## Calcium Hydrides

## A Cationic Calcium Hydride Cluster Stabilized by Cyclen-Derived Macrocyclic N,N,N,N Ligands\*\*

Phillip Jochmann, Julien P. Davin, Thomas P. Spaniol, Laurent Maron,\* and Jun Okuda\*

Metal hydride complexes of the d and f block metals are precatalysts in many important homogeneous transformations.<sup>[1,2]</sup> Much less is known about molecular main group metal, in particular s block metal hydrides.<sup>[3]</sup> Recently, a few well-defined examples of magnesium hydride complexes were reported in the context of hydrogen storage and for pyridine functionalization.<sup>[4,5]</sup> Since the discovery of the homogeneous calcium-based hydrogenation catalysts by Harder et al.,  $[{Ca(DIPP-nacnac)(H)(thf)}_2]$ (DIPP = 2, 6-diisopropylphenyl; DIPP-nacnac = CH{(CMe)(2.6-iPr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N)}<sub>2</sub>) remained the only fully characterized molecular calcium hydride to date.<sup>[6,7]</sup> [{Ca(DIPP-nacnac)(H)(thf)}<sub>2</sub>] was extensively tested in homogeneous catalysis and various ligand exchange reactions. A crucial issue is to stabilize heteroleptic hydride species by an appropriate ligand set to prevent formation of insoluble [CaH<sub>2</sub>]<sub>∞</sub>. The latter saline hydride forms easily in a Schlenk type equilibrium.<sup>[6a]</sup> We report herein the isolation and characterization of three ion pairs, each containing a monocationic trinuclear calcium hydride.

Starting from calcium precursors  $[CaR_2(thf)_x]$  (1a: R =  $N(SiMe_3)_2, x = 2;^{[8]}$  **1b**:  $R = C_3H_5, x = 0;^{[9]}$  **1c**:  $R = CH_2Ph, x =$ 0.25<sup>[10]</sup>), reactions with the tetradentate proligand  $(Me_3TACD)H$   $((Me_3TACD)H = Me_3[12]aneN_4:$  1,4,7-trimethyl-1,4,7,10-tetraazacyclododecane) afforded the mono-(ligand) complexes  $[(Me_3TACD)CaR]_n$  (2a, 2c: n = 1; 2b: n =2) (Scheme 1). The amide **2a** was reported previously.<sup>[11]</sup> Subsequent reactions of the precursors 2a-c with  $Ph_2SiH_2$  in THF at 25 °C led to the formation of the trinuclear cationic calcium hydride  $[(Me_3TACD)_3Ca_3(\mu_3-H)_2]^+$ , with different silicon-containing counteranions [A]-. These anions are either an amide [N(SiMe<sub>3</sub>)(SiPh<sub>3</sub>)]<sup>-</sup> (3a), a hydridosilicate  $[Ph_3SiH_2]^-$  (3b), or a carbanion  $[(Ph_2SiH)CHPh]^-$  (3c). Hitherto, only very few examples of trinuclear compounds of calcium have been structurally characterized.<sup>[12]</sup> The hydrides 3a-c were isolated by crystallization from the



 $c: R = CH_2Ph, x = 0.25, n = 1, A = (Ph_2SiH)CHPh$ 

**Scheme 1.** Synthesis of  $Me_3TACD$ -stabilized calcium hydride complexes 3a-c from 2a-c.

reaction mixtures in yields up to 32%. Attempts to increase the yield by precipitation with pentane or drying of the crude reaction mixtures gave product mixtures. These consisted of the cationic part of **3** and a broad variety of aryl-substituted anions, as evident from <sup>1</sup>H NMR spectroscopy.

X-ray crystal structure determination and NMR spectroscopy of hydrides 3a-c indicate the formation of identical cationic hydride units  $[(Me_3TACD)_3Ca_3(\mu_3-H)_2]^+$ , irrespective of the starting compound 2a-c. Compound 3a gave the best refinement parameters, and its C3-symmetric cation is depicted in Figure 1. The central Ca<sub>3</sub>H<sub>2</sub> core forms a trigonal bipyramid. The metal atoms are bridged by amido nitrogen atoms, resulting in an almost planar Ca<sub>3</sub>N<sub>3</sub> ring. Further coordination to the nitrogen atoms of the macrocyclic ligand leads to a coordination number of seven for the metal atoms. Ca-Ca distances of 3.3551(10) Å (3a) were found in the crystal structure, and DFT calculations indicate direct interaction between these atoms. This formally increases the coordination number of the metal centers to nine. As expected, shorter bonds are observed between calcium and the bridging amido nitrogen atoms N1 (2.438(2) and 2.471(3) Å) compared to the amine nitrogen atoms N2-N4 (2.578(3) to 2.627(3) Å). The Ca-H bond lengths of 2.36(4) Å (Ca-H1) and 2.37(4) Å (Ca-H2) in **3a** are virtually equal but longer than reported for  $[{Ca(DIPP-nacnac)(H)(thf)}_2]^{[7]}$ Ca-H bond lengths observed for 3b and 3c show larger variations (2.03(8) to 2.50(9) Å), resulting in an overall average Ca-H<sub>av</sub> value of 2.33(9) Å. The structural motif is

<sup>[\*]</sup> Dr. P. Jochmann, J. P. Davin, Dr. T. P. Spaniol, Prof. Dr. J. Okuda Institute of Inorganic Chemistry, RWTH Aachen University Landoltweg 1, 52056 Aachen (Germany)
E-mail: jun.okuda@ac.rwth-aachen.de
Prof. Dr. L. Maron
Université de Toulouse et CNRS, INSA, UPS, CNRS; UMR 5215
LPCNO, 135 avenue de Rangueil, 31077 Toulouse (France)
E-mail: laurent.maron@irsamc.ups-tlse.fr

<sup>[\*\*]</sup> Financial support by the DFG and the Cluster of Excellence "Tailor-Made Fuels from Biomass" is gratefully acknowledged. P.J. thanks the NRW Forschungsschule "BrenaRo" for a scholarship. L.M. is member of the Institut Universitaire de France. Cyclen = 1,4,7,10tetraazacyclododecane.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201200690.



**Figure 1.** Molecular structure of the cationic calcium hydride cluster [(Me<sub>3</sub>TACD)<sub>3</sub>Ca<sub>3</sub>( $\mu_3$ -H)<sub>2</sub>]<sup>+</sup> in **3 a**. Ellipsoids are set at 50% probability; hydrogen atoms except for those of the Ca<sub>3</sub>H<sub>2</sub> core are omitted for clarity.

reminiscent of the one reported for the lanthanide hydrides  $[{Ln(Me_3TACD)(\mu_2-H)_2}_3]$  (Ln = Y, Ho, Lu).<sup>[13]</sup> Up to four non-coordinating THF molecules were found in the crystal packing of **3a–c**. These THF molecules can be removed by drying of **3a–c** in vacuo.

Compound **3b** contains a rare example of an isolated organosilicate with a five-coordinate silicon atom.<sup>[14]</sup> Bonding parameters compare well to the those reported for  $[K([18]crown-6)][Ph_3SiH_2]$ , which is the only known example of a structurally characterized dihydridotriphenylsilicate anion.<sup>[14]</sup>

The new precursors 2b and c are sparingly soluble in THF and were obtained by slow diffusion of a THF solution of 1b or 1c into that of (Me<sub>3</sub>TACD)H. Compound 2b was obtained as single crystals at ambient temperature and single-crystal X-ray analysis established a dimeric solid-state structure. Although disorder of the Me<sub>3</sub>TACD ligands and poor crystal quality prevent discussion of bonding parameters, connectivity is unambiguous.  $\mu_2$ -N bridges provided by the tetradentate macrocyclic ligands are observed, whereas the allyl ligands coordinate to the calcium centres in an  $\eta^3$ -fashion. This contrasts with bridging allyl ligands observed for other multinuclear allyl complexes of Group 2 metals.<sup>[15]</sup> In solution, compound **2c** shows the expected  $\eta^1$  coordination mode for the benzyl ligand, and signals characteristic for the Me<sub>3</sub>TACD ligand (see the Supporting Information). Although <sup>1</sup>H NMR resonances ( $[D_8]$ THF, 24°C) match the formulae  $[\{(Me_3TACD)Ca(\eta^3-C_3H_5)\}_2]$ (2b)and [(Me<sub>3</sub>TACD)Ca(CH<sub>2</sub>Ph)] (2c), low solubility prevented detailed assignment of the observed signals.

Compounds  $3\mathbf{a}$ -c have low solubility in THF and are insoluble in hydrocarbons. In more polar solvents (DMSO, CH<sub>3</sub>CN) they undergo immediate decomposition. NMR spectroscopic analysis of compounds  $3\mathbf{a}$ -c is in agreement with the structure in the solid state and indicate the presence of trinuclear  $[(Me_3TACD)_3Ca_3(\mu_3-H)_2]^+$  in THF solution. <sup>1</sup>H NMR spectra  $([D_8]THF, 24^{\circ}C)$  show a singlet for the hydrido ligands at 3.99 ppm. This is 0.46 ppm upfield of the hydride chemical shift reported for  $[\{Ca(DIPP-nacnac)(H)-(thf)\}_2]$   $(C_6D_6, 20^{\circ}C)$ .<sup>[7]</sup> The methyl groups of the Me<sub>3</sub>TACD ligands show singlets at 2.22 and 2.55 ppm with an integration ratio of 1:2. The CH<sub>2</sub> protons of the macrocycle appear as broad signals in the range of 1.9–3.3 ppm. This suggests dynamic behavior of the CH<sub>2</sub>CH<sub>2</sub> groups in Me<sub>3</sub>TACD.

The anionic part of **3a**,  $[N(SiMe_3)(SiPh_3)]^-$ , shows unexceptional proton resonances,<sup>[16]</sup> whereas the anion in **3b**  $[Ph_3SiH_2]^-$  shows a singlet at 5.95 ppm, which is consistent with the chemical shift reported for the hydridic hydrogen atoms of the anion in  $[K([18]crown-6)][Ph_3SiH_2]$ .<sup>[14a]</sup> This finding for **3b** suggests separated ion pairs in THF solution. The anionic part of **3c**,  $[(Ph_2SiH)CHPh]^-$ , shows a doublet for the silicon-bound hydrogen atom at 5.31 ppm ( ${}^{3}J_{HH} = 3.5$  Hz,  ${}^{1}J_{SiH} = 171.4$  Hz).

The formation of **3** was investigated by in situ NMR spectroscopic reaction monitoring, using different silanes (Ph<sub>3</sub>SiH, Ph<sub>2</sub>SiH<sub>2</sub>, PhSiH<sub>3</sub>, Et<sub>3</sub>SiH) as hydride transfer agents. Common observations for reactions of **2a**-**c** with these silanes were: 1) the cationic hydride cluster [(Me<sub>3</sub>TACD)<sub>3</sub>Ca<sub>3</sub>-( $\mu^3$ -H)<sub>2</sub>]<sup>+</sup> is formed at early stages in high yield and appears to be favored; 2) complex mixtures of silanes Ph<sub>x</sub>SiH<sub>x-4</sub> in varying ratios are formed owing to facile substituent scrambling; and 3) orange to red reaction solutions and H<sub>2</sub> evolution were observed. Relative reaction rates for different silanes were Ph<sub>2</sub>SiH<sub>2</sub>  $\approx$  PhSiH<sub>3</sub> > Ph<sub>3</sub>SiH  $\gg$  Et<sub>3</sub>SiH. For a given silane, **2a** and **2c** react faster than the allyl **2b**. The scrambling process is crucial for the production of **3**. Such exchange processes are known to be catalyzed by metal hydrides.<sup>[17]</sup>

Although complex mixtures and side reactions prevent assessment of the detailed mechanism, we propose that the formation of products 3 is induced by the initial formation of neutral [(Me<sub>3</sub>TACD)CaH] according to the silane route.<sup>[7]</sup> The energetically favored formation of a cationic trimer requires a hydride transfer to an acceptor molecule. The latter is provided by different species resulting from groups R (from starting compounds 2), the corresponding silane, and ligand exchange products thereof. Only one anion-cation match with high lattice energy crystallizes from the reaction mixture to give products **3a–c**. Evolution of  $H_2$  is proposed to arise from silane coupling side reactions to give di- or oligosilanes. This reaction has precedence and is usually catalyzed by transition and lanthanide complexes.<sup>[18]</sup> The fate of the calcium-bound group R is obscured by hydrosilylation reactions. Indeed, reactions of 2b with phenylsilanes showed proton resonances, which were attributed to propane-1,2divlbis(triphenylsilane).

To investigate the stability of complexes **3**, a bonding analysis was carried out using DFT methods on **3a**. The geometry of the ion pair was optimized at the DFT (B3PW91/ 6-311G(d,p)) level of theory. The geometrical parameters are in excellent agreement with the experimental data. The Ca– Ca distances are found to be 3.35 Å, in perfect agreement with the experimental value (3.35 Å). Similarly, the distance between the calcium atoms and the bridging nitrogen atoms



are reproduced (2.47 and 2.43 Å vs. 2.47 and 2.44 Å) as well as the distance to the other nitrogen atoms of the ring (2.61 vs. 2.57–2.62 Å). The Ca-H distances are also well-reproduced (2.34 vs. average value of 2.35 Å). The bonding situation was analyzed using NBO analysis: three three-center bonds were found, each involving two sp hybrid orbitals of Ca and one sp<sup>2</sup> hybrid orbital of the bridging nitrogen. At the second order, these bonds are delocalized into Ca d orbitals (up to 0.15 electrons per Ca). These d orbitals overlap, leading to a direct Ca–Ca interaction (50.71 kcal mol<sup>-1</sup> at the second-order NBO analysis). Both hydrogen atoms also interact with the three calcium atoms, as demonstrated by the formation of strongly delocalized Ca-H interactions at the NBO level (interaction of more than 85 kcalmol<sup>-1</sup> at the second order NBO level). No direct interaction between the two hydrogen atoms were located at the NBO level. Thus, based on this analysis, we conclude that the cohesion of the trinuclear core is ensured by strong Ca-Ca direct interactions, supported by the presence of the bridging amido nitrogen atoms. The three Ca atoms form a triangle, where each edge is capped by a bridging nitrogen and each face is capped by an hydrogen atom.

Compound **3b** was tested in a catalytic hydrosilylation and hydrogenation of 1,1-diphenylethene (DPE) using  $Ph_2SiH_2$ and  $H_2$ , respectively (Scheme 2). Preliminary results show that **3b** catalyzes the hydrosilylation of DPE with  $Ph_2SiH_2$ (5 mol%, 25 °C). After 18 h, 95% of DPE was selectively



Scheme 2. Catalytic hydrogenation and hydrosilylation of DPE.

converted into the anti-Markovnikov addition product, as determined by in situ <sup>1</sup>H NMR spectroscopy. The catalytic hydrogenation of DPE with **3b** (19 mol %) proceeded under mild conditions (60 °C, 1 bar H<sub>2</sub>) but is slow (13 d, >99 % conversion). It is noteworthy that the reaction mixture turned dark red as soon as **3b** and DPE were reacted. NMR spectroscopic data suggested the formation of 1,1-diphenyl-ethane and  $[Ca_3(Me_3TACD)_3(H)_2][C(Ph)_2Me]$ . A related complex was isolated by Harder et al. from the reaction of DPE with [{Ca(DIPP-nacnac)(H)(thf)}\_2], and found to be highly active in catalytic hydrogenation of DPE under somewhat more forcing conditions (20 bar H<sub>2</sub>).<sup>[6b,c]</sup>

In summary, we have presented the preparation and full characterization of the first cationic calcium hydrides. Their preparation utilizes different silanes as hydride sources, resulting in silicon-containing anions. The macrocyclic ligand was found suitable for the stabilization of the thermodynamically favored cationic  $Ca_3H_2$  core in  $[(Me_3TACD)_3Ca_3(\mu_3-H)_2]^+$ . Activity in the catalytic hydrosilylation and hydrogenation of 1,1-diphenylethene was

noted, but conditions need to be optimized. The role of silicon-based anions is currently under investigation in our laboratories.

## **Experimental Section**

All operations were performed under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques. Deuterated solvents were distilled under argon from sodium/benzophenone ketyl prior to use and stored in a glovebox. All other solvents were purified using a MB SPS-800 solvent purification system. Glassware and vials were dried in an oven at 120 °C overnight and exposed to a vacuumargon cycle three times. (Me<sub>3</sub>TACD)H,<sup>[19]</sup> **1a**,<sup>[8]</sup> **1b**,<sup>[9]</sup> **1c**,<sup>[10]</sup> and **2a**<sup>[11]</sup> were synthesized following literature procedures. NMR spectra were recorded on a Bruker DRX 400 spectrometer (<sup>1</sup>H: 400.1 MHz) at 24 °C unless otherwise stated. Chemical shifts for <sup>1</sup>H NMR spectra were referenced internally using the residual solvent resonances and reported relative to tetramethylsilane. Owing to low solubility, no <sup>13</sup>C NMR data were obtained.

**3a**: Neat Ph<sub>2</sub>SiH<sub>2</sub> (18.4 mg, 18.5 µL, 0.1 mmol) was added via microliter syringe to a solution of **2a** (41.4 mg, 0.1 mmol) in 0.5 mL of THF. The mixture was allowed to stand at 25 °C. The color of the solution changed to yellow after 5 min and colorless crystals formed within 1 h. The mixture was stored at -30 °C overnight to complete crystallization. The supernatant was decanted and the crystals (4.0 mg, 0.004 mmol, 4%) were dried under reduced pressure. <sup>1</sup>H NMR (400.1 MHz, [D<sub>8</sub>]THF):  $\delta = -0.14$  (s, 9H, N(SiMe<sub>3</sub>)(SiPh<sub>3</sub>)), 2.23 (s, 9H, NCH<sub>3</sub>), 2.45–2.90 (br m, 24H, CH<sub>2</sub>), 2.56 (s, 18H, NCH<sub>3</sub>), 3.00–3.15 (br, 6H, CH<sub>2</sub>), 3.99 (s, 2H, CaH), 6.95–7.10 (m, 9H, N(SiMe<sub>3</sub>)(SiPh<sub>3</sub>)), 7.76–7.71 ppm (m, 6H, N(SiMe<sub>3</sub>)(SiPh<sub>3</sub>)). C,H,N analysis calcd (%) for C<sub>54</sub>H<sub>101</sub>Ca<sub>3</sub>N<sub>13</sub>Si<sub>2</sub> (1108.87 gmol<sup>-1</sup>): C 58.49, H 9.18, N 16.42; found: C 57.78, H 8.80, N 17.45.

**3b**: A solution of Ph<sub>2</sub>SiH<sub>2</sub> (21 mg, 0.11 mmol) in 0.5 mL of THF was added to a suspension of **2b** (30 mg, 0.05 mmol) in 0.5 mL of THF. A color change to red and gas evolution were observed. After 3 h, all **2b** was consumed and the reaction mixture was placed in the freezer (-35 °C). The product was isolated as light yellow, plate-like single crystals by decantation, washing with pentane, and drying under reduced pressure (11 mg, 0.011 mmol, 32 %). <sup>1</sup>H NMR (400.1 MHz, [D<sub>8</sub>]THF):  $\delta = 1.90-2.45$  (br m, 18H, *CH*<sub>2</sub>), 2.20 (s, 9H, N*CH*<sub>3</sub>), 2.45–2.90 (br m, 24H, *CH*<sub>2</sub>), 2.54 (s, 18H, N*CH*<sub>3</sub>), 2.95–3.20 (br, 6H, *CH*<sub>2</sub>), 3.99 (s, 2H, CaH), 5.95 (s, 2H, Ph<sub>3</sub>SiH<sub>2</sub>), 6.91 (tt, 3H, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, <sup>4</sup>J<sub>HH</sub> = 1.6 Hz, *p*-C<sub>6</sub>H<sub>5</sub>), 6.99 (t, 6H, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, *m*-C<sub>6</sub>H<sub>5</sub>), 8.12 ppm (dd, 6H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, <sup>4</sup>J<sub>HH</sub> = 1.5 Hz, *o*-C<sub>6</sub>H<sub>5</sub>). C,H,N analysis calcd (%) for C<sub>51</sub>H<sub>94</sub>Ca<sub>3</sub>N<sub>12</sub>Si (1023.96 gmol<sup>-1</sup>): C 59.84, H 9.26, N 16.42; found: C 59.53, H 8.90, N 15.92.

3c: A solution of Ph<sub>2</sub>SiH<sub>2</sub> (8.0 mg, 0.044 mmol) in 0.5 mL of THF was added to a suspension of 2c (15 mg, 0.044 mmol) in 0.5 mL of THF. The mixture was shaken, the color immediately turned to red, and the solution became homogeneous. After filtration, 0.5 mL of toluene were added and the mixture was stored at -30°C overnight. The supernatant was decanted and the red crystals (7.5 mg, 21.5%) were dried under reduced pressure. <sup>1</sup>H NMR (400.1 MHz, [D<sub>8</sub>]THF):  $\delta = 1.90-2.45$  (br m, 18H, CH<sub>2</sub>), 2.20 (s, 9H, NCH<sub>3</sub>), 2.28 (d, <sup>3</sup>J<sub>HH</sub> = 3.5 Hz, 1H, CHC<sub>6</sub>H<sub>5</sub>), 2.45–2.90 (br m, 24H, CH<sub>2</sub>), 2.54 (s, 18H,  $NCH_3$ ), 2.95–3.20 (br, 6H,  $CH_2$ ), 3.99 (s, 2H, CaH), 5.28 (tt,  ${}^{3}J_{HH} =$ 6.7 Hz,  ${}^{4}J_{\text{HH}} = 1.4$  Hz, 1 H, *p*-CHC<sub>6</sub>H<sub>5</sub>), 5.31 (d,  ${}^{3}J_{\text{HH}} = 3.5$  Hz,  ${}^{1}J_{\text{HSi}} =$ 171.4 Hz, 1 H, SiH), 6.10 and 6.17 (2 br, 4 H, o- and m-CHC<sub>6</sub>H<sub>5</sub>), 7.05 (m, 6H, *m*- and *p*-C<sub>6</sub> $H_5$ ), 7.63 (dd,  ${}^{3}J_{HH} = 7.8$  Hz,  ${}^{4}J_{HH} = 1.8$  Hz, 4H, *o*- $C_6H_5$ ). C,H,N analysis calcd (%) for  $C_{52}H_{94}Ca_3N_{12}Si$ (1035.70 gmol<sup>-1</sup>): C 60.30, H 9.15, N 16.23; found: C 59.78, H 7.79, N 12.40.

CCDC 861124, 861125, 861126 (**3a-c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

Received: January 25, 2012 Published online: March 23, 2012

**Keywords:** alkaline earth metals · calcium · homogeneous catalysis · hydrides · hydrogen storage

- a) E. L. Muetterties, B. A. Frenz, J. A. Ibers, J. P. Jesson, R. A. Schunn, C. A. Tolman in *Transition Metal Hydrides, Vol. 1* (Ed.: E. L. Muetterties), Marcel Dekker, New York, **1971**; b) *Transition Metal Hydrides, Vol. 167*, Advances in Chemistry Series (Ed.: R. Bau), American Chemical Society, Washington, DC, **1978**; c) *Transition Metal Hydrides* (Ed.: A. Dedieu), VCH, Weinheim, **1992**; d) M. A. Esteruelas, L. A. Oro, *Chem. Rev.* **1998**, 98, 577–588; e) A. J. Hoskin, D. W. Stephan, *Coord. Chem. Rev.* **2002**, *233–234*, 107–129; f) G. S. McGrady, G. Guilera, *Chem. Soc. Rev.* **2003**, *32*, 383–392.
- [2] a) M. Konkol, J. Okuda, *Coord. Chem. Rev.* 2008, 252, 1577–1591; b) M. Nishiura, Z. Hou, *Nat. Chem.* 2010, 2, 257–268; c) A. Venugopal, W. Fegler, T. P. Spaniol, L. Maron, J. Okuda, *J. Am. Chem. Soc.* 2011, *133*, 17574–17577; d) M. Nishiura, J. Baldamus, T. Shima, K. Mori, Z. Hou, *Chem. Eur. J.* 2011, *17*, 5033–5044.
- [3] a) A. J. Downs, Coord. Chem. Rev. 1999, 189, 59-100; b) S. Aldridge, A. J. Downs, Chem. Rev. 2001, 101, 3305-3366; c) E. Rivard, P. P. Power, Dalton Trans. 2008, 4336-4343; d) H. Nöth, A. Schlegel, J. Knizek, H. Schwenk, Angew. Chem. 1997, 109, 2754-2758; Angew. Chem. Int. Ed. Engl. 1997, 36, 2640-2643; e) D. Hoffmann, T. Kottke, R. J. Lagow, R. D. Thomas, Angew. Chem. 1998, 110, 1630-1633; Angew. Chem. Int. Ed. 1998, 37, 1537-1539; f) D. R. Armstrong, W. Clegg, R. P. Davies, S. T. Liddle, D. J. Linton, P. R. Raithby, R. Snaith, E. H. Wheatley, Angew. Chem. 1999, 111, 3568-3570; Angew. Chem. Int. Ed. 1999, 38, 3367-3370; g) S. R. Boss, M. P. Coles, R. Haigh, P. B. Hitchcock, R. Snaith, A. E. H. Wheatley, Angew. Chem. 2003, 115, 5751-5754; Angew. Chem. Int. Ed. 2003, 42, 5593-5596.
- [4] a) R. Han, G. Parkin, Inorg. Chem. 1992, 31, 983-988; b) L. Schlapbach, A. Züttel, Nature 2001, 414, 353-358; c) D. J. Gallagher, K. W. Henderson, A. R. Kennedy, C. T. O'Hara, R. E. Mulvey, R. B. Rowlings, Chem. Commun. 2002, 376-377; d) 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; e) 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; f) S. P. Green, C. Jones, A. Stasch, Angew. Chem. 2008, 120, 9219-9223; Angew. Chem. Int. Ed. 2008, 47, 9079-9083; g) M. Arrowsmith, M. S. Hill, D. J. MacDougall, M. F. Mahon, Angew. Chem. 2009, 121, 4073-4076; Angew. Chem. Int. Ed. 2009, 48, 4013-4016; h) S. J. Bonyhady, C. Jones, S. Nembenna, A. Stasch, A. J. Edwards, G. J. McIntyre, Chem. Eur. J. 2010, 16, 938-955; i) S. Harder, J. Spielmann, J. Intemann, H. Bandmann, Angew. Chem. 2011, 123, 4242-4246; Angew. Chem. Int. Ed. 2011, 50, 4156-4160.
- [5] a) M. S. Hill, G. Kociok-Köhn, D. J. MacDougall, M. F. Mahon, C. Weetman, *Dalton Trans.* 2011, 40, 12500–12509; b) M. Arrowsmith, M. S. Hill, T. Hadlington, G. Kociok-Köhn, C. Weetman, *Organometallics* 2011, 30, 5556–5559.

- [6] a) S. Harder, *Chem. Rev.* 2010, *110*, 3852–3876; b) J. Spielmann,
  S. Harder, *Chem. Eur. J.* 2007, *13*, 8928–8938; c) J. Spielmann, S. Harder, *Eur. J. Inorg. Chem.* 2008, 1480–1486; d) J. Spielmann,
  F. Buch, S. Harder, *Angew. Chem.* 2008, *120*, 9576–9580; *Angew. Chem. Int. Ed.* 2008, *47*, 9434–9438.
- [7] S. Harder, J. Brettar, Angew. Chem. 2006, 118, 3554–3558; Angew. Chem. Int. Ed. 2006, 45, 3474–3478.
- [8] T. K. Panda, C. G. Hrib, P. G. Jones, J. Jenter, P. W. Roesky, M. Tamm, *Eur. J. Inorg. Chem.* **2008**, 4270–4279.
- [9] P. Jochmann, T. S. Dols, T. P. Spaniol, L. Perrin, L. Maron, J. Okuda, Angew. Chem. 2009, 121, 5825-5829; Angew. Chem. Int. Ed. 2009, 48, 5715-5719.
- [10] a) S. Harder, S. Müller, E. Hübner, Organometallics 2004, 23, 178-183; b) A. M. Johns, S. C. Chmely, T. P. Hanusa, Inorg. Chem. 2009, 48, 1380-1384.
- [11] J.-C. Buffet, J. P. Davin, T. P. Spaniol, J. Okuda, New J. Chem. 2011, 35, 2253–2257.
- [12] a) K. G. Caulton, M. H. Chisholm, S. R. Drake, K. Folting, J. C. Huffman, W. E. Streib, *Inorg. Chem.* **1993**, *32*, 1970–1976; b) V.-C. Arunasalam, S. R. Drake, M. B. Hursthouse, K. M. A. Malik, S. A. S. Miller, D. M. P. Mingos, *J. Chem. Soc. Dalton Trans.* **1996**, 2435–2442; c) S.-M. Ho, C.-S. Hsiao, A. Datta, C.-H. Hung, L.-C. Chang, T.-Y. Lee, J.-H. Huang, *Inorg. Chem.* **2009**, *48*, 8004–8011.
- [13] M. Ohashi, M. Konkol, I. Del Rosal, R. Poteau, L. Maron, J. Okuda, J. Am. Chem. Soc. 2008, 130, 6920-6921.
- [14] a) P. D. Prince, M. J. Bearpark, G. S. McGrady, J. W. Steed, *Dalton Trans.* 2008, 271–282; b) M. J. Bearpark, G. S. McGrady, P. D. Prince, J. W. Steed, *J. Am. Chem. Soc.* 2001, *123*, 7736– 7737; c) E. P. A. Couzijn, A. W. Ehlers, M. Schakel, K. Lammertsma, *J. Am. Chem. Soc.* 2006, *128*, 13634–13639.
- [15] a) C. Lichtenberg, P. Jochmann, T. P. Spaniol, J. Okuda, Angew. Chem. 2011, 123, 5872-5875; Angew. Chem. Int. Ed. 2011, 50, 5753-5756; b) P. J. Bailey, S. T. Liddle, C. A. Morrison, S. Parsons, Angew. Chem. 2001, 113, 4595-4598; Angew. Chem. Int. Ed. 2001, 40, 4463-4466.
- [16] a) Y. Tang, L. N. Zakharov, W. S. Kassel, A. L. Rheingold, R. A. Kemp, *Inorg. Chim. Acta* 2005, *358*, 2014–2022; b) J. F. Dunne, S. R. Neal, J. Engelkemier, A. Ellern, A. D. Sadow, *J. Am. Chem. Soc.* 2011, *133*, 16782–16785.
- [17] a) B. Becker, R. J. P. Corriu, C. Guérin, B. J. L. Henner, J. Organomet. Chem. **1989**, 369, 147–154; b) M. Itoh, K. Inoue, J.-i. Ishikawa, K. Iwata, J. Organomet. Chem. **2001**, 629, 1–6.
- [18] a) C. M. Forsyth, S. P. Nolan, T. J. Marks, Organometallics 1991, 10, 2543-2545; b) L. Rosenberg, C. W. Davis, J. Yao, J. Am. Chem. Soc. 2001, 123, 5120-5121; c) L. S. Chang, J. Y. Corey, Organometallics 1989, 8, 1885-1893; d) J. Garcia, D. J. M. Meyer, D. Guillaneux, J. J. E. Moreau, M. W. C. Man, J. Organomet. Chem. 2009, 694, 2427-2433; e) P. Boudjouk, A. B. Rajkumar, W. L. Parker, J. Chem. Soc. Chem. Commun. 1991, 245-246.
- [19] a) E. Abinet, D. Martin, S. Standfuss, H. Kulinna, T. P. Spaniol, J. Okuda, *Chem. Eur. J.* **2011**, *17*, 15014–15026; b) J.-F. Pilichowski, J.-M. Lehn, J.-P. Sauvage, J.-C. Gramain, *Tetrahedron* **1985**, *41*, 1959–1964.