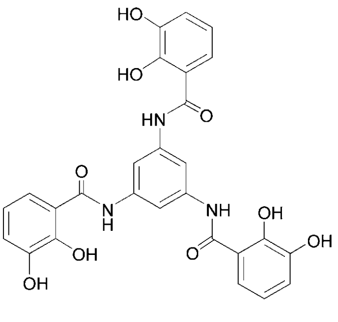
DOI: 10.1002/chem.200901443

Assembly of a Tetranuclear Host with a Tris(benzene-*o*-dithiolato) Ligand

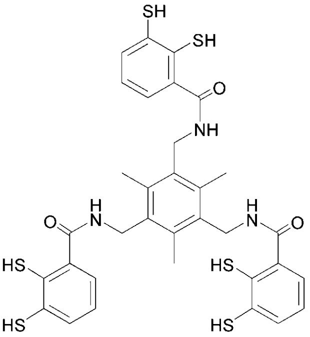
Birgit Birkmann,[a] Roland Fröhlich,[b] and F. Ekkehardt Hahn*[a]

Metallosupramolecular chemistry combines versatile polydentate organic ligands and transition metals in the design and synthesis of sophisticated assemblies of noncovalently attached components.[1] Various supramolecular architectures, such as helicates,[1e,2] boxes,[3] grids,[4] squares,[5] molecular containers,[6] and others,[7] have been obtained from metal-directed spontaneous self-assembly reactions. Among these, metallohelicates[1e,2] have gathered special interest due to the presence of the helical structure in nature. The DNA motif has been transferred to metallosupramolecular dinuclear double- and triple-stranded helical complexes by using ligands with amine or catecholato[2,8] donor groups. Recently, we prepared the first dinuclear triple-stranded helicates based on bis(benzene-*o*-dithiolato)[9] and mixed benzene-*o*-dithiolato/catecholato ligands.[10]

Raymond et al. introduced a 1,5-naphthalene-bridged dicatechol ligand H_4-L,[6d,11] which was designed to prevent the formation of a dinuclear triple-standed helicate $[M_2(L)_3]^{n-}$ and thus reacted with metal ions to yield tetranuclear tetrahedral clusters of type $[M_4(L)_6]^{2n-}$ in which the dicatecholato ligands bridge the vertices of the tetrahedron.[6d,11] We showed that the analogous bis(benzene-*o*-dithiol) ligand, against our expectations, reacts with Ti^{4+} to yield a dinuclear triple-standed helicate.[12] Since linear bis(benzene-*o*-dithiol) ligands appear unsuitable for the generation of a tetrahedral tetranuclear cluster, we turned to tripodal tris(benzene-*o*-dithiol) ligands. Raymond et al.[6c,11] and Albrecht et al.[13] have shown that tripodal tricatechol ligands like H_6-**A** are capable of forming tetranuclear tetrahedral clusters of type $[M_4(\mathbf{A})_4]^{m-}$. We have transferred this design principle to tris(benzene-*o*-dithiol) ligands. Ligand H_6-**B**, however, is flexible enough to react with Ti^{4+} to yield the mononuclear siderophor analogue[14] complex anion $[Ti(\mathbf{B})]^{2-}$.[15] Reduction of the lengths of the ligand arms by one methylene group each leads to the essentially planar ligand H_6-**1**, which like H_6-**A** is incapable of forming mononuclear chelate complexes. We report here on the preparation of ligand H_6-**1**, its reaction with Ti^{4+}, and on the unusual structural properties of the tetranuclear pseudo-tetrahedral cluster $[Ti_4(\mathbf{1})_4]^{8-}$ obtained in this reaction (Scheme 1).



H_6-**A**



H_6-**B**

The synthesis of the C_3-symmetric ligand H_6-**1** was achieved by following a previously published procedure (Scheme 1). 1,3,5-Triaminobenzene (**2**),[6c] obtained by reduction of 3,5-dinitroaniline with Raney-Ni, was reacted with 2,3-di(isopropylmercapto)benzoic acid chloride (**3**)[16] to produce the S-alkylated ligand precursor **4**. Elimination of the isopropyl groups with sodium/naphthalene provided ligand H_6-**1** in a yield of 82 % (see Supporting Information).[16]

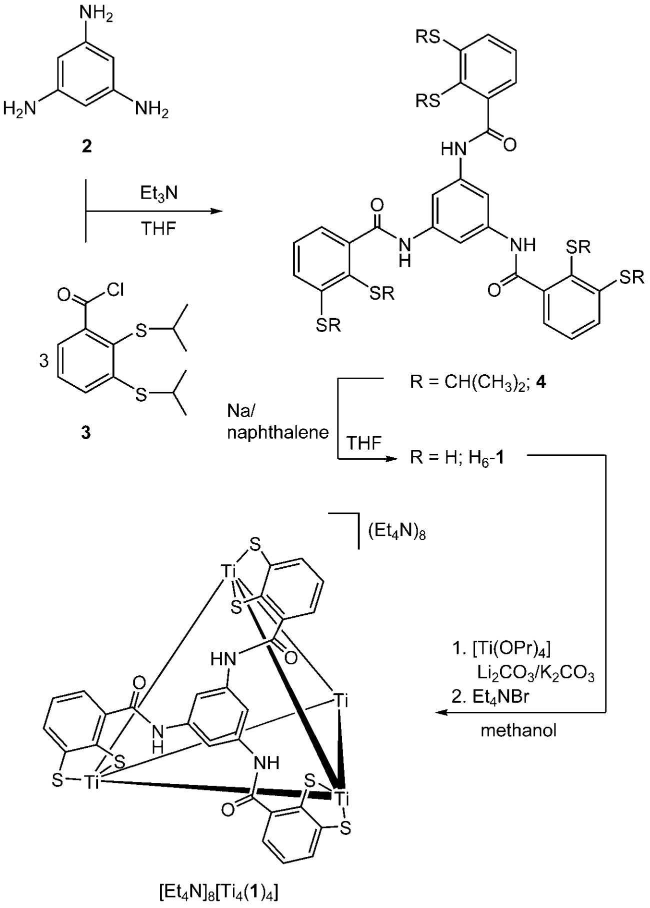
Reaction of ligand H_6-**1** with $[Ti(OPr)_4]$ in methanol, in the presence of Li_2CO_3/K_2CO_3, led to the formation of a dark red solution ($\lambda_{max} = 542$ nm), indicating the formation of the $\{TiS_6\}^{2-}$ chromophore (Scheme 1).[17] Complex $Li_xK_{8-x}[Ti_4(\mathbf{1})_4]$ was not isolated. Instead the alkali metal

---

[a] Dr. B. Birkmann, Prof. Dr. F. E. Hahn
Institut für Anorganische und Analytische Chemie
Westfälische Wilhelms-Universität Münster
Corrrensstrasse 36, 48149 Münster (Germany)
Fax: (+49) 251-833-3108
E-mail: fehahn@uni-muenster.de

[b] Dr. R. Fröhlich
Organisch-Chemisches Institut
Westfälische Wilhelms-Universität Münster
Corrensstrasse 40, 48149 Münster (Germany)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200901443.



Scheme 1. Synthesis of ligand H_6-**1** and of the tetranuclear complex $[Et_4N]_8[Ti_4(\mathbf{1})_6]$.

cations were exchanged for tetraethylammonium cations. The use of the organic cations led to a red precipitate and allowed for the isolation of the complex as a red solid. Since a ligand:metal ratio of 1:1 was used and ligand H_6-**1** is not capable of forming mononuclear complexes, formation of the tetranuclear complex $[Et_4N]_8[Ti_4(\mathbf{1})_4]$ can be assumed.

The small number of resonances in the ^{1}H NMR spectrum of $[Et_4N]_8[Ti_4(\mathbf{1})_4]$ (in [D$_7$]DMF/[D$_3$]acetonitrile, Figure 1) indicates the presence of only one highly symmetric species in solution. In case of encapsulation of some tetraethylammonium cations within the cavity of complex ion $[Ti_4(\mathbf{1})_4]^{8-}$, two sets of proton resonances with a highfield shift for those of the encapsulated cations would be expected.[6d] However, only one set of sharp resonances ($\delta = 1.14$ (t) and 3.18 ppm (q)) was observed for all tetraethylammonium cations at ambient temperature.

All signals corresponding to the ligand framework in compound $[Et_4N]_8[Ti_4(\mathbf{1})_4]$ are only slightly shifted relative to those observed for the free ligand. The resonance for the amide protons was detected as a singlet at $\delta = 10.17$ ppm and is slightly shifted highfield compared to the value recorded for the free ligand ($\Delta\delta = 0.51$ ppm). This observation excludes the formation of strong intramolecular N–H···S hydrogen bonds in solution.[9a,c] The spectrum also reveals the

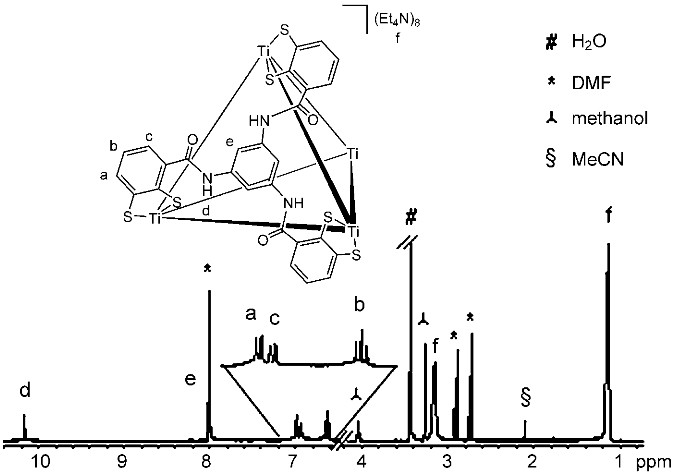
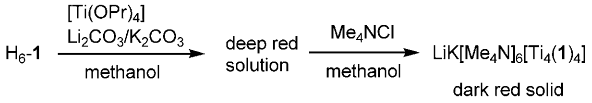


Figure 1. ^{1}H NMR spectrum of $[Et_4N]_8[Ti_4(\mathbf{1})_4]$ at ambient temperature.

characteristic set of signals for the proton resonances of the benzene-*o*-dithiolato donor unit, two doublet of doublets at $\delta = 7.01$ and 6.96 ppm, respectively, and one triplet at $\delta = 6.65$ ppm, reflecting the AMX spin system.

In a second attempt, ligand H_6-**1** was treated with [Ti(OPr)$_4$] in the presence of Li_2CO_3/K_2CO_3 to give again a deep red solution (Scheme 2). Addition of Me_4NCl yielded



Scheme 2. Synthesis of $LiK[Me_4N]_6[Ti_4(\mathbf{1})_4]$.

a dark red precipitate. The ESI(negative ions) mass spectrum showed peaks for the anions $[[Me_4N]_3[Ti_4(\mathbf{1})_4]]^{5-}$ and $[[Me_4N]_5[Ti_4(\mathbf{1})_4]]^{3-}$ at $m/z = 580.2$, and 1016.7 amu with the correct isotope distribution, respectively (see Supporting Information). Recrystallization of this precipitate from DMF/CH_3CN yielded red crystals of $LiK[Me_4N]_6[Ti_4(\mathbf{1})_4]\cdot 6\,DMF$ that were suitable for an X-ray diffraction analysis.

Complex $LiK[Me_4N]_6[Ti_4(\mathbf{1})_4]\cdot 6\,DMF$ crystallizes in the monoclinic space group *C*2/*c* with the octaanion residing on a crystallographic twofold axis (Figure 2). The asymmetric unit contains $^1/_2$ of the octaanion, three Me_4N^+ ions, and three DMF molecules. The potassium cation resides on the twofold axis passing through the center of the octaanion. One half of a positive charge per asymmetric unit could not be located. We assume that each asymmetric unit either contains $^1/_2$ of a disordered lithium cation or that a lithium cation is also located on the twofold axis. We have previously described similar problems in locating the light lithium cation in X-ray diffraction studies on dinuclear triple-stranded helicates.[10c] Each titanium atom is coordinated by six sulfur atoms in a strongly distorted octahedral fashion with calculated twist angles of $\Phi = 33.0°$ (Ti1) and 39.6° (Ti2). Two titanium atoms adopt the Δ configuration (Ti1, Ti1*) and the other two the Λ configuration (Ti2, Ti2*), which is a

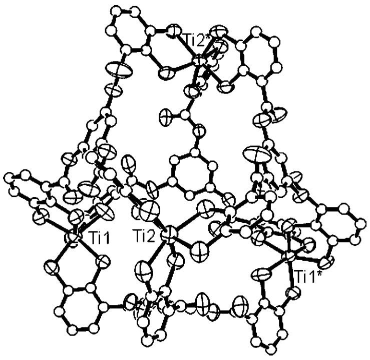


Figure 2. Molecular structure of the octaanion $[Ti_4(\mathbf{1})_4]^{8-}$ in $LiK[Me_4N]_6$-$[Ti_4(\mathbf{1})_4]\cdot6DMF$. Hydrogen atoms, counterions and solvent molecules have been omitted and ellipsoids for phenyl carbon atoms have been drawn at an arbitrary small scale for clarity.

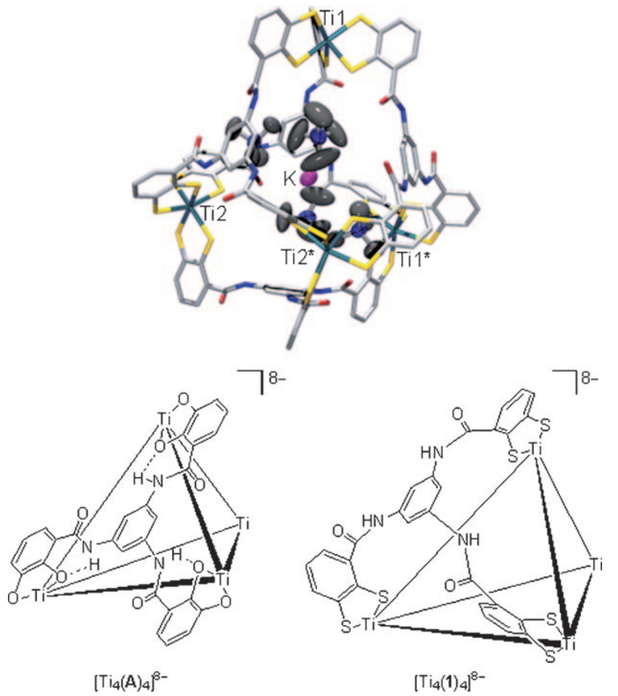


Figure 3. Molecular structure of the $[Ti_4(\mathbf{1})_4]^{8-}$ ion with the encapsulated cations and schematic representation of the C_3-symmetric ligands in the anions $[Ti_4(\mathbf{A})_4]^{8-}$ and $[Ti_4(\mathbf{1})_4]^{8-}$.

rare feature for supramolecular tetrahedral clusters of type $[M_4(L)_4]^{n-}$ that normally possess four homochiral metal centers.

Long and variable N···S separations in the range of 3.309 to 4.127 Å confirm the absence of intramolecular N–H···S hydrogen bonds in the solid state as was already concluded from the ^1H NMR spectrum for the situation in solution. The Ti–S bond lengths fall in the range previously reported for titanium complexes with three amide-substituted benzene-*o*-dithiolato ligands.[9,10] The C_2S_2Ti heterocycle is bent along the S–S vector (range of dihedral angles between the $C_6H_3S_2$ and S_2Ti planes 2.7–15.2°) as has been observed earlier for related complexes.[9,10,12,17]

The $[Ti_4(\mathbf{1})_4]^{8-}$ ion contains not only a potassium cation, but also an additional four Me_4N^+ ions (Figure 3, top). This behavior is in remarkable contrast to the situation described for complex ion $[Ti_4(\mathbf{A})_4]^{8-}$ with the tricatecholato ligand,[6c] for which no encapsulation of any cations has been observed due to the limited space within the cluster anion. The tricatecholato ligand in $[Ti_4(\mathbf{A})_4]^{8-}$ is essentially planar with strong intramolecular N–H···O hydrogen bonds that cause the coplanar orientation of the phenylene backbone with the catecholato donor groups (Figure 3, bottom left).[6c] Ligand $\mathbf{1}^{6-}$ in $[Ti_4(\mathbf{1})_4]^{8-}$ is not planar and no N–H···S hydrogen bonds have been observed. The benzene-*o*-dithiolato donor groups are oriented essentially perpendicular to the central phenylene group (range of dihedral angles between the C_6H_3 and $C_6H_3S_2$ planes 73.5–89.9°, see ligand bridging Ti1, Ti1* and Ti2* in Figure 3, top). This ligand conformation (Figure 3, bottom right) together with the nonplanar C_2S_2Ti heterocycles generates a much larger and much more open cavity in $[Ti_4(\mathbf{1})_4]^{8-}$ than was found for $[Ti_4(\mathbf{A})_4]^{8-}$, which in turn allows the encapsulation of the five cations (one K^+ and four NMe_4^+).

Molecular containers like complex anion $[Ga_4(L)_6]^{12-}$ have found applications as molecular flasks in both catalysis and reaction control.[18] Encouraged by the encapsulation of tetramethylammonium cations observed with $[Ti_4(\mathbf{1})_4]^{8-}$, we tried to encapsulate the larger benzimidazolium cation. Benzimidazolium salts can be converted into benzimidazolin-2-ylidenes upon C2 deprotonation.[19]

Reaction of ligand H_6-$\mathbf{1}$ with $[Ti(OPr)_4]$ and Li_2CO_3/K_2CO_3 in methanol followed by addition of four equivalents of *N*,*N*'-dimethylbenzimidazolium bromide gave a red precipitate. The ^1H NMR spectrum of this solid in $[D_7]DMF$/CD_2Cl_2 (Figure 4, black line) showed the signals for the $[Ti_4(\mathbf{1})_4]^{8-}$ ion (vide supra) and four broad resonances for the benzimidazolium cation. Compared to the ^1H NMR

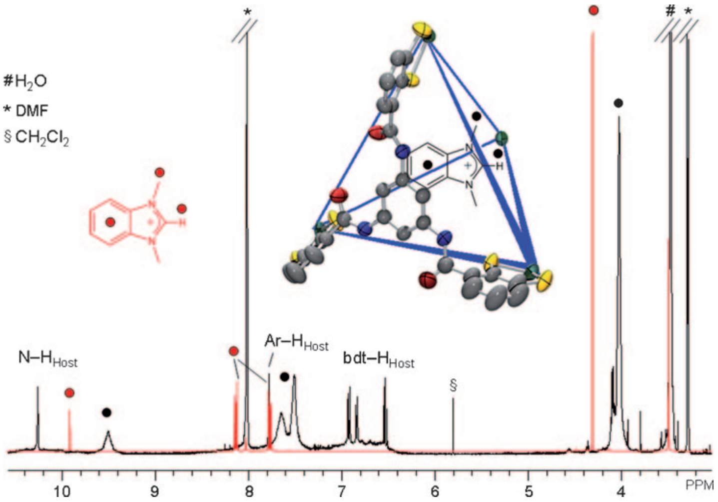


Figure 4. ^1H NMR spectra of benzimidazolium bromide in the absence (red) and in the presence (black) of the tetranuclear host $[Ti_4(\mathbf{1})_4]^{8-}$ at ambient temperature.

spectrum of benzimidazolium bromide, measured in the absence of complex anion $[Ti_4(\mathbf{1})_4]^{8-}$ (Figure 4, red line), all resonances for the benzimidazolium cations are shifted highfield in the presence of $[Ti_4(\mathbf{1})_4]^{8-}$. Both, the highfield shift of the resonances of the benzimidazolium cation and the observed line broadening are indications for a fast exchange of benzimidazolium cations between the inside and the outside of the octanuclear $[Ti_4(\mathbf{1})_4]^{8-}$ octaanion.[20] Formation of a contact ion pair by π–π interactions of the benzimidazolium cation with aromatic rings at the outside of the cluster anion are not likely due to the substitution pattern of both the benzimidazolium cation and the aromatic rings of ligand $\mathbf{1}^{6-}$.

We have prepared the tris(benzene-*o*-dithiol) ligand H_6-**1**, which reacts with Ti^{4+} to give the tetranuclear cluster anion $[Ti_4(\mathbf{1})_4]^{8-}$. This cluster anion exhibits some unusual properties when compared to the analogous derivative with a tricatecholato ligand. The $[Ti_4(\mathbf{1})_4]^{8-}$ ion contains simultaneously metal centers with the Δ and the Λ configuration and the tris(benzene-*o*-dithiolato) ligand is due to a lack of intramolecular hydrogen bonds not planar, but contains $C_6H_3S_2$ donor groups which are rotated by about 90° relative to the central phenylene linker. This leads to an enlarged and much more open cavity of the cluster anion, which has been shown to be capable of hosting different cations. As we have already described for dinuclear triple-stranded helicates,[12] the exchange of catacholato donor groups against benzene-*o*-dithiolato donor groups also leads to a significant change in the coordination chemistry of phenylene-bridged tripodal ligands with three aromatic bidentate donors.

Experimental Section

Details of the synthesis and characterization of the compounds described herein can be found in the Supporting Information.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft (IRTG 1444) and the Fonds der Chemischen Industrie. We thank Dr. Alexander Hepp for measuring the NMR spectra and Dr. Heinrich Luftmann for measuring the mass spectra.

Keywords: coordination chemistry · host–guest systems · metallosupramolecular architectures · self-assembly · S ligands · titanium

---

[1] a) J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim **1995**; b) R. W. Saalfrank, B. Demleitner in *Transition Metals in Supramolecular Chemistry, Vol. 5* (Ed.: J.-P. Sauvage), Wiley-VCH, Weinheim **1999**, pp. 1–51; c) M. M. Conn, J. Rebek, Jr., *Chem. Rev.* **1997**, *97*, 1647–1668; d) S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853–908; e) T. Kreickmann, F. E. Hahn, *Chem. Commun.* **2007**, 1111–1120.

[2] a) C. Piguet, G. Bernardinelli, G. Hopfgartner, *Chem. Rev.* **1997**, *97*, 2005–2062; b) M. Albrecht, *Chem. Rev.* **2001**, *101*, 3457–3497; c) M. Meyer, B. Kersting, R. E. Powers, K. N. Raymond, *Inorg. Chem.* **1997**, *36*, 5179–5191; d) E. J. Enemark, T. D. P. Stack, *Angew. Chem.* **1995**, *107*, 1082–1084; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 996–998.

[3] a) P. Baxter, J.-M. Lehn, A. DeCian, J. Fischer, *Angew. Chem.* **1993**, *105*, 92–95; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 69–72; b) E. Leize, A. Van Dorsselaer, R. Krämer, J.-M. Lehn, *J. Chem. Soc. Chem. Commun.* **1993**, 990–993.

[4] a) P. N. W. Baxter, J.-M Lehn, J. Fischer, M.-T. Youinou, *Angew. Chem.* **1994**, *106*, 2432–2434; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2284–2287; b) M. Ruben, J. Rojo, F. J. Romero-Salguero, L. H. Uppadine, J.-M. Lehn, *Angew. Chem.* **2004**, *116*, 3728–3747; *Angew. Chem. Int. Ed.* **2004**, *43*, 3644–3662.

[5] a) F. Würthner, C.-C. You, C. R. Saha-Möller, *Chem. Soc. Rev.* **2004**, *33*, 133–146; b) M. Fujita, M. Tominaga, A. Hori, B. Therrien, *Acc. Chem. Res.* **2005**, *38*, 369–380.

[6] a) C. J. Jones, *Chem. Soc. Rev.* **1998**, *27*, 289–299; b) X. Sun, D. W. Johnson, D. L. Caulder, K. N. Raymond, E. H. Wong, *J. Am. Chem. Soc.* **2001**, *123*, 2752–2763; c) C. Brückner, R. E. Powers, K. N. Raymond, *Angew. Chem.* **1998**, *110*, 1937–1940; *Angew. Chem. Int. Ed.* **1998**, *37*, 1837–1839; d) D. L. Caulder, R. E. Powers, T. N. Parac, K. N. Raymond, *Angew. Chem.* **1998**, *110*, 1940–1943; *Angew. Chem. Int. Ed.* **1998**, *37*, 1840–1843; e) T. Beissel, R. E. Powers, K. N. Raymond, *Angew. Chem.* **1996**, *108*, 1166–1168; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1084–1086; f) M. Yoshizawa, T. Kusukawa, M. Fujita, S. Sakamoto, K. Yamaguchi, *J. Am. Chem. Soc.* **2001**, *123*, 10454–10459.

[7] a) G. F. Swiegers, T. J. Malefetse, *Chem. Rev.* **2000**, *100*, 3483–3537; b) C. A. Schalley, A. Lützen, M. Albrecht, *Chem. Eur. J.* **2004**, *10*, 1072–1080; c) X.-Y. Cao, J. Harrowfield, J. Nitschke, J. Ramírez, A.-M. Stadler, N. Kyritsakas-Gruber, A. Madalan, K. Rissanen, L. Russo, G. Vaughan, J.-M. Lehn, *Eur. J. Inorg. Chem.* **2007**, 2944–2965; d) S. K. Dey, T. S. M. Abedin, L. N. Dawe, S. S. Tandon, J. L. Collins, L. K. Thompson, A. V. Postnikov, M. S. Alam, P. Müller, *Inorg. Chem.* **2007**, *46*, 7767–7781.

[8] a) M. Albrecht, *Chem. Soc. Rev.* **1998**, *27*, 281–287; b) I. Janser, M. Albrecht, K. Hunger, S. Burk and K. Rissanen, *Eur. J. Inorg. Chem.* **2006**, 244–251.

[9] a) F. E. Hahn, T. Kreickmann, T. Pape, *Dalton Trans.* **2006**, 769–771; b) F. E. Hahn, T. Kreickmann and T. Pape, *Eur. J. Inorg. Chem.* **2006**, 535–539; c) T. Kreickmann, C. Diedrich, T. Pape, H. V. Huynh, S. Grimme, F. E. Hahn, *J. Am. Chem. Soc.* **2006**, *128*, 11808–11819.

[10] a) F. E. Hahn, C. Schulze Isfort, T. Pape, *Angew. Chem.* **2004**, *116*, 4911–4915; *Angew. Chem. Int. Ed.* **2004**, *43*, 4807–4810; b) C. Schulze Isfort, T. Kreickmann, T. Pape, R. Fröhlich, F. E. Hahn, *Chem. Eur. J.* **2007**, *13*, 2344–2357; c) F. E. Hahn, M. Offermann, C. Schulze Isfort, T. Pape, R. Fröhlich, *Angew. Chem.* **2008**, *120*, 6899–6902; *Angew. Chem. Int. Ed.* **2008**, *47*, 6794–6797.

[11] a) D. L. Caulder, K. N. Raymond, *Acc. Chem. Res.* **1999**, *32*, 975–981; b) D. L. Caulder, K. N. Raymond, *Dalton Trans.* **1999**, 1185–1200.

[12] a) F. E. Hahn, B. Birkmann, T. Pape, *Dalton Trans.* **2008**, 2100–2102; b) B. Birkmann, A. W. Ehlers, R. Fröhlich, K. Lammertsma, F. E. Hahn, *Chem. Eur. J.* **2009**, *15*, 4301–4311.

[13] a) M. Albrecht, I. Janser, S. Meyer, P. Weis, R. Fröhlich, *Chem. Commun.* **2003**, 2854–2855; b) M. Albrecht, I. Janser, J. Runsink, G. Raabe, P. Weis, R. Fröhlich, *Angew. Chem.* **2004**, *116*, 6832–6836; *Angew. Chem. Int. Ed.* **2004**, *43*, 6662–6666; c) M. Albrecht, I. Janser, R. Fröhlich, *Chem. Commun.* **2005**, 157–165; d) M. Albrecht, I. Janser, S. Burk, P. Weis, *Dalton Trans.* **2006**, 2875–2880; e) M. Albrecht, R. Fröhlich, *Bull. Chem. Soc. Jpn.* **2007**, *80*, 797–808; f) M. Albrecht, S. Burk, P. Weis, C. A. Schalley, M. Kogej, *Synthesis* **2007**, 3736–3740.

[14] a) K. N. Raymond, C. J. Carrano, *Acc. Chem. Res.* **1979**, *12*, 183–190; b) K. N. Raymond, E. A. Dertz, S. S. Kim, *Proc. Natl. Acad. Sci. USA* **2003**, *100*, 3584–3588.

[15] B. Birkmann, W. W. Seidel, T. Pape, A. W. Ehlers, K. Lammertsma, F. E. Hahn, *Dalton Trans.* DOI: 10.1039/b911014n.

[16] a) F. E. Hahn, W. W. Seidel, *Angew. Chem.* **1995**, *107*, 2938–2941; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2700–2703; b) H. V. Huynh, C. Schulze Isfort, W. W. Seidel, T. Lügger, R. Fröhlich, O. Kataeva, F. E. Hahn, *Chem. Eur. J.* **2002**, *8*, 1327–1335; c) H. V. Huynh, W. W. Seidel, T. Lügger, R. Fröhlich, B. Wibbeling, F. E. Hahn, *Z. Naturforsch. B* **2002**, *57*, 1401–1408.

[17] M. Könemann, W. Stüer, K. Kirschbaum, D. M. Giolando, *Polyhedron* **1994**, *13*, 1415–1425.

[18] a) D. Fiedler, R. G. Bergman, K. N. Raymond, *Angew. Chem.* **2004**, *116*, 6916–6919; *Angew. Chem. Int. Ed.* **2004**, *43*, 6748–6751; b) D. H. Leung, D. Fiedler, R. G. Bergman, K. N. Raymond, *Angew. Chem.* **2004**, *116*, 981–984; *Angew. Chem. Int. Ed.* **2004**, *43*, 963–966; c) D. Fiedler, H. van Halbeek, R. G. Bergman, K. N. Raymond, *J. Am. Chem. Soc.* **2006**, *128*, 10240–10252; d) V. M. Dong, D. Fiedler, B. Carl, R. G. Bergman, K. N. Raymond, *J. Am. Chem. Soc.* **2006**, *128*, 14464–14465; e) M. D. Pluth, R. G. Bergman, K. N. Raymond, *Science* **2007**, *316*, 85–88; f) M. D. Pluth, R. G. Bergman, K. N. Raymond, *Angew. Chem.* **2007**, *119*, 8741–8743; *Angew. Chem. Int. Ed.* **2007**, *46*, 8587–8589; g) D. Fiedler, D. H. Leung, R. G. Bergman, K. N. Raymond, *Acc. Chem. Res.* **2005**, *38*, 349–360.

[19] a) F. E. Hahn, M. C. Jahnke, *Angew. Chem.* **2008**, *120*, 3166–3216; *Angew. Chem. Int. Ed.* **2008**, *47*, 3122–3172; b) F. E. Hahn, L. Wittenbecher, D. Le Van, R. Fröhlich, *Angew. Chem.* **2000**, *112*, 551–554; *Angew. Chem. Int. Ed.* **2000**, *39*, 541–544.

[20] M. D. Pluth, K. N. Raymond, *Chem. Soc. Rev.* **2007**, *36*, 161–171.

Received: May 29, 2009