Nanoclusters

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Discrete Magnesium Hydride Aggregates: A Cationic $Mg_{13}H_{18}$ Cluster Stabilized by NNNN-Type Macrocycles**

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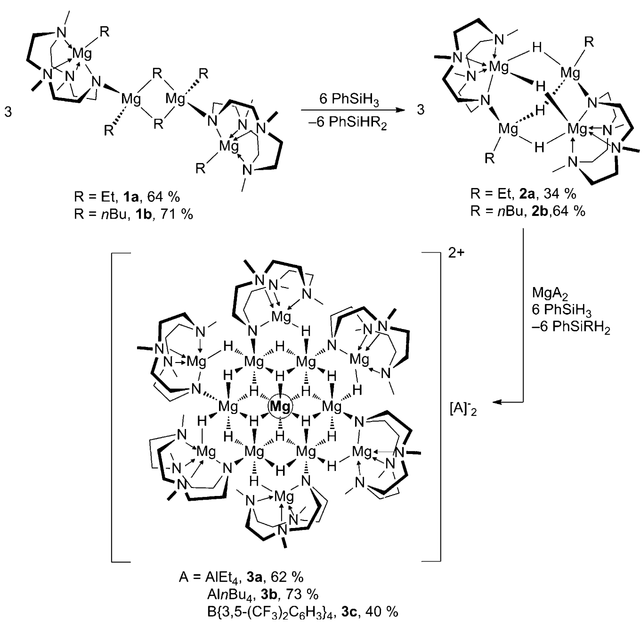
Dedicated to Professor Richard R. Schrock on the occasion of his 70th birthday

Abstract: *Large magnesium hydride aggregates $[Mg_{13}(Me_3TACD)_6(\mu_2\text{-}H_{12})(\mu_3\text{-}H_6)][A]_2$ ($(Me_3TACD)H = 1,4,7$-trimethyl-1,4,7,10-tetraazacyclododecane; $A = AlEt_4$, $AlnBu_4$, $B\{3,5\text{-}(CF_3)_2C_6H_3\}_4$) were synthesized stepwise from alkyl complexes $[Mg_2(Me_3TACD)R_3]$ (R = Et, nBu) and phenylsilane in the presence of additional Mg^{II} ions. The central magnesium atom is octahedrally coordinated by six hydrides as in solid α-MgH_2 of the rutile type. Further coordination to six magnesium atoms leads to a substructure of seven edge-sharing octahedra as found in the hexagonal layer of brucite ($Mg(OH)_2$). Upon protonolysis in the presence of 1,2-dimethoxyethane (DME), this cluster was degraded into a tetranuclear dication $[Mg_2(Me_3TACD)(\mu\text{-}H)_2(DME)]_2[A]_2$.*

Solid-state magnesium hydride MgH_2 is a potential energy carrier, because it is able to store hydrogen (7.6 wt %) in a reversible manner.[1] However, bulk MgH_2 is thermodynamically stable ($T_{dec} \geq 284\,°C$) with slow uptake und release kinetics.[2] Theoretical calculations suggest that the temperature required for the desorption of hydrogen drops by 100 K when the particle size is reduced from bulk to small clusters $(MgH_2)_n$ with $n \leq 19$.[3] This has recently been confirmed by Harder et al. using defined magnesium hydride clusters with $n \leq 10$ stabilized with β-diketiminate (nacnac).[4]

Molecular magnesium hydrides are rare, because Schlenk equilibria easily lead to insoluble saline MgH_2 with a high lattice energy ($\Delta H = 2709\ kJ\,mol^{-1}$).[5] In 1992, Michalzcyk reported on magnesium hydride aggregates of unknown size that are soluble in donor solvents.[6] The first molecular magnesium hydrides $[Mg_2M_2(NiPr_2)_4(\mu\text{-}H)_2(toluene)_x]$ (M = Na: $x = 0$, 2; K: $x = 2$) were described by Mulvey et al. in 2002.[7] Use of nacnac-derived ligands led to the controlled synthesis of mono-,[8] di-,[9] tetra-,[4,10] and octanuclear[11] derivatives. The amido–hydrido cluster $[Mg_4(IPr)_2(\mu\text{-}H)_6[N(SiMe_3)_2]_2]$ (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene) is stabilized by an N-heterocyclic carbene ligand.[12]

We have now managed to construct molecular magnesium hydride clusters by using the monoanionic amidotriamine ligand of $L_{3+1}X$-type Me_3TACD ($(Me_3TACD)H = Me_3[12]aneN_4 = 1,4,7$-trimethyl-1,4,7,10-tetraazacyclododecane)[13] and studied their properties (Scheme 1). The magnesium alkyls $[Mg_2(Me_3TACD)R_3]_2$ (R: Et, **1a**; *n*Bu: **1b**), accessible from $(Me_3TACD)H$ and 2 equiv of $[MgR_2]$ in THF, reacted with one equiv of phenylsilane to give the mixed alkyl–hydrido complexes $[Mg_2(Me_3TACD)(\mu_2\text{-}H)_2R]_2$ (R: Et, **2a**; *n*Bu, **2b**).



Scheme 1. Synthesis of Me_3TACD-stabilized clusters.

The solubility of **2a** is very low in standard solvents, but reliable NMR spectra were obtained for the soluble *n*-butyl derivative **2b**. ^1H NMR spectra in [D$_8$]THF reveals one broad singlet at δ 3.25 ppm for three inequivalent magnesium-bound hydrides.[12] The Me_3TACD and the alkyl ligands lead to two sets of signals, indicating a dynamic structure in

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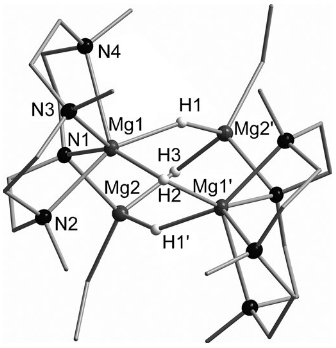


Figure 1. Molecular structure of $[Mg_2(Me_3TACD)(\mu_2\text{-}H)_2Et]_2$ (**2a**). Displacement parameters are drawn at 50% probability. The hydrogen atoms except for those of the $Mg_4H_4N_2$ core are omitted for clarity.

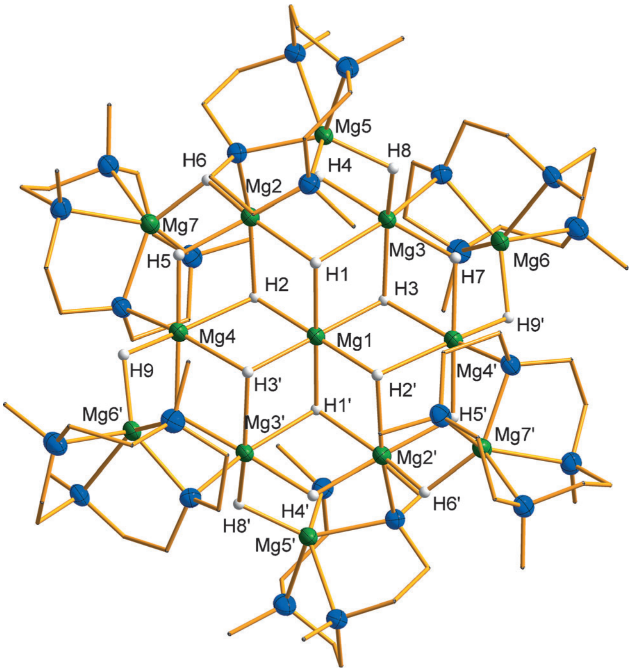


Figure 2. Molecular structure of the cationic cluster $[Mg_{13}(Me_3TACD)_6(\mu_2\text{-}H)_{12}(\mu_3\text{-}H)_6]^{2+}$ in **3c**. Ellipsoids are set at 50%. The anion and hydrogen atoms except for those of the $Mg_{13}H_{18}$ core are omitted for clarity.

solution that may be due to Schlenk equilibria involving both the hydride and *n*Bu ligands.

Despite the different solubility of **2a** and **2b**, single-crystal X-ray diffraction studies reveal similar molecular structures. The ethyl derivative **2a** shows crystallographic C_2 symmetry with a C_2 axis through the hydrogen atoms H2 and H3 (Figure 1). The structures contain an adamantane-like $Mg_4H_4N_2$ core. Similar frameworks were reported for related magnesium hydrides.[4,12] Both amido functions of the two Me_3TACD ligands (N1 and N1′) bridge two magnesium atoms. Unlike other mixed alkyl/hydride compounds with NN-bridged bis-β-diketiminate ligands such as $[Mg_4(NN)_2H_2(nBu)_2]$,[4a] further reaction with excess silane gave an insoluble yellow material.

Most remarkably, neutral **2a** and **2b** reacted in the presence of a magnesium aluminate or borate MgA_2 (A = $[AlEt_4]$, $[AlnBu_4]$, $[B\{1,3\text{-}(CF_3)_2C_6H_3\}_4]$) with phenylsilane reproducibly to dicationic aggregates of composition $[Mg_{13}(Me_3TACD)_6(\mu_2\text{-}H)_{12}(\mu_3\text{-}H)_6]A_2$ (A = $[AlEt_4]$ (**3a**), $[AlnBu_4]$ (**3b**), $[B\{1,3\text{-}(CF_3)_2C_6H_3\}_4]$ (**3c**)). The structure of these compounds was established by *X*-ray diffraction of single crystals of **3b** and **3c** (Figure 2).

The structures contain the dication $[Mg_{13}(Me_3TACD)_6(\mu_2\text{-}H)_{12}(\mu_3\text{-}H)_6]^{2+}$ with crystallographic C_i symmetry. The central $[Mg(\mu_3\text{-}H)_6Mg_6(\mu_2\text{-}H)_6]^{2+}$ core fragment is planar (largest deviation from the mean plane formed by the seven Mg atoms: 0.0708(6) Å) and resembles Anderson-type polyoxo metal clusters[14] $[Mg_7(OR)_{12}]^{2+}$ that contain alkoxo instead of hydrido ligands.[15] The "Mg_7H_{12}" unit in **3** can therefore be considered as a section of an infinite layer in the $Mg(OH)_2$ (brucite) structure. The relationship between this fragment and the structure of bulk metallic magnesium that crystallizes in hexagonal symmetry is also obvious: the Mg⋯Mg distances of 3.1722(14)–3.2102(14) Å in **3c** are comparable to that of 3.17 Å observed within a layer of metallic magnesium. This central fragment is encapsulated by a shell of six "$Mg(Me_3TACD)H$" units that coordinate via μ-H and μ-N bonds. The outer magnesium centers are situated alternately above and below the central Mg_7 plane, leading to non-crystallographic C_{3i} (S_6) symmetry. This leads to three different environments for the magnesium atoms, as observed for the aluminum atoms in the structurally related nanocluster $[Al_{13}(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{12}\{N(CH_2CO_2H)_2(CH_2CH_2OH)\}_6(H_2O)_6]^{3+}$.[16] The central atom Mg1 is octahedrally coordinated by six hydride ligands, formally leading to a $[MgH_6]^{4-}$ unit, followed by six octahedrally coordinated atoms in the second coordination shell as well as by six magnesium atoms on the periphery that are bonded to one hydride and four nitrogen atoms of an Me_3TACD ligand. The large cluster size is reflected by the distance between two external symmetry related Mg atoms of 9.986(2)–10.008(2) Å. A view along the $\bar{3}$ axis (Figure 2) shows that the $Mg_{13}H_{18}$ fragment is derived from the hexagonally closest-packed structure of bulk magnesium but not from α-MgH_2 (rutile type), which would be predicted for clusters with more than 19 Mg atoms.[3] The geometry of the ligand is ideally suited to stabilize the metal hydride cluster (Supporting Information, Figure S25).

The ^1H NMR spectra of **3b** confirm that the structure remains intact in solution. Cluster **3b** shows three distinct broad singlets for the hydrido ligands, in agreement with three coordination modes for the symmetry-related hydrides. A ^1H–^1H COSY NMR spectrum (Figure 3) reveals that the signal H_b at δ 3.66 ppm is coupled to both the resonance H_a at δ 4.20 and that for H_c at 3.18 ppm. In contrast to the earlier reported Mg_8H_{10} cluster $[Mg_8(PARA)_3H_{10}]$, for which H–H coupling was observed even at 100 °C (4–5 Hz),[11] the cationic $Mg_{13}H_{18}$ cluster does not show a coupling pattern (not even at −80 °C). The ligand shows no symmetry, revealing a discrete ^{13}C signal for every carbon atom in the backbone.

The optimized structures obtained from DFT calculations (B3PW91/6-311++G**(Mg), 6-31G**(other atoms)) for the cationic aggregates in **3** agree well with those obtained from crystal structure analysis. The Mg–H bond distances and the

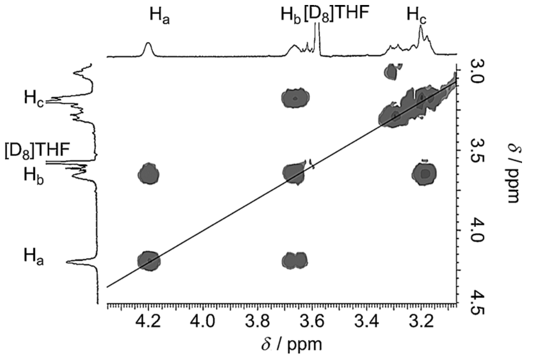
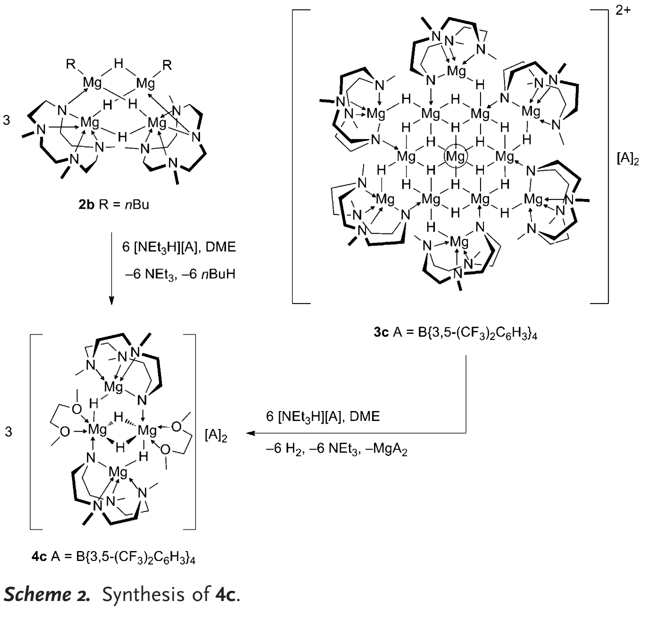


Figure 3. ^{1}H–^{1}H COSY spectrum in [D$_8$]THF (400 MHz, 25 °C) showing the three hydride signals in **3b** at δ 4.20, 3.66, and 3.18 ppm.

interatomic Mg···Mg distances were also reproduced well (see the Supporting Information). Calculations on the second order NBO level do not show substantial direct Mg···Mg interaction, but reveal significant contributions from Mg–H···Mg donation with an average bonding energy of 40–50 kcal mol^{-1}. Wiberg indices of 0.29 between each bridging hydrogen atom and the two connected magnesium centers indicate 3c,2e$^-$ Mg–H–Mg bonding. This type of interaction was found to stabilize lanthanide hydride clusters.[13c,f]

Protonolysis of **2b** with 2 equiv of the weak Brønsted acid [NEt$_3$H][B{1,3-(CF$_3$)$_2$C$_6$H$_3$}$_4$] in the presence of 1,2-dimethoxyethane (DME) gave the dicationic [Mg$_2$(Me$_3$TACD)(μ-H)$_2$(DME)$_2$]$_2$[B{1,3-(CF$_3$)$_2$C$_6$H$_3$}$_4$]$_2$ (**4c**). Cation **4c** was also obtained from **3c** by protonation with 6 equiv of [NEt$_3$H][B{1,3-(CF$_3$)$_2$C$_6$H$_3$}$_4$] under release of dihydrogen (Scheme 2). X-ray diffraction shows that **4c** contains two units of [MgH(Me$_3$TACD)MgH]$^+$ related by crystallographic inversion symmetry (Figure 4). The fragment "Mg$_2$(Me$_3$TACD)H$_2$" is derived from the "Mg$_{13}$H$_{18}$" nanocluster. Edge-sharing magnesium octahedra in **4c** (Mg2, Mg2′) form the second coordination sphere of **3c**. Five-fold coordination of Mg1 (Mg1′) in **4c** exists for the magnesium atoms in the periphery of **3c**. All four metal atoms of **4c** are located within a plane. This structure may be considered as an inverse crown that stabilizes the two hydrides H2 as in [M$_2$Mg$_2$(N*i*Pr$_2$)$_4$(μ$_2$-H)$_2$(toluene)$_x$] (M = Na, x = 0, 2; M = K, x = 2).[7] Related structures are known for magnesium chloride and alkoxide clusters.[17] DFT calculation of **4c** reproduced the structure (see the Supporting Information).



Scheme 2. Synthesis of **4c**.

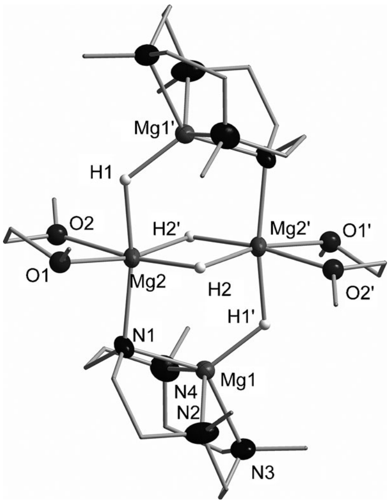


Figure 4. Structure of the molecular cation [Mg$_2$(Me$_3$TACD)(μ$_2$-H)$_2$(DME)]$_2^{2+}$ in **4c**. Ellipsoids are set at 50% probability. The hydrogen atoms except for those of the Mg$_4$H$_4$ core are omitted for clarity.

DSC measurements of compounds **3c** and **4c** revealed an exothermic transition that is accompanied by a visible gas evolution when the experiment was performed in a volume reduced NMR tube as described by Harder et al.[4] The dicationic species [Mg$_2$(Me$_3$TACD)(μ$_2$-H)$_2$]$_2$[B{1,3-(CF$_3$)$_2$C$_6$H$_3$}$_4$]$_2$ (**4c**) decomposed at 197 °C. This is slightly higher than that found for the neutral tetrameric magnesium hydride [Mg$_2$(DIPP-nacnac)H$_2$]$_2$ (175 °C).[4] The large aggregate [Mg$_{13}$(Me$_3$TACD)$_6$(μ$_2$-H)$_{12}$(μ$_3$-H)$_6$][B{1,3-(CF$_3$)$_2$C$_6$H$_3$}$_4$]$_2$ (**3c**) decomposed at 234 °C, a temperature higher than that observed for Harder's [Mg$_8$(PARA)$_3$H$_{10}$] (200 °C).[11] The higher decomposition temperature of **3c** agrees with calculated predictions,[11] although the cluster size may not be the only factor affecting the decomposition temperature. ^{1}H NMR spectroscopy showed dihydrogen as the main fraction in the gas evolved; ethylene also formed. Attempts to identify the solid decomposition products were not successful. The residue was insoluble in any common solvent.

In summary, we have reported the stepwise formation of the largest molecular magnesium hydride cluster known to date, which has thirteen magnesium atoms: [Mg$_{13}$(Me$_3$TACD)$_6$(μ$_2$-H)$_{12}$(μ$_3$-H)$_6$]A$_2$ (A = [AlEt$_4$] (**3a**), [Al*n*Bu$_4$] (**3b**), [B{1,3-(CF$_3$)$_2$C$_6$H$_3$}$_4$] (**3c**)). The NNNN macrocyclic ligand allows the central [Mg$_7$H$_{12}$]$^{2+}$ fragment to be stabilized, the structure of which is formally derived from Mg(OH)$_2$ (brucite) and thereby markedly different to that in salt-like MgH$_2$. The essential building block in the cationic clusters **3** and **4** is identified as [Mg$_2$(Me$_3$TACD)H$_2$]$^+$. Although the compounds decompose to give dihydrogen at lower temperatures compared than with bulk MgH_2, the detailed mechanism remains to be clarified.

Keywords: cluster compounds · hydrides · hydrogen · macrocylic ligands · magnesium

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[1] a) U. Eberle, M. Felderhoff, F. Schüth, *Angew. Chem. Int. Ed.* **2009**, *48*, 6608–6630; *Angew. Chem.* **2009**, *121*, 6732–6757; b) I. P. Jain, C. Lal, A. Jain, *Int. J. Hydrogen Energy* **2010**, *35*, 5133–5144; c) K.-F. Aguey-Zinsou, J.-R. Ares-Fernandez, *Energy Environ. Sci.* **2010**, *3*, 526–543; d) B. Bogdanović, A. Ritter, B. Spliethoff, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 223–234; *Angew. Chem.* **1990**, *102*, 239–250.

[2] J. F. Stampfer, C. E. Holley, J. F. Suttle, *J. Am. Chem. Soc.* **1960**, *82*, 3504–3508.

[3] R. W. P. Wagemans, J. H. van Lenthe, P. E. de Jongh, A. J. van Dillen, K. P. de Jong, *J. Am. Chem. Soc.* **2005**, *127*, 16675–16680.

[4] a) J. Intemann, J. Spielmann, P. Sirsch, S. Harder, *Chem. Eur. J.* **2013**, *19*, 8478–8489; b) E. Hevia, R. E. Mulvey, *Angew. Chem. Int. Ed.* **2011**, *50*, 9242–9243; *Angew. Chem.* **2011**, *123*, 9410–9411.

[5] a) S. Harder, *Chem. Commun.* **2012**, *48*, 11165–11177; b) C. M. Stander, R. A. Pacey, *J. Phys. Chem. Solids* **1978**, *39*, 829–832.

[6] M. J. Michalczyk, *Organometallics* **1992**, *11*, 2307–2309.

[7] a) D. J. Gallagher, K. W. Henderson, A. R. Kennedy, C. T. O'Hara, R. E. Mulvey, R. B. Rowlings, *Chem. Commun.* **2002**, 376–377; b) P. C. Andrikopoulos, D. R. Armstrong, A. R. Kennedy, R. E. Mulvey, C. T. O'Hara, R. B. Rowlings, *Eur. J. Inorg. Chem.* **2003**, 3354–3362; c) D. V. Graham, A. R. Kennedy, R. E. Mulvey, C. T. O'Hara, *Acta Crystallogr. C* **2006**, *62*, m366–m368.

[8] S. J. Bonyhady, C. Jones, S. Nembenna, A. Stasch, A. J. Edwards, G. J. McIntyre, *Chem. Eur. J.* **2010**, *16*, 938–955.

[9] S. P. Green, C. Jones, A. Stasch, *Angew. Chem. Int. Ed.* **2008**, *47*, 9079–9083; *Angew. Chem.* **2008**, *120*, 9219–9223.

[10] S. Harder, J. Spielmann, J. Intemann, *Dalton Trans.* **2014**, *43*, 14284–14290.

[11] S. Harder, J. Spielmann, J. Intemann, H. Bandmann, *Angew. Chem. Int. Ed.* **2011**, *50*, 4156–4160; *Angew. Chem.* **2011**, *123*, 4242–4246.

[12] M. Arrowsmith, M. S. Hill, D. J. MacDougall, M. F. Mahon, *Angew. Chem. Int. Ed.* **2009**, *48*, 4013–4016; *Angew. Chem.* **2009**, *121*, 4073–4076.

[13] a) P. Jochmann, J. P. Davin, T. P. Spaniol, L. Maron, J. Okuda, *Angew. Chem. Int. Ed.* **2012**, *51*, 4452–4455; *Angew. Chem.* **2012**, *124*, 4528–4531; b) D. Martin, J. Kleemann, E. Abinet, T. P. Spaniol, L. Maron, J. Okuda, *Eur. J. Inorg. Chem.* **2013**, 3987–3992; c) H. Kulinna, T. P. Spaniol, L. Maron, J. Okuda, *Chem. Eur. J.* **2013**, *19*, 9468–9471; d) H. Kulinna, T. P. Spaniol, L. Maron, J. Okuda, *Inorg. Chem.* **2012**, *51*, 12462–12472; e) E. Abinet, D. Martin, S. Standfuss, H. Kulinna, T. P. Spaniol, J. Okuda, *Chem. Eur. J.* **2011**, *17*, 15014–15026; f) J.-C. Buffet, J. Okuda, *Dalton Trans.* **2011**, *40*, 7748–7754; g) J.-C. Buffet, J. P. Davin, T. P. Spaniol, J. Okuda, *New J. Chem.* **2011**, *35*, 2253–2257; h) S. Standfuss, T. P. Spaniol, J. Okuda, *Eur. J. Inorg. Chem.* **2010**, 2987–2991; i) M. Ohashi, M. Konkol, I. Del Rosal, R. Poteau, L. Maron, J. Okuda, *J. Am. Chem. Soc.* **2008**, *130*, 6920–6921.

[14] J. S. Anderson, *Nature* **1937**, *140*, 850.

[15] a) M. Linnert, C. Bruhn, H. Schmidt, R. Herzog, D. Steinborn, *Polyhedron* **2008**, *27*, 151–156; b) Z. Janas, L. B. Jerzykiewicz, P. Sobota, J. Utko, *New J. Chem.* **1999**, *23*, 185–188.

[16] S. L. Heath, P. A. Jordan, I. D. Johnson, G. R. Moore, A. K. Powell, M. Helliwell, *J. Inorg. Biochem.* **1995**, *59*, 785–794.

[17] a) S. Sakamoto, T. Imamoto, K. Yamaguchi, *Org. Lett.* **2001**, *3*, 1793–1795; b) P. Sobota, J. Utko, K. Sztajnowska, J. Ejfler, L. B. Jerzykiewicz, *Inorg. Chem.* **2000**, *39*, 235–239.

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