1); Al(1)−N(2) 1.900(1); Al(1)−S(1), 2.234(1); Al(1)−S(2), 2.223(1); S(1)−Si(1), 2.128(1); S(2)−Si(2), 2.138(1); O(1)−Si(1), 1.641(1); O(1)−Si(2), 1.639(1); N(1)−Al(1)−N(2), 96.6(1); S(1)−Al(1)−S(2), 113.1(1); Al(1)−S(1)−Si(1), 106.0(1); Al(1)−S(2)−Si(2), 106.6(1); S(1)−Si(1)−O(1), 111.3(1); S(2)−Si(2)−O(1), 110.3(1); Si(1)−O(1)−Si(2), 135.9(1).

In summary, the imidazolium cation is an ideal system for the stabilization of unusual anions. $[C_xH^+][LAl(SH)(S)]^-$ and $[C_mH^+]_2[LAl(S)_2]^{2-}$ are promising precursors for further reactions and are, together with their oxidation products, the subject of our ongoing research.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie and is dedicated to Professor Narayan S. Hosmane.

Supporting Information Available: All experimental details (S1−S5); crystal data collection, structure solution, and refinement details for compounds **4**, **6**, and **7** (S6) (pdf); and X-ray structural information in CIF format for **4**, **6**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC050693Q

---

(7) (a) Wehmschulte, R. J.; Power, P. P. *J. Chem. Soc., Chem. Commun.* **1998**, 335−336. (b) Wehmschulte, R. J.; Power, P. P. *J. Am. Chem. Soc.* **1997**, *119*, 9566−9567. (c) Uhl, W.; Vester, A.; Hiller, W. *J. Organomet. Chem.* **1993**, *443*, 9−17. (d) Zheng, W.; Hohmeister, H.; Mösch-Zanetti, N. C.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Inorg. Chem.* **2001**, *40*, 2363−2367. (e) Paek, C.; Kang, S. O.; Ko, J.; Carroll, P. J. *Organometallics* **1997**, *16*, 2110−2115. (f) Nöth, H.; Konrad, P. *Chem. Ber.* **1983**, *116*, 3552−558. (g) Daniel, S.; Hoffman, D. M. *Inorg. Chem.* **2002**, *41*, 3843−3849. (h) Ruhlandt-Senge, K.; Power, P. P. *Inorg. Chem.* **1991**, *30*, 2633−2637. (i) Reddy, N. D.; Kumar, S. S.; Roesky, H. W.; Vidovic, D.; Magull, J.; Noltemeyer, M.; Schmidt, H.-G. *Eur. J. Inorg. Chem.* **2003**, 442−448. (j) Wehmschulte, R. J.; Ruhlandt-Senge, K.; Power, P. P. *Inorg. Chem.* **1995**, *34*, 2593−2595.

(8) Jancik, V.; Peng, Y.; Roesky, H. W.; Li, J.; Neculai, D.; Neculai, A. M.; Herbst-Irmer, R. *J. Am. Chem. Soc.* **2003**, *125*, 1452−1453.

(9) Taghiof, M.; Heeg, M. J.; Bailey, M.; Dick, D. G.; Kumar, R.; Hendershot, D. G.; Rahbarnoohi, H.; Oliver, J. P. *Organometallics* **1995**, *14*, 2903−2917.

(10) Jancik, V.; Moya Cabrera, M. M.; Roesky, H. W.; Herbst-Irmer, R.; Neculai, D.; Neculai, A. M.; Noltemeyer, M.; Schmidt, H.-G. *Eur. J. Inorg. Chem.* **2004**, 3508−3512.

(11) For shortest (a and b) and longest (c and d) Si−S bonds, see: (a) Gruber, H.; Müller, U. *Z. Anorg. Allg. Chem.* **1997**, *623*, 957−961. (b) Becker, B.; Baranowska, K.; Chojnacki, J.; Wojnowski, W. *Chem. Commun.* **2004**, 620−621. (c) Sydora, O. L.; Wolczanski, P. T.; Lobkovsky, E. B.; Rumberger, E.; Hendrickson, D. N. *Chem. Commun.* **2004**, 650−651. (d) Osakada, K.; Hataya, K.; Yamamoto, T. *Chem. Commun.* **1995**, 2315−2316.