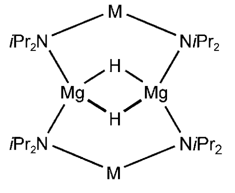
DOI: 10.1002/anie.200900878

Cluster Chemistry

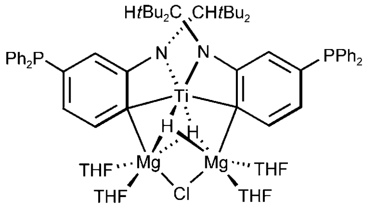
A Hydride-Rich Magnesium Cluster**

Merle Arrowsmith, Michael S. Hill, Dugald J. MacDougall, and Mary F. Mahon*

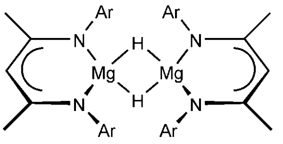
Matrix isolation studies have allowed the identification of molecular magnesium dihydride, MgH_2, as a linear species with Mg–H bonds of 1.718 Å.[1,2] This simple binary compound is more commonly encountered, however, as a typical ionic solid and in the condensed phase both tetragonal (rutile, α-MgH_2) and high-pressure orthorhombic (γ-MgH_2) modifications have been identified by X-ray and neutron diffraction experiments respectively.[3,4] Although a weight % of 7.6 % of hydrogen has recently reinvigorated interest in MgH_2 as a potential solid-state hydrogen-storage medium,[5] there are no reports of well-defined and tractable molecular magnesium hydrides with H:Mg ratios greater than 1. While a variety of heteroleptic magnesium hydride species, XMgH (X = halide, alkyl, aryl, cyclopentadienyl, alkoxo, amido) have been known for some time, and have been shown to have some use in effecting reductive transformations, their structures are incompletely defined and, most likely, poly- or oligomeric.[6] More recently, several molecular species containing Mg-(μ-H)-Mg bridges have been described. These examples are either constituents of more complex heterobimetallic species (**I**–**IV**)[7,8] or are reliant upon the presence of a sterically demanding anionic supporting ligand to enforce a reduced nuclearity (**V**).[9] The rational synthesis of **V**, achieved by treatment of a β-diketiminato magnesium butyl precursor with an excess of phenylsilane, echoed earlier reports by Michalczyk of reactions of dibutylmagnesium with an identical hydride source.[10] In this latter case, reactions in the presence of donor ligands, such as dimethoxyethane (DME) or *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), led to the precipitation of amorphous, insoluble, and pyrophoric materials, which were reasoned to exist as distributions of polymeric $[MgH_2L_x]_n$ capped by the bidentate ligand L. As the isolated hydride materials were deficient in the neutral ligand, L, it is evident that the isolation of more tractable compounds $[LMgH_2]_n$ will require a neutral supporting environment in terms of kinetic/steric constraints and σ-donor ability to the otherwise uncongested magnesium centers.



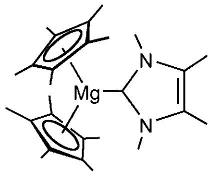
I: M = Na(C_7H_8); **II**: Na; **III**: K(C_7H_8)



IV

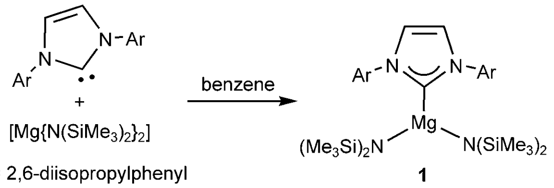


V



VI

N-heterocyclic carbenes (NHCs) typically bind as potent two-electron σ-donors and their steric demands can be easily modulated by manipulation of the steric demands of the N-bound imidazolyl organic residues.[11] Although NHCs have a growing pedigree for the stabilization of low-coordinate and/or low oxidation state p-block metal centers, their use in s-block systems is still relatively limited.[12] To date, only a small number of complexes in which magnesium is bound to a neutral NHC ligand have been reported and are limited to a handful of dialkylmagnesium and magnesocene adducts such as **VI**.[13] We have recently reported a number of NHC adducts of the homoleptic bis(trimethylsilyl)amides of the heavier alkaline-earth metals, Ca, Sr, and Ba[14] and have now found that this synthesis is readily extended to the formation of lighter magnesium analogues. Treatment of $[Mg\{N(SiMe_3)_2\}_2]$ with a single equivalent of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) in benzene provided the expected adduct $[Mg\{N(SiMe_3)_2\}_2(IPr)]$ (**1**) in high yield after crystallization from the reaction mixture [Eq. (1)].



Ar = 2,6-diisopropylphenyl

(1)

A single-crystal X-ray diffraction analysis performed upon crystals of compound **1** confirmed its three-coordinate and mononuclear formulation (Figure 1). The coordination geometry at the three-coordinate magnesium center is only distorted from trigonal planar ($\Sigma_{angles} = 360°$) by a widening of the angle between the two silyl amide ligands (N2-Mg1-N2′ 124.93(8)°), which may be ascribed to the larger steric demands of these substituents. The Mg1–C1 bond (2.276(2) Å) is at the upper limit of the range (2.194–2.279 Å) derived from reported values for Mg–NHC bond lengths,[13] perhaps reflecting the crowded nature of the magnesium coordination environment.

---

[*] M. Arrowsmith, Dr. M. S. Hill, Dr. D. J. MacDougall, Dr. M. F. Mahon
Department of Chemistry, University of Bath
Claverton Down, Bath, BA2 7AY (UK)
E-mail: m.s.hill@bath.ac.uk

[**] We thank the EPSRC for the provision of a project studentship.

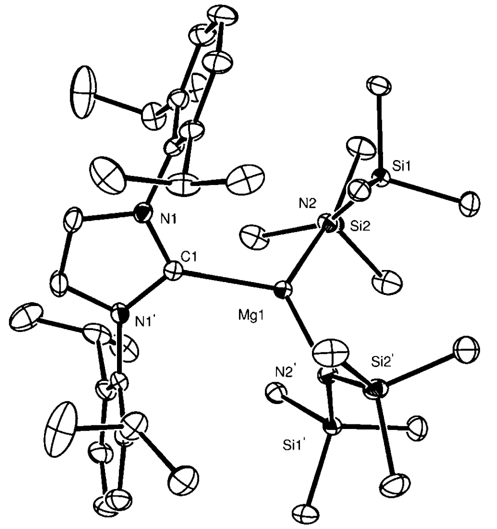


Figure 1. ORTEP plot of **1**. H atoms removed for clarity. Thermal ellipsoids set at 30% probability. Selected bond lengths [Å] and angles [°]: Mg1–C1 2.276(2), Mg1–N2 2.0295(13); C1-Mg1-N2 117.53(4), C1-Mg1-N2′ 117.53(4), N2-Mg1-N2′ 124.93(8). Symmetry transformations used to generate equivalent atoms: $1-x$, y, $-z+{}^1/_2$.

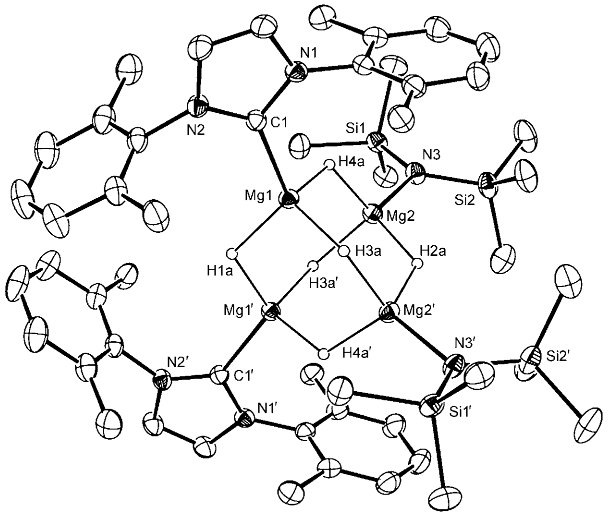


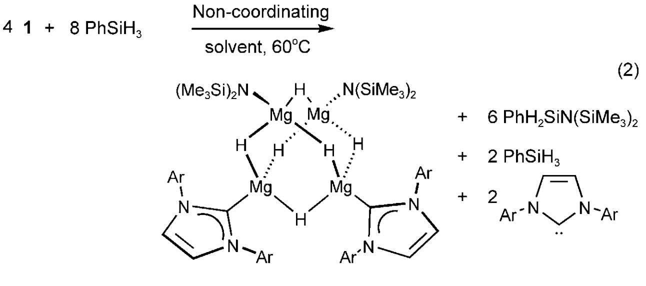
Figure 2. ORTEP plot of **2**. H atoms, apart from those associated with the Mg_4H_6 core, and isopropyl methyl groups removed for clarity. Thermal ellipsoids set at 30% probability. Selected bond lengths [Å] and angles [°]: C1–Mg1 2.2063(19), N3–Mg2 2.0049(17), Mg1–H1a 1.902(11), Mg1–H4a 1.855(13), Mg1–H3a 1.858(13), Mg2–H2a 1.881(11), Mg2–H4a 1.869(13); C1-Mg1-H1a 121.5(5), C1-Mg1-H4a 108.9(5), H1a-Mg1-H4a 103.6(7), C1-Mg1-H3a 107.3(6), H1a-Mg1-H3a 104.8(8), H4a-Mg1-H3a 110.5(9), N3-Mg2-H2a 118.0(7), N3-Mg2-H4a 116.7(5), H2a-Mg2-H4a 101.7(8). Symmetry transformations used to generate equivalent atoms: #1 $1-x$, y, $-z+{}^1/_2$; #2 $-x+1$, y, $-z+{}^1/_2$.

An NMR-scale reaction in C_6D_6 of **1** with two molar equivalents of $PhSiH_3$ revealed that a small amount of phenylsilane (<10%) had been consumed before the first point of analysis at room temperature. This change was accompanied by the appearance of a single new resonance at $\delta = 5.16$ ppm in the ^{1}H NMR spectrum, assigned to an Si-H group. After heating at 60 °C for 16 h the concentration of this new species had continued to increase until approximately 75% of the starting $PhSiH_3$ had been consumed and was associated with the emergence of two new resonances at $\delta =$ 0.21 and 0.34 ppm in a 3:1 ratio by integration and assigned to silylmethyl groups. It was apparent that 50% of the IPr ligand was present as the free uncomplexed carbene while the remainder was in a single environment at room temperature with resonances subjected to upfield shifts reminiscent of the data of compound **1**. In contrast to the completely homogeneous nature of this reaction solution, a further NMR-scale experiment between [(Mg{N(SiMe$_3$)$_2$}$_2$)] and two molar equivalents of $PhSiH_3$ deposited a gelatinous precipitate, presumed to be polymeric MgH_2, in a matter of minutes. The sole soluble product from this reaction was $PhH_2SiN(SiMe_3)_2$, which provided ^{1}H NMR chemical shift data identical to the silane product observed in the initial reaction of **1** and $PhSiH_3$.

This reaction between [(Mg{N(SiMe$_3$)$_2$}$_2$)] and two molar equivalents of $PhSiH_3$ confirmed that the presence of the IPr ligand was crucial to maintain the homogeneity of the reaction solution. A subsequent preparative scale reaction between **1** and $PhSiH_3$ provided a moderate yield of a new colorless complex, **2**. Recrystallization of this material from toluene provided crystals suitable for an X-ray diffraction analysis (Figure 2). Compound **2** is a magnesium hydride cluster [Mg$_4$H$_6$(IPr)$_2${N(SiMe$_3$)$_2$}$_2$] and comprises a Mg_4H_6 adamantane-like core constructed about four pseudotetrahedral magnesium centers and six μ-H bridging interactions. The asymmetric unit is composed of half of a molecule of the magnesium cluster plus half of a molecule of toluene. The hydrides bridging the tetrahedral Mg_4 core were located and refined. H1a and H2a were found to be located on a two-fold rotation axis intrinsic in the space group symmetry and the Mg--H distances were restrained to being similar in the final least-squares cycle. The cluster displays crystallographically imposed C_{2v} symmetry and may be rationalized as a combination of two [MgH$_2$(IPr)] (that is {Mg1/Mg1′}) and two [MgH{N(SiMe$_3$)$_2$}] (that is, {Mg2/Mg2′}) units. Although they must be treated with some caution, all the Mg–H distances (range: 1.858(13)–1.902(11) Å) in **2** are at the short end of the range established for the less hydride-rich compounds **I**–**V** (1.88(2) Å in (**I**) to 2.045(15) Å in (**IV**)).[7–9] It is also notable that the Mg(μ-H)Mg interactions between the Mg1 centers that are coordinated by the strongly σ-donating IPr ligands provide the longest Mg–H distances in the cluster. The resultant Mg···Mg separations in **2** (3.1764(12)–3.3905(12) Å) are considerably longer than those either within the Mg–Mg bonded compounds of Jones and Stasch (2.8508(12), 2.8457(8) Å) or the hydride-bridged dimer **V** (2.890(2) Å) and do not imply any level of Mg–Mg bonding within the oligomeric unit.[15,9]

NMR spectroscopic analysis of isolated crystals of compound **2** in [D$_8$]toluene suggested that the integrity of the cluster was retained in this non-coordinating solvent. In the ^{1}H nOesy spectrum at 298 K a nuclear Overhauser effect was observed between the silylmethyl resonances and the isopropyl and aryl resonances of the IPr ligand indicating that both sets of resonances arose from the same molecular entity. The hydride resonance at this temperature appeared as a broad feature at approximately $\delta = 2.52$ ppm and was partly obscured by the isopropyl septet signal arising from the coordinated IPr ligand. This chemical shift value is, therefore, similar to, but to slightly higher field than those observed in derivatives containing a Mg(μ-H)Mg interaction (e.g. **III**; $\delta = 3.78$: **V**; $\delta = 4.03$ ppm). Although the remaining IPr and silylmethyl resonances were somewhat broad at 298 K, the resonances in the ^{1}H spectra of compound **2** sharpened considerably and underwent a series of decoalescence events down to the low temperature limit of the experiment (218 K). While the hydride resonances were still not be unambiguously resolved at this temperature, the isopropyl methyl doublets and methine septets, which could be correlated by a 2D (COSY) experiment, were each split into a complex series of at least eight separate signals of varying intensity. Although the same low-temperature ^{1}H spectra demonstrated that the silylmethyl resonances were split into a pair of signals of similar intensity, on the basis of the variation in the methyl doublet integral ratios, we postulate that this behavior is suggestive of the presence of several energetically similar conformational isomers rather than a "locking" of a specific conformation of the cluster species on the NMR time scale.

In summary, we have prepared a magnesium hydride species, **2**, which displays a higher magnesium to hydride ratio, 1:1.5, than any complex described to date. The formation of this species is remarkably specific and the reaction may be realistically represented by the stoichiometry illustrated in Equation (2). Complex **2** is robust in solution and has, thus far, proved resistant to further Si-H/Mg{N(SiMe$_3$)$_2$} metathesis to form a molecular dihydride species. This goal may require the application of more potent sources of the hydride ligand or variations of the supporting NHC architecture.



Experimental Section

All reactions and manipulations were performed under rigorous exclusion of water and oxygen, either on a double manifold vacuum line or an Ar-filled drybox operating at less than 1 ppm O$_2$. All reagents and solvents were purified by standard procedures.

1: IPr (195 mg, 0.50 mmol) and [Mg{N(SiMe$_3$)$_2$}$_2$] (175 mg, 0.50 mmol) were dissolved in benzene (5 mL). Concentration and slow cooling of a hot saturated solution resulted in the formation of compound **1** as colorless crystals, 250 mg, 73 %. M.p. discolors 208 °C, melts 214 °C: Elemental analysis (%) for $C_{39}H_{72}MgN_4Si_4$: calcd: C 63.85, H 9.89, N 7.64; found C 63.79, H 9.85, N 7.63; ^{1}H NMR (300 MHz, C_6D_6, 298 K): $\delta = 0.20$ (s, 36 H, SiCH_3), 0.88 (d, 12 H, CH(CH_3)$_2$, $^{2}J_{HH} = 6.9$ Hz), 1.43 (d, 12 H, CH(CH_3)$_2$, $^{2}J_{HH} = 6.6$ Hz), 2.82 (sept, 4 H, CH(CH$_3$)$_2$), 6.33 (s, 2 H, CH), 7.13–7.25 ppm (m, 6 H, *m*, *p*-C$_6$$H_3$). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 298 K): $\delta = 7.4$ (SiCH$_3$), 23.9 (CH(CH$_3$)$_2$), 26.5 (CH(CH$_3$)$_2$), 29.2 (CH(CH$_3$)$_2$), 125.4 (*m*-C_6H$_3$), 126.2 (*p*-C_6H$_3$), 131.3 (*o*-C_6H$_3$), 137. 0 (*i*-C_6H$_3$), 146.0 ppm (CH), C^{1} NHC carbon not observed.

2: Compound **1** (0.72 g, 0.98 mmol) and PhSiH$_3$ (0.21 g, 1.96 mmol) were combined in hexane (30 mL) and heated to 60 °C for 3 h. The solution was allowed to cool and filtered to remove a small quantity of precipitated colorless material. Concentration to incipient crystallization and storage at −30 °C produced analytically pure compound **2** as a colorless crystalline material (0.21 g, 66 %). Recrystallization of a small sample from toluene provided crystals suitable for an X-ray diffraction analysis. M.p. discolors 150 °C, melts 158 °C (dec): Elemental analysis (%) for $C_{66}H_{114}Mg_4N_6Si_4$: calcd: C 65.99, H 9.57, N 7.00; found C 65.97, H 9.41, N 7.02; ^{1}H NMR (300 MHz, C_6D_6, 298 K): $\delta = 0.34$ (s, 36 H, SiCH_3), 1.01 (d, 24 H, CH(CH_3)$_2$, $^{2}J_{HH} = 6.9$ Hz), 1.27 (d, 12 H, CH(CH_3)$_2$, $^{2}J_{HH} = 6.7$ Hz), 2.45 (sept, 4 H, CH(CH$_3$)$_2$), 2.52 (br. s, 6 H, MgH) 6.35 (s, 4 H, CH), 7.14–7.28 (m, 12 H, *m*, *p*-C$_6$$H_3$). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 298 K): $\delta = 6.9$ (SiCH$_3$), 24.7 (CH(CH$_3$)$_2$), 25.3 (CH(CH$_3$)$_2$), 29.3 (CH(CH$_3$)$_2$), 124.9 (*m*-C_6H$_3$), 131.6. (*p*-C_6H$_3$), 134.9 (*o*-C_6H$_3$), 137. 2 (*i*-C_6H$_3$), 145.7 (CH), 184.7 (Mg-C_{NHC}).

Crystallographic data for **1** at 150(2) K: ($C_{39}H_{72}MgN_4Si_4$, $M_r = 733.68$) crystal dimensions $0.20 \times 0.10 \times 0.10$ mm^3: monoclinic, space group $C2/c$, $a = 21.0644(3)$, $b = 11.0175(2)$, $c = 22.1341(3)$ Å, $\beta = 114.339(1)°$, $V = 4680.27(13)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.041$ g cm^{-3}, $\mu = 0.169$ mm^{-1}. Of 41227 reflections measured ($3.51 < \theta < 27.47°$), 5361 were independent ($R_{int} = 0.0664$), $R1 = 0.045$, $wR2 = 0.1045$ [for 4158 reflections with $I > 2\sigma(I)$], $R1 = 0.0644$, $wR2 = 0.1174$ (all data) GOF = 1.035. The asymmetric unit is composed of half of a molecule, the central magnesium and the carbene carbon both located on a crystallographic 2-fold rotation axis. Crystallographic data for **2** at 150(2) K: ($C_{73}H_{121}Mg_4N_6Si_4$, $M_r = 1292.36$) crystal dimensions $0.40 \times 0.40 \times 0.20$ mm^3: orthorhombic, space group $Pbcn$, $a = 20.0590(2)$, $b = 22.6650(2)$, $c = 18.6250(2)$ Å, $V = 8467.62(14)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.014$ g cm^{-3}, $\mu = 0.139$ mm^{-1}. Of 139073 reflections measured ($3.55 < \theta < 27.48°$), 9657 were independent ($R_{int} = 0.1322$), $R1 = 0.0524$, $wR2 = 0.1287$ [for 7120 reflections with $I > 2\sigma(I)$], $R1 = 0.0783$, $wR2 = 0.1556$ (all data) GOF = 1.112. In **2**, the asymmetric unit comprises half of a molecule of the magnesium cluster plus half of a molecule of toluene. The hydrides bridging the magnesium core were located and refined (H1a and H2a were found to be located on a 2-fold rotation axis intrinsic to the space group symmetry). Mg-H distances were restrained to being similar in the final least squares. The toluene fragment was also found to be proximate to a 2-fold rotation axis and, consequently, the methyl group attached to C(36) is disordered over two sites. The arene hydrogen sharing the disorder with this methyl could not be reliably located and, hence, was omitted. Residual electron density in this model is centered on the solvent region, so there is likely to be additional disorder present. Planarity restraints were included for this fragment, as were distance restraints. CCDC 720135 (**1**) and 720136 (**2**) 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: February 13, 2009

Keywords: amides · carbene ligands · cluster compounds · hydrides · magnesium

---

[1] For a comprehensive review of main-group hydride chemistry, see, S. Aldridge, A. J. Downs, *Chem. Rev.* **2001**, *101*, 3305.

[2] a) J. A. Pople, B. T. Luke, M. J. Frisch, J. S. Binkely, *J. Chem. Phys.* **1985**, *89*, 2198; b) T. J. Tague, Jr., L. Andrews, *J. Phys. Chem.* **1994**, *98*, 8611.

[3] W. H. Zachariasen, C. E. Holley, Jr., J. F. Stamper, Jr., *Acta Crystallogr. A* **1963**, *16*, 352.

[4] M. Bortz, B. Bertheville, G. Böttger, K. Yvon, *J. Alloys Compd.* **1999**, *290*, L8.

[5] a) F. Schüth, B. Bogdanović, M. Felderhoff, *Chem. Commun.* **2004**, 2249; b) S. A. Shevlin, Z. X. Guo, *Chem. Soc. Rev.* **2008**, *38*, 211; c) J.-G. Roqufere, J.-L. Bobet, *Z. Naturforsch. B* **2007**, *62*, 907; d) M. Pozzo, D. Alfè, *Phys. Rev. B* **2008**, *77*, 104103.

[6] a) R. Bauer, *Z. Naturforsch. B* **1962**, *17*, 2.1; b) R. G. Beach, E. C. Ashby, *Inorg. Chem.* **1971**, *10*, 906; c) E. C. Ashby, A. B. Goel, *J. Chem. Soc. Chem. Commun.* **1977**, 169; d) E. C. Ashby, A. B. Goel, *Inorg. Chem.* **1977**, *16*, 1441; e) E. C. Ashby, A. B. Goel, *Inorg. Chem.* **1977**, *16*, 1863; f) E. C. Ashby, A. B. Goel, *Inorg. Chem.* **1977**, *16*, 2941; g) E. C. Ashby, A. B. Goel, *J. Org. Chem.* **1977**, *42*, 3480; h) E. C. Ashby, A. B. Goel, J. J. Lin, *Tetrahedron Lett.* **1977**, *18*, 3133; i) E. C. Ashby, A. B. Goel, *Inorg. Chem.* **1979**, *18*, 1306; j) A. B. Goel, E. C. Ashby, *J. Organomet. Chem.* **1981**, *214*, C1.

[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; 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; c) D. V. Graham, A. R. Kennedy, R. E. Mulvey, C. T. O'Hara, *Acta Crystallogr. Sect. C* **2006**, *62*, m366.

[8] Q. F. Mokuolu, P. A. Duckmanton, A. J. Blake, C. Wilson, J. B. Love, *Organometallics* **2003**, *22*, 4387.

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

[10] M. J. Michalczyk, *Organometallics* **1992**, *11*, 2307.

[11] D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39.

[12] Selected recent examples from *p*-block chemistry; a) Y. Wang, B. Quillian, P. R. Wei, C. S. Wannere, Y. Xie, R. B. King, H. F. Shaefer, P. v. R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2007**, *129*, 12412; b) Y. Wang, B. Quillian, P. R. Wei, Y. Xie, R. B. King, H. F. Shaefer, P. v. R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2008**, *130*, 14970; c) Y. Wang, B. Quillian, P. R. Wei, Y. Xie, R. B. King, H. F. Schaefer, P. v. R. Schleyer, G. H. Robinson, *Science* **2008**, *321*, 1069.

[13] a) A. J. Arduengo, H. V. Rasika-Dias, R. Davidson, R. L. Harlow, *J. Organomet. Chem.* **1993**, *462*, 13; b) A. J. Arduengo, F. Davidson, R. Krafczyk, W. J. Marshall, M. Tamm, *Organometallics* **1998**, *17*, 3375; c) H. Schumann, J. Gottriedsen, M. Glanz, S. Dechert, J. Demtschuk, *J. Organomet. Chem.* **2001**, *617*, 588.

[14] A. G. M. Barrett, M. R. Crimmin, M. S. Hill, G. Kociok-Köhn, D. J. MacDougall, M. F. Mahon, P. A. Procopiou, *Organometallics* **2008**, *27*, 3939.

[15] S. P. Green, C. Jones, A. Stasch, *Science* **2007**, *318*, 1754.