A banana-shaped dinuclear complex with a tris(benzene-*o*-dithiolato) ligand†

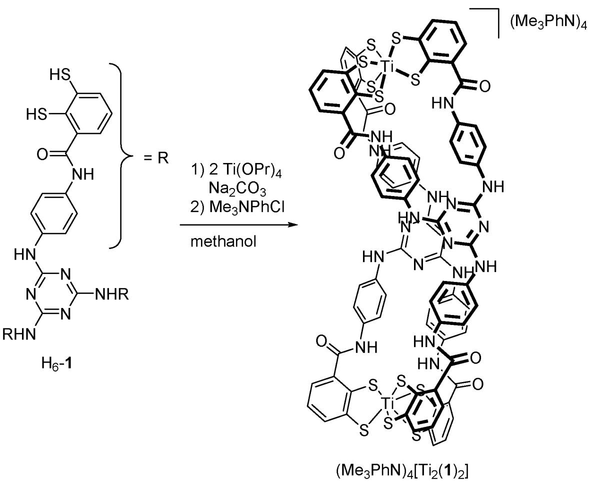
Florian Hupka and F. Ekkehardt Hahn*

Received 22nd December 2009, Accepted 9th April 2010
First published as an Advance Article on the web 23rd April 2010
DOI: 10.1039/b926939h

Reaction of the C_3-symmetric triazine bridged tris(benzene-*o*-dithiol) ligand H_6-1 with Ti^{4+} leads to the unexpected formation of the dinuclear complex $(Me_3PhN)_4[Ti_2(1)_2]$ while other C_3-symmetric ligands are reported to form either mono- or tetranuclear complexes.

Supramolecular self-assembly facilitates the creation of large and complex structures from relatively simple precursors.[1,2] Based on reversible weak interactions, such as hydrogen bonding or metal–ligand interactions, an array of self-assembled structures have been synthesized and this type of coordination chemistry has been reviewed.[3–9] Some of these structures possess an internal cavity, whose interior provides a specific chemical environment, distinctly different from the exterior surrounding.[10–13] The development of new container molecules which can be used as reaction chambers or for trapping of short living reaction intermediates currently constitutes an important synthetic target.

Raymond *et al.*[14] and Albrecht *et al.*[15] have synthesized C_3-symmetric tricatechol ligands, suitable for the formation of tetranuclear clusters of type $[M_4L_4]^{m-}$. However, if the backbone in such ligands is flexible enough, the entropically favored mononuclear complexes of type $[ML]^{n-}$ are formed.[16] Recently, we have described the formation of a tetranuclear cluster derived from a C_3-symmetric tris(bdt)$^{6-}$ ligand (bdt = benzene-*o*-dithiolato dianion)[17] while a similar ligand with a more flexible backbone leads to the formation of the mononuclear complex.[18] The tetranuclear cluster has been shown to serve as a container molecule capable to encapsulate small cationic guest molecules. Here we describe a C_3-symmetric tris(benzene-*o*-dithiol) ligand (H_6-1) which is surprisingly capable of forming a dinuclear complex when reacted with $Ti(OPr)_4$ and Me_3PhNCl.



Scheme 1 Synthesis of the dinuclear complex $(Me_3PhN)_4[Ti_2(\mathbf{1})_2]$.

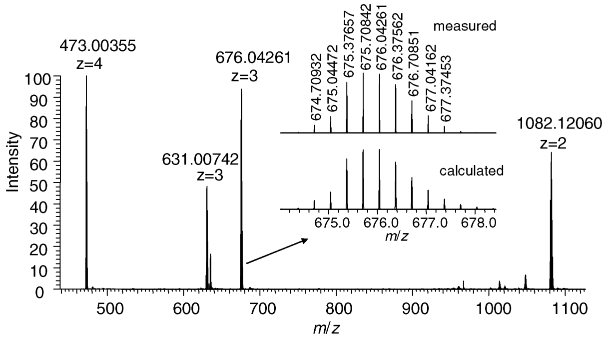


Fig. 1 High-resolution electrospray mass spectrum of $H_x(Me_3PhN)_y[Ti_2(\mathbf{1})_2]$, for peak assignment see text.

Ligand H_6-1 has been prepared according to previously published procedures.[19,20] Two equivalents of H_6-1 react with two equivalents of $Ti(OPr)_4$‡ in the presence of Na_2CO_3 in methanol§ resulting in the formation of a deep red solution (λ_{max} = 540 nm), typical for the $[Ti(bdt)_3]^{2-}$ chromophore.[21] Addition of Me_3PhNCl to the methanol solution yields a deep red precipitate which was identified as the dinuclear complex $[Ti_2(\mathbf{1})_2]^{4-}$ (Scheme 1). The high-resolution ESI(−) MS spectrometry data confirm the $[Ti_2(\mathbf{1})_2]^{4-}$ stoichiometry. Fig. 1 shows the ESI mass spectrum with major peaks at m/z = 473.0 $[Ti_2(\mathbf{1})_2]^{4-}$, 631.0 $\{H[Ti_2(\mathbf{1})_2]\}^{3-}$, 676.0 $\{(Me_3PhN)[Ti_2(\mathbf{1})_2]\}^{3-}$, and 1082.1 $\{(Me_3PhN)_2[Ti_2(\mathbf{1})_2]\}^{2-}$.

Single crystals of $(Me_3PhN)_4[Ti_2(\mathbf{1})_2]\cdot 2DMSO\cdot 6DMF$ suitable for an X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into a solution of $(Me_3PhN)_4[Ti_2(\mathbf{1})_2]$ in MeOH/DMF/DMSO (10 : 1 : 1, v : v : v).¶ Fig. 2 shows the molecular structure of the trianion $[Me_3PhN\subset Ti_2(\mathbf{1})_2]^{3-}$, with one Me_3PhN^+ cation encapsulated within the interior of the cavity.

To the best of our knowledge, complex $[Ti_2(\mathbf{1})_2]^{4-}$ constitutes the first example of two C_3-symmetric ligands forming a dinuclear complex, with two ligand arms of each ligand coordinating to one metal center and the remaining one coordinating to the second metal center (and *vice versa*).

Institut für Anorganische und Analytische Chemie, Universität Münster, Corrensstraße 30, D-48149 Münster, Germany. E-mail: fehahn@uni-muenster.de; Fax: +49-251-8333108; Tel: +49-251-8333111

† Electronic supplementary information (ESI) available: Details of the crystal structure determination. CCDC 759471. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b926939h

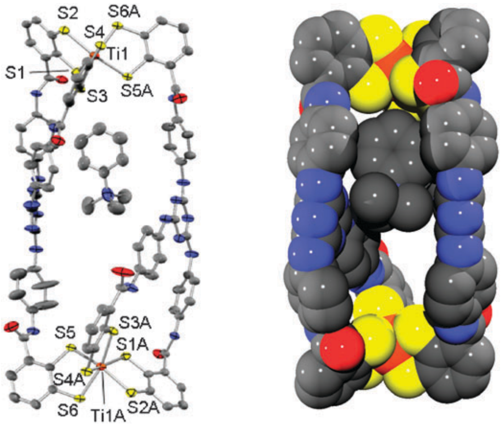


Fig. 2 Molecular structure of the complex anion $[Me_3PhN \subset Ti_2(\mathbf{1})_2]^{3-}$ (left ORTEP drawing with 50% probability ellipsoids; right space filling model), hydrogen atoms, solvent molecules and cations (except for the encapsulated Me_3PhN^+) have been omitted for clarity. Selected bond lengths [Å] and angles [°]: range Ti1–S 2.391(2)–2.446(2), Ti1A–S 2.381(2)–2.449(2), Ti1···Ti2 18.956(2); bite angle S–Ti1–S 81.00(6)–83.02(6), S–Ti1A–S 80.62(6)–82.92(6).

Complex $(Me_3PhN)_4[Ti_2(\mathbf{1})_2]\cdot 2DMSO\cdot 6DMF$ crystallizes in the centrosymmetric space group $P\bar{1}$. Each titanium atom is coordinated by six sulfur atoms in a strongly distorted octahedral fashion with a calculated twist angle of $\phi = 36.1°$ (Ti1) and $\phi = 36.8°$ (Ti2). Both titanium atoms exhibit the same absolute configuration, namely Δ in the depicted complex anion. Each $\{TiS_6\}$ moiety in complex anion $[Ti_2(\mathbf{1})_2]^{4-}$ shows two long (N···S separations in the range of 3.5 Å) and one short N···S separation (∼2.9 Å) indicative for the formation of just one N–H···S hydrogen bond per $\{TiS_6\}$ unit.

The side view of the crystal structure (Fig. 3, left) shows an uncommon banana like shape where both ligands point in the same direction. Remarkable is the very long Ti–Ti distance of about 19 Å which is about twice as large as seen for other dinuclear helical complexes.[19d–g]

Since the separation of the triazine moieties measures about 9 Å, the two ligands span a large groove and the complex anion can serve as a molecular host. The molecular structure determination shows one Me_3PhN^+ cation located inside this cavity (Fig. 3, right), while the other three cations remain outside maintaining no remarkable interactions with the complex anion.

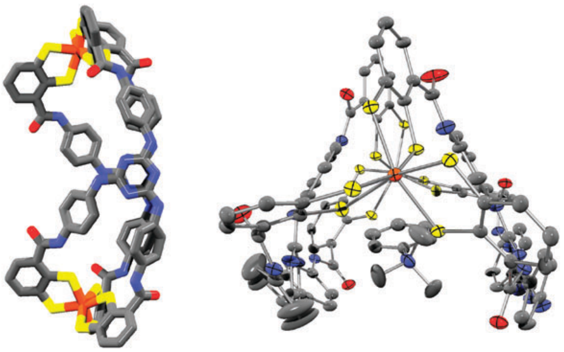


Fig. 3 Plot of the $[Ti_2(\mathbf{1})_2]^{4-}$ anion in a side view showing its banana-shape and plot of the $[Me_3PhN \subset Ti_2(\mathbf{1})_2]^{3-}$ anion viewed down the Ti–Ti axis (right).

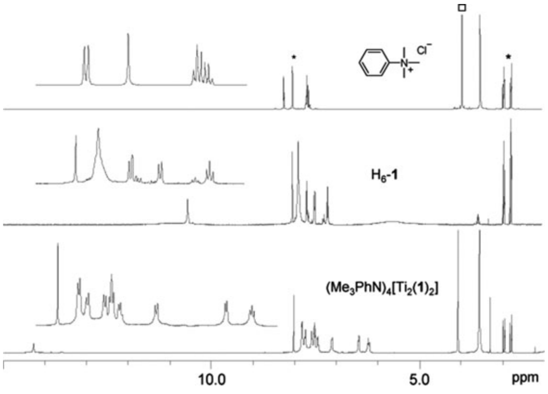


Fig. 4 ^1H NMR spectra (400 MHz, 25 °C, δ, ppm) of Me_3PhNCl (top), ligand H_6-**1** (middle) and complex $(Me_3PhN)_4[Ti_2(\mathbf{1})_2]$ (bottom) in DMF-d_7 (* = DMF, □ = H_2O).

Encapsulation and release from the cavity in solution is too fast to be detected by NMR spectroscopy. Even at low temperatures neither a broadening of the proton resonances nor a chemical shift to higher field was observed for the Me_3PhN^+ cation as would be expected for the encapsulated ion (Fig. 4).

The small numbers of resonances in the ^1H NMR spectrum of $(Me_3PhN)_4[Ti_2(\mathbf{1})_2]$ (Fig. 4, bottom) indicate the presence of only one highly symmetric species in solution. The spectrum reveals the characteristic set of signals for the proton resonances of the benzene-*o*-dithiolato donor unit reflecting the AMX spin system at $\delta = 7.11$ (dd), 6.46 (dd) and 6.22 (t) ppm. The resonance for the amide protons is detected as a singlet at $\delta = 14.27$ ppm and is shifted to low field compared to the value recorded for the free ligand ($\Delta\delta = 3.27$ ppm). This observation indicates, in contrast to the findings in the solid state, the formation of intramolecular N–H···S hydrogen bonds in solution.

In conclusion, we have described the use of a novel tris-(benzene-*o*-dithiol) ligand to form a self-assembled M_2L_2 complex, the first dinuclear complex based on a C_3-symmetric ligand showing a banana-shape geometry. This homochiral complex possesses an internal cavity which can encapsulate one Me_3PhN^+ cation which was detected in the solid state but not in solution. Further studies concerning the possibility to encapsulate other small molecules are underway.

This work was supported by the Fonds der Chemischen Industrie and the NRW International Graduate School of Chemistry. We thank Dr A. Hepp for measuring the NMR spectra and Dr H. Luftmann for measuring the mass spectra.

Notes and references

‡ Commercially available $Ti(OPr)_4$ (Aldrich) was used without further purification. 2,3-Di(isopropylmercapto)benzoic acid chloride[19] and 2,4,6-tris(*p*-aminoanilino)-1,3,5-triazine[20] were prepared as described previously.

§ Preparation of 2,4,6-tris{*p*-[2,3-di(isopropylmercapto)benzamido-anilino]}-1,3,5-triazine: freshly prepared 2,3-di(isopropylmercapto)-benzoic acid chloride (1.0 g, 3.47 mmol) was dissolved in THF (20 mL) and this solution was added to a solution of 2,4,6-tris-(*p*-aminoanilino)-1,3,5-triazine (462 mg, 1.16 mmol) and Et_3N (1.20 mL, 8.70 mmol) in THF (40 mL). The reaction mixture was stirred for 12 h at ambient temperature. Subsequently, insoluble material was removed by filtration and the solvent was removed from the filtrate under vacuum. The solid residue was purified by column chromatography (silica gel, CH_2Cl_2/ethyl acetate 1 : 1, v : v). Yield: 1.18 g (1.02 mmol, 88%); ^{1}H NMR (400.1 MHz, $CDCl_3$, ppm): δ = 7.55 (m, 12H, phenylene-H), 7.42 (m, 3H, bdt-H), 7.30 (m, 6H, bdt-H), 3.43 (m, 6H, $C\mathit{H}(CH_3)_2$), 2.92 (s, br, 3H, N–H), 1.34 (d, ^3J = 6.6 Hz, 18H, $CH(C\mathit{H}_3)_2$), 1.16 (d, ^3J = 6.6 Hz, 18H, $CH(C\mathit{H}_3)_2$). ^{13}C NMR (100.6 MHz, $CDCl_3$, ppm): δ = 170.8 (C(O)NH), 168.1 (triazene-C), 149.6, 146.8, 139.0, 137.5, 133.0, 132.9, 132.0, 129.2, 125.6, 124.5 (phenylene- and bdt-C), 44.7 (SCH), 40.0 (SCH), 26.9 ($CH(\mathit{C}H_3)_2$), 26.5 ($CH(\mathit{C}H_3)_2$). MS (MALDI, positive ions): m/z = 1156 $[M + H]^+$, 1178 $[M + Na]^+$.

Preparation of ligand H_6-**1**: dry, freshly distilled THF (60 mL) was added to a mixture of 2,4,6-tris{*p*-[2,3-di(isopropylmercapto)benzamidoanilino]}-1,3,5-triazine (1.18 g, 1.02 mmol), sodium (352 mg, 15.3 mmol) and naphthalene (979 mg, 7.65 mmol). The reaction mixture was stirred for 12 h at ambient temperature. Subsequently, methanol (10 mL) was added to destroy unreacted sodium. All solvents were then removed under vacuum and the solid residue was dissolved in degassed water and washed three times with degassed diethyl ether (20 mL each). Insoluble material was removed by filtration. The clear aqueous solution was treated dropwise with HCl (37%) until a white precipitate formed. The precipitate was isolated by filtration and washed with water and diethyl ether. The solid residue was dried under vacuum. Yield: 755 mg (0.84 mmol, 82%); ^{1}H NMR (400.1 MHz, DMF-d_7, ppm): δ = 11.0 (s, br, 3H, N-H), 10.55 (s, 3H, N-H), 7.88 (s, br, 12H, phenylene-H), 7.67 (dd, ^3J = 7.7, ^4J = 1.0, 3H, bdt-H), 7.49 (dd, ^3J = 7.7, ^4J = 1.0, 3H, bdt-H), 7.17 (t, ^3J = 7.7, 3H, bdt-H), 5.61 (s, br, 6H, S-H). ^{13}C NMR (100.6 MHz, DMF-d_7, ppm): δ = 168.0 (C(O)NH), 137.4 (triazine-C), 135.0, 134.9, 132.1, 130.9, 128.4, 126.7, 126.3, 126.0, 125.4, 121.1 (phenylene- and bdt-C). MS (MALDI, positive ions): m/z = 904 $[M + H]^+$, 926 $[M + Na]^+$.

Preparation of $(Me_3PhN)_4[Ti_2(\mathbf{1})_2]$: a sample of $Ti(OPr)_4$ (15.7 mg, 0.055 mmol) was added to a solution of H_6-**1** (50 mg, 0.055 mmol) and Na_2CO_3 (11.7 mg, 0.110 mmol) in degassed methanol (20 mL). The solution was stirred under argon at ambient temperature for 12 h and filtered. Addition of Me_3PhNCl (18.9 mg, 0.11 mmol) to the filtrate yielded a dark red precipitate, which was isolated by filtration, washed with methanol (2 × 10 mL) and dried under vacuum. Yield: 57 mg (0.03 mmol, 55%); ^{1}H NMR (400 MHz, DMF-d_7, ppm): δ = 14.27 (s, 6H, (C(O)NH)), 7.78 (d, ^3J = 8.0 Hz, 8H, Me_3NPh-H), 7.71 (d, ^3J = 8.6 Hz, 12H, phenylene-H), 7.55 (d, ^3J = 8.6 Hz, 12H, phenylene-H), 7.52 (t, ^3J = 8.0 Hz, 8H, Me_3NPh-H), 7.41 (m, 4H, Me_3NPh-H), 7.11 (dd, ^3J = 7.7 Hz, ^4J = 1.2 Hz, 6H, bdt-H), 6.42 (dd, ^3J = 7.7 Hz, ^4J = 1.2 Hz, 6H, bdt-H), 6.18 (t, ^3J = 7.7 Hz, 6H, bdt-H), 3.56 (s, 36H, PhNMe-H); ^{13}C NMR (400 MHz, DMF-d_7, ppm): δ = 167.7 (C(O)NH), 163.5 (triazine-C), 160.1, 157.5 (C–S), 147.5 (Me_3NPh-C), 135.9, 134.9 (phenylene-C), 130.7, 130.6, 120.3 (Me_3NPh-C), 119.6, 119.5 (phenylene-C), 114.7, 114.1, 113.4, 112.6 (bdt-C), 57.1 ($PhNMe_3$-C); MS (ESI, negative ions) m/z: 473.0 $[Ti_2(\mathbf{1})_2]^{4-}$, 631.0 $\{H[Ti_2(\mathbf{1})_2]\}^{3-}$, 676.0 $\{(Me_3PhN)[Ti_2(\mathbf{1})_2]\}^{3-}$, 1082.1 $\{(Me_3PhN)_2[Ti_2(\mathbf{1})_2]\}^{2-}$.

¶ Crystal data for $(Me_3PhN)_4[Ti_2(\mathbf{1})_2]\cdot 2DMSO\cdot 6DMF$: $C_{142}H_{164}N_{28}O_{14}S_{14}Ti_2$, M = 3031.65, T = 153(1) K, λ = 1.54178 Å, μ(Cu-K$_\alpha$) = 3.167 mm^{-1}, triclinic, a = 14.6767(10), b = 21.0095(12), c = 25.8753(8) Å, α = 84.555(4)°, β = 78.851(4)°, γ = 87.166(4)°, V = 7788.8(8) Å^3, space group $P\bar{1}$, Z = 2, 45 721 measured intensities, 26 396 unique intensities (R_{int} = 0.0687), all reflections used in refinement against $|F^2|$, R = 0.0900, wR = 0.2586 (for all data).

1 J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Voegtle and J.-M. Lehn, *Comprehensive Supramolecular Chemistry*, Pergamon, Oxford, 1996.

2 J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, 1995.

3 D. S. Lawrence, T. Jiang and M. Levett, *Chem. Rev.*, 1995, **95**, 2229.

4 S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853.

5 M. M. Conn and J. Rebek, Jr., *Chem. Rev.*, 1997, **97**, 1647.

6 M. A. Mateos-Timoneda, M. Crego-Calama and D. N. Reinhoudt, *Chem. Soc. Rev.*, 2004, **33**, 363.

7 T. D. Hamilton and L. R. MacGillivray, *Cryst. Growth Des.*, 2004, **4**, 419.

8 M. Albrecht, *Chem. Rev.*, 2001, **101**, 3457.

9 T. Kreickmann and F. E. Hahn, *Chem. Commun.*, 2007, 1111.

10 L. Garel, J.-P. Dutasta and A. Collet, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1169.

11 J. C. Sherman and D. J. Cram, *J. Am. Chem. Soc.*, 1989, **111**, 4527.

12 F. Hof, S. L. Craig, C. Nuckolls and J. Rebek, Jr., *Angew. Chem., Int. Ed.*, 2002, **41**, 1488.

13 W.-Y. Sun, M. Yoshizawa, T. Kusukawa and M. Fujita, *Curr. Opin. Chem. Biol.*, 2002, **6**, 757.

14 (*a*) C. Brückner, R. E. Powers and K. N. Raymond, *Angew. Chem., Int. Ed.*, 1998, **37**, 1837; (*b*) D. L. Caulder and K. N. Raymond, *Acc. Chem. Res.*, 1999, **32**, 975; (*c*) D. L. Caulder and K. N. Raymond, *J. Chem. Soc., Dalton Trans.*, 1999, 1185.

15 (*a*) M. Albrecht, I. Janser, S. Meyer, P. Weis and R. Fröhlich, *Chem. Commun.*, 2003, 2854; (*b*) M. Albrecht, I. Janser, J. Runsink, G. Raabe, P. Weis and R. Fröhlich, *Angew. Chem., Int. Ed.*, 2004, **43**, 6662; (*c*) M. Albrecht, I. Janser and R. Fröhlich, *Chem. Commun.*, 2005, 157; (*d*) M. Albrecht, I. Janser, S. Burk and P. Weis, *Dalton Trans.*, 2006, 2875; (*e*) M. Albrecht and R. Fröhlich, *Bull. Chem. Soc. Jpn.*, 2007, **80**, 797; (*f*) M. Albrecht, S. Burk, P. Weis, C. A. Schalley and M. Kogej, *Synthesis*, 2007, 3736.

16 (*a*) W. R. Harris, F. L. Weitl and K. N. Raymond, *J. Chem. Soc., Chem. Commun.*, 1979, 177; (*b*) K. N. Raymond and C. J. Carrano, *Acc. Chem. Res.*, 1979, **12**, 183; (*c*) K. N. Raymond, E. A. Dertz and S. S. Kim, *Proc. Natl. Acad. Sci. U. S. A.*, 2003, **100**, 3584; (*d*) A. R. Bulls, C. G. Pippin, F. E. Hahn and K. N. Raymond, *J. Am. Chem. Soc.*, 1990, **112**, 2627; (*e*) T. M. Garrett, T. J. McMurry, M. W. Hosseini, Z. E. Reyes, F. E. Hahn and K. N. Raymond, *J. Am. Chem. Soc.*, 1991, **113**, 2965.

17 B. Birkmann, R. Fröhlich and F. E. Hahn, *Chem.–Eur. J.*, 2009, **15**, 9325.

18 B. Birkmann, W. W. Seidel, T. Pape, A. W. Ehlers, K. Lammertsma and F. E. Hahn, *Dalton Trans.*, 2009, 7350.

19 (*a*) F. E. Hahn and W. W. Seidel, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2700; (*b*) H. V. Huynh, C. Schulze Isfort, W. W. Seidel, T. Lügger, R. Fröhlich, O. Kataeva and F. E. Hahn, *Chem.–Eur. J.*, 2002, **8**, 1327; (*c*) H. V. Huynh, W. W. Seidel, T. Lügger, R. Fröhlich, B. Wibbeling and F. E. Hahn, *Z. Naturforsch., B*, 2002, **57**, 1401; (*d*) F. E. Hahn, C. Schulze Isfort and T. Pape, *Angew. Chem., Int. Ed.*, 2004, **43**, 4807; (*e*) T. Kreickmann, C. Diedrich, T. Pape, H. V. Huynh, S. Grimme and F. E. Hahn, *J. Am. Chem. Soc.*, 2006, **128**, 11808; (*f*) C. Schulze Isfort, T. Kreickmann, T. Pape, R. Fröhlich and F. E. Hahn, *Chem.–Eur. J.*, 2007, **13**, 2344; (*g*) F. E. Hahn, M. Offermann, C. Schulze Isfort, T. Pape and R. Fröhlich, *Angew. Chem., Int. Ed.*, 2008, **47**, 6794.

20 K. Takagi, T. Hattori, H. Kunisada and Y. Yuki, *J. Polym. Sci., Part A: Polym. Chem.*, 2000, **38**, 4385.

21 M. Könemann, W. Stüer, K. Kirschbaum and D. M. Giolando, *Polyhedron*, 1994, **13**, 1415.