

Synthesis, Structure and Theoretical Studies of the Hydrido Inverse Crown $[\text{K}_2\text{Mg}_2(\text{NiPr}_2)_4(\mu\text{-H})_2(\text{toluene})_2]$: a Rare Example of a Molecular Magnesium Hydride with a $\text{Mg}(\mu\text{-H})_2\text{-Mg}$ Double Bridge

Prokopis C. Andrikopoulos,^[a] David R. Armstrong,^[a] Alan R. Kennedy,^[a] Robert E. Mulvey,^[a] Charles T. O'Hara,^{*[a]} and René B. Rowlings^[a]

Dedicated to the memory of Ron Snaith who for DRA and REM was an inspirational teacher, a pre-eminent researcher and a revered colleague and friend

Keywords: Potassium / Magnesium / N ligands / Hydride ligands / Density functional calculations

Reaction of benzylpotassium, *n,s*-dibutylmagnesium and diisopropylamine in boiling toluene produces a rare example of a molecular magnesium hydride with a $\text{Mg}(\mu\text{-H})_2\text{-Mg}$ double bridge, in $[\text{K}_2\text{Mg}_2(\text{NiPr}_2)_4(\mu\text{-H})_2(\text{toluene})_2]$ (**1**). In an effort to rationalise the formation of **1**, a series of DFT calculations were performed. This report of **1** establishes the first isostructural pair of Na and K complexes solvated by toluene to be reported in the Cambridge Crystallographic Database.

In comparison with its previously reported Na analogue, **2**, the metal-arene centroid distances are considerably shorter (by 0.159 Å) in the new complex reported here. It was found that a hydrocarbon solution of **1** is capable of reducing benzophenone to benzhydrol in moderate yields (74%).

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2003)

Introduction

Main group metal hydrides, in particular those containing aluminium are widely utilised by the synthetic chemist as highly efficient reducing agents.^[1] Commercially available reagents such as lithium aluminium hydride, lithium tri-*tert*-butoxyaluminumhydride and Red-Al® [sodium bis(2-methoxyethoxy)aluminium hydride] can effect the reduction of many polarised organic functional groups easily and efficiently. The structural chemistry of molecules containing an Al–H–Al linkage is also well developed.^[2] However, unlike their aluminium counterparts, magnesium hydrides have thus far not been the subject of intensive research. To the best of our knowledge, only one genuine molecular magnesium hydride, which contains a $\text{Mg}(\mu\text{-H})_2\text{-Mg}$ bridge, has been prepared and crystallographically characterised^[3] (see below). Synthetically, it has been shown that magnesium hydride-containing species (such as RMgH , ROMgH or R_2NMgH ; where $\text{R} = \text{Me}$, Et , $i\text{Pr}$ or C_5H_5 for the alkylmagnesium hydrides and $\text{R} = \text{Me}$, $i\text{Pr}$, $t\text{Bu}$, $t\text{BuCH}_2$, PhCH_2CH_2 , Ph , Ph_3C , $2,6\text{-Me}_2\text{C}_6\text{H}_3$, $2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$ or $2,6\text{-}t\text{Bu}_2\text{-4-MeC}_6\text{H}_2$ for the alkoxy or aryloxy-magnesium hydrides and $\text{R} = \text{Et}$, $i\text{Pr}$, $n\text{Bu}$ or Ph for the dialkyl or diarylamino-magnesium hydrides) are useful in effecting reductive transformations.^[4] Unsolvated magnesium

bis(diisopropylamide)^[5] is also capable of converting aldehydes/ketones to alcohols and converting nitro compounds to amines via hydride transfer from the carbon positioned beta to the magnesium centre.

Herein we report the synthesis and structural analysis of $[\text{K}_2\text{Mg}_2(\text{NiPr}_2)_4(\mu\text{-H})_2(\text{toluene})_2]$ (**1**). Complex **1** represents the first structurally characterised potassium-containing heterobimetallic diisopropylamide and only the second molecular magnesium hydrido species which contains an $\text{Mg}(\mu\text{-H})_2\text{-Mg}$ bridge, the first being the Na analogue of **1**, $[\text{Na}_2\text{Mg}_2(\text{NiPr}_2)_4(\mu\text{-H})_2(\text{toluene})_2]$ (**2**). This complex was reported in a recent communication.^[3] Here we provide further details of the structure of **2**. Complex **1** is only the second example of a crystallographically characterised potassium diisopropylamide, the first example being the simple dimeric, TMEDA solvate $[(\text{KNiPr}_2\cdot\text{TMEDA})_2]$ (**3**).^[6] Recent work in our laboratory has focused on the synergistic chemistry of combining an alkali metal amide with its magnesium (or zinc) bis(amide) analogue. The major consequence of these studies thus far has been the development of a series of heterobimetallic macrocyclic amide complexes that have become known collectively as “inverse crowns.”^[7] A subset of the inverse crowns (IC) are the inverse crown ethers (ICE). This non-precise nomenclature was chosen because the ICE complexes show an inverse topological relationship to conventional crown ether complexes — the Lewis acidic metal sites and Lewis basic oxygen centres are mutually interchanged. IC complexes are distinguished

^[a] Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, G1 1XL, UK

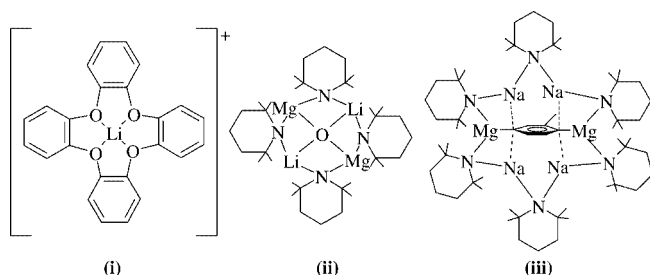


Figure 1. Examples of a conventional crown ether complex (i), an inverse crown ether (ii)^[8] and an "oxygen-free" inverse crown complex (iii)^[9]

from ICE complexes by the fact that the former do not contain any oxygen-containing anions (Figure 1).

As well as forming complexes with aesthetically pleasing crystal structures, a special chemistry that is otherwise irreproducible has been uncovered using these synergistic metal amide bases. Employing "NaMg(NiPr₂)₃", the tris(amido) species prepared from the in situ reaction of BuNa, Bu₂Mg and HNiPr₂ in a 1:1:3 molar ratio, the unprecedented 1,1',3,3'-tetrametallation of ferrocene was accomplished.^[10] Returning to **1**, this molecule is the most recent addition to the inverse crown family. Although essentially isostructural with its sodium analogue, in the potassium variant, the alkali metal exhibits stronger coordination to the arene molecule, indicated by the fact that the mean arene-M (where M = Na or K) length is *shorter* for the K analogue. Alkali metal- π interactions have recently been the subject of considerable research.^[11] The importance of these interactions has been realised in zeolite-supported processes,^[12] in the interaction of alkali metal cations with aromatic side chains of proteins,^[13] and in the selectivity of superbases,^[14] via the coordination of an arene molecule to a group 1 metal centre.

Results and Discussion

Preparation and Spectra

Complex **1** was prepared by heating a 1:1:3 mixture of benzylpotassium, *n,s*-dibutylmagnesium and diisopropylamine, in a toluene/heptane medium. This synthesis marks a significant departure from that of most of the other members of the inverse crown family prepared to date^[15] — a *MnBu* (where M = Li, Na or K) reagent has not been utilised in the preparation. The synthesis of **1** was initially attempted using *n*-butylpotassium; however, on the addition of amine to the heterobimetallic alkyl mixture, a significant quantity of an insoluble, black solid was obtained. The formation of this impurity can be attributed to the fact that *n*-butylpotassium is not thermally stable being readily susceptible to β -hydride elimination. Ironically, a similar decomposition pathway is vital to the formation of **1** (vide infra), but at this early stage in the synthetic procedure, it appears to be highly detrimental. On changing the potassi-

ating reagent from butyl- to benzyl- (i.e. ruling out β -hydride elimination as a potential decomposition pathway) the reaction proceeded in a seemingly more controlled manner, resulting in the observation of a discernible colour change without the precipitation of an undesired solid by-product. Although less reactive than its butyl counterpart, the activity of benzylpotassium is adequate for our needs, and this easily prepared reagent will undoubtedly be utilised by our group in various reactions in the future. Interestingly, if the heterobimetallic amide mixture is not subjected to intense heating, complex **1** is not formed — instead the unsolvated tris(amido) species KMg(NiPr₂)₃ is produced. Details of the preparation and structural analysis of this complex and two other related compounds can be found in the preceding paper in this issue.^[16]

The by-product of amine deprotonation by benzylpotassium is toluene and since the bulk of the reaction medium is composed of this solvent, the by-product does not have a disadvantageous effect on the reaction. Indeed, toluene is actually incorporated into the molecular structure of **1**. The shielding of the potassium and magnesium centres by the isopropyl groups and the former by toluene molecules results in the entire molecule being highly lipophilic.^[17] As a consequence the complex is highly hydrocarbon soluble, explaining why the isolated yield of the crystals of **1** was relatively low.

Table 1 contains the ¹H NMR spectroscopic data for **1** along with those of **2** for comparison. The chemical shifts for the potassium analogue **1** are systematically at a higher frequency than those for the sodium variant **2**, although the differences are rather small. The hydride shift in both complexes is similar indicating that changing the alkali metal has little effect on the Mg–H–Mg bridge. This supports our interpretation that there is essentially no K–H bonding in **1** (see below). Unfortunately, the relative chemical shifts of the complexed toluene molecules in **1** and **2** cannot be directly compared. For **1** the acquired spectrum in C₆D₆ clearly shows that the correct stoichiometric amount of toluene is present, consistent with that in the crystal structure; however, for **2** in the same solvent virtually no toluene can be observed, meaning that the vast majority of the toluene is lost on isolation. When **2** is dissolved in C₆D₅CD₃, two distinct methyl resonances are observed. These are attributed to uncomplexed toluene (δ = 2.09 ppm) and toluene which has been incorporated into the structure of **1** (δ = 2.11 ppm).

Table 1. ¹H NMR spectroscopic data for **1** and **2**; spectra acquired at 400.13 MHz in [D₆]benzene

Fragment	Chemical shift for 1	Chemical shift for 2
(CH ₃) ₂ CH	1.29	1.22
(CH ₃) ₂ CH	3.35	3.19
Mg–H–Mg	3.78	3.76
CH ₃ –Ph	2.11	2.11 (in C ₆ D ₅ CD ₃)

X-ray Crystallography

The molecular structure of **1** (Figure 2) is essentially isostructural with its sodium analogue **2**. Listed in Table 2 are the key structural dimensions of **1**, alongside those of **2** for comparison.

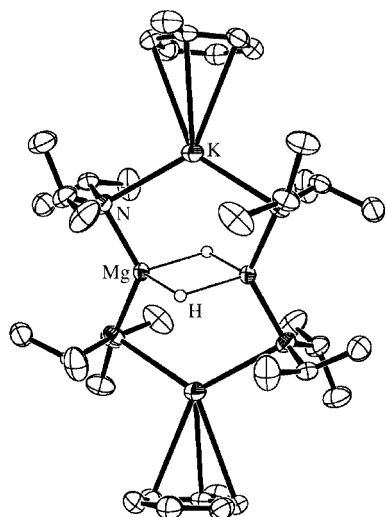


Figure 2. Molecular structure of **1**

Table 2. Key structural dimensions of **1** and **2**

Selected bonds and bond angles	Bond lengths (Å) and bond angles (°)	
	M = K (1)	M = Na (2)
M1–N1	2.7754(16)	2.4807(18)
Mg1–N1	2.0595(15)	2.0651(18)
M···H	2.96(3)	2.68(3)
Mg1–H1	1.94(2)	1.89(2)
Mg···Mg	2.9437(14)	2.8921(19)
M- <i>ipso</i> -C	3.107(3)	3.157(4)
M- <i>ortho</i> -C	3.1840(19)	3.275(3)
M- <i>meta</i> -C	3.339(2)	3.531(3)
M- <i>para</i> -C	3.422(3)	3.663(4)
M-centroid	2.955	3.114
N–M–N	119.55(6)	132.08(10)
N–Mg–N	126.55(9)	133.16(11)
Mg–H–Mg	98.7(14)	100(2)

The eight-membered metal-amide ring of **1** is chair-shaped. As for **2**, the N–Mg–N···N–Mg–N “chair-seat” is strictly planar, whilst the “head-” and “foot-rest” positions (signified by N–K–N in **1**) are tilted at an angle of 154.70(11)° compared to 153.5(2)° in **2** (Figure 3). At this juncture it is important to mention that the bridging hydride ions were independently refined. The Mg–H bond length in **1** is the same within experimental error as that in **2**. These dimensions resemble those of the Mg–H bonds present in a selection of other heterobimetallic hydride complexes: [(C₅Me₅)₂Ti(μ-H)₂]₂Mg,^[18] (mean, 1.88 Å); [(C₅HMe₄)₂Ti(μ-H)₂Mg(THF)(μ-Cl)]₂,^[19] (mean, 1.91 Å); and [(Me₂Si(C₅Me₄)₂)Zr{η²-C₂H₄}H)₂Mg],^[20] (mean, 1.82 Å). The magnesium atoms in **1** are forced into a highly

distorted tetrahedral coordination environment [the angles around the magnesium centres range from 104.1(9) to 126.55(9)°; mean, 115.57°].

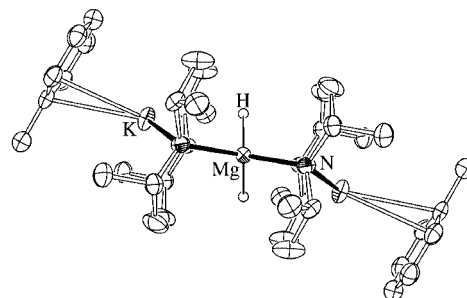


Figure 3. Alternative view of the molecular structure of **1** highlighting the planar “seat” and tilted “head-” and “foot-rest” arrangements

The closest K···H contact in **1** is 2.96(3) Å. This value can be compared with those in [K(*fac*-RuH₃{Cy₂P(CH₂)₄PCy₂}{CO})KBHsBu₃],^[17] [mean, 2.63 Å; range, 2.44(6)–2.82(5) Å], and in [(C₅Me₅)Sm(μ-H)₂]₆{(μ-H)K(THF)₂}]₃,^[21] [2.58(4) and 2.89(7) Å]. Unlike **1**, these complexes exhibit both short and long K···H contacts. The short contacts are significantly shorter than those found in **1**; however, the longer contacts, especially those in the latter complex, are similar to those in **1**. Therefore it appears that the K···H contacts in **1** appear to be too long to be considered significant.

The K–N bond length in **1** [2.7754(16) Å] is of the same order as those in the aforementioned TMEDA solvate **3** (mean, 2.7715 Å). The K centres in each form two bonds to diisopropylamido bridges, therefore it can be assumed that the TMEDA chelation and toluene π-interactions stabilise the respective molecules to a similar extent. To elaborate, the K coordination sphere in **1** is completed by an η³ (*ipso* and two equivalent *ortho* C atoms) π-interaction to a toluene molecule [bond lengths: K–C_{*ipso*}, 3.107(3) Å; K–C_{*ortho*}, 3.1840(19) Å; all other K···C separations are 3.339(2) Å or longer]. There are no agostic bonds evident in the molecule, presumably as a consequence of the strong K-arene interactions which are present. Arguably the most interesting feature of the dimensions is that the K–C_{*ipso*} bond lengths are approximately 0.05 Å shorter than the corresponding Na–C_{*ipso*} bonds in **2**. Also, the K–C_{*ortho*} bonds are approximately 0.09 Å shorter than their Na counterparts in **2**, seemingly contrary to the fact that the ionic radius of K (1.52 Å) is larger than that of Na (1.16 Å).^[22] These short metal-carbon contacts may help to explain some anomalies in the chemical analysis of **1** and **2**. Firstly, the elemental analysis results for **2** were found to be extremely variable — this was attributed to the rapid loss of toluene upon isolation of the inverse crown. In contrast, the elemental analysis results for **1** were reproducible and accurate, possibly as a reflection of the stronger complexation of the toluene to the larger alkali metal. Secondly, the ¹H NMR spectroscopic studies of **1** and **2** in C₆D₆ seem to confirm this assertion, namely that the spectra indicate

that for the sodium analogue **2**, there is much less toluene present than expected in comparison from the stoichiometry in the crystal structure, whereas for **1**, the spectrum indicates that no toluene had been lost during the isolation procedure.

To determine whether or not this apparently surprising anomaly in the M-arene distances has been observed previously, a search of the Cambridge Crystallographic Database^[23] was conducted. This search uncovered no examples of an isostructural pair of Na and K toluene solvated species that could be used as a direct comparison to **1** and **2**. However, it revealed five complexes^[3,24] that contain a sodium atom solvated by a neutral toluene molecule — as opposed to a benzyl fragment — and there are fourteen examples^[11c,24a,25] of complexes that contain a potassium atom solvated by a toluene molecule. Examples of such Na-toluene(centroid) distances found in the search are 2.664^[24a] and 2.746 Å^[24b] for the hexameric thiolate $[(\text{NaSSiPh}_3)_6 \cdot (\text{toluene})_2]$ and the monomeric aluminate $[\text{NaAl}(\text{SiMe}_3)_4 \cdot (\text{toluene})_2]$, respectively. These are 0.368–0.450 Å shorter than the Na-toluene(centroid) distances found for **2**. In the former complex two of the six sodium centres interact strongly with a molecule of toluene, whilst in the latter complex the Na cation is sandwiched between two arene molecules rendering it separate from its aluminate anion. The range of K-toluene(centroid) distances is 2.936^[25d]–3.128^[25f] Å. It is therefore evident that the K-toluene(centroid) distance in **1** is representative of those for the other complexes, whilst the Na-toluene(centroid) distance in **2** is much longer (and by implication weaker) than previously observed.

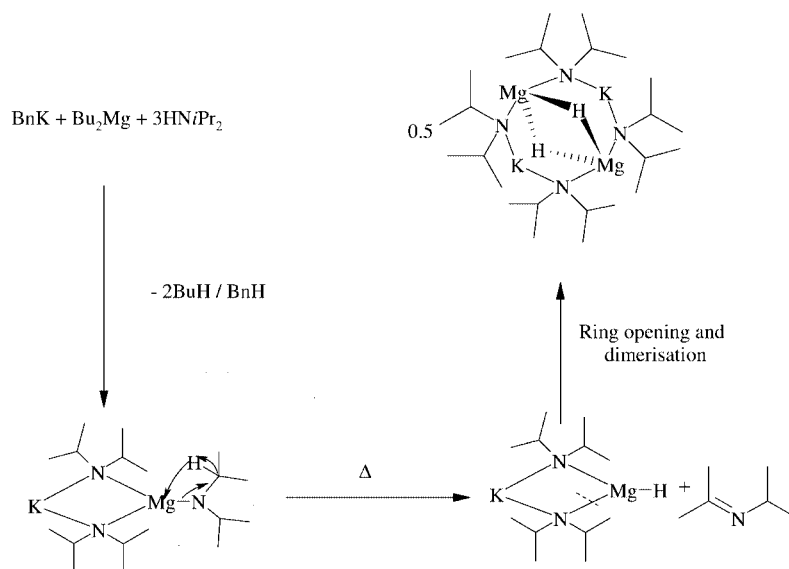
The N–K–N endocyclic bond angle in **1** [119.55(6)°] compares to that of 100.54(5)° in **3**, and the N–Na–N angles of 132.08(10)° in **2**. Therefore on changing from Na to K there is a significant narrowing of the N–M–N angle. The consequence of this narrowing, coupled with the longer

K–N bonds, creates a greater N···N separation of 4.796 Å compared to 4.534 Å in **2**, resulting in the K atom being pushed out further from the core of the structure. Concomitantly, a wider separation of the diisopropylamido groups occurs to give a larger coordination arc, which allows for a closer approach of the toluene molecule compared to that in **2**. The N–Mg–N bond angles in **1** are also less obtuse than those in **2** [126.55(9)° vs. 133.169(11)°].

Returning to the point made earlier, the formation of **1** and **2** can be explained by a β -hydride elimination process (Scheme 1). Thus, on heating a solution of the heterobimetallic tris(amido) species to reflux, it is proposed that hydride elimination could take place from an amido group to yield a hydrido intermediate and a molar equivalent of imine [$i\text{Pr-N}=\text{C}(\text{Me})_2$]. The resultant relaxation in steric crowding about the magnesium centre would then allow dimerisation to take place. To ascertain whether the process proposed is a realistic possibility, a series of ab initio MO calculations were performed. The findings of this theoretical study are discussed in the next subsection.

DFT Calculations

As described previously, complex **1** was prepared by reacting a 1:1:3 mixture of benzylpotassium and dibutylmagnesium with diisopropylamine, and then boiling in toluene. Although the reaction was carried out in situ, according to the proposed mechanism it can be thought of as proceeding in five stages. Stage I involves the formation of the monometallic amides, which is accompanied by butane and toluene generation. Stage II involves the formation of the single tris(amido) species from its two component monometallic amides. Stage III involves the β -hydride elimination from a diisopropylamide group and transfer of the hydride ion to the magnesium centre with concomitant elimination of imine. Stage IV involves ring opening and dimerisation to give the eight-membered inverse crown ring. The final stage,



Scheme 1. Proposed reaction pathway for the preparation of **1**; for clarity, the solvating toluene molecules in the final product have been omitted

stage V, involves the completion of the K coordination sphere by the docking of a toluene solvent molecule.

Relevant starting molecules, intermediates and final products (Figure 4) were initially modelled^[26] at the Hartree–Fock (HF) level, using the 6–31G(d)^[27–31] basis set and subjected to a frequency analysis. Using the HF-optimised structures, the geometry of molecules were then refined at the DFT^[32] level, using the B3LYP^[33,34] method and the 6–311G(d, p)^[35,36] basis set. The geometrical values reported here are taken exclusively from the DFT calculations while the energy values^[37] are the DFT results modified by the scaled (0.91) zero point energy correction abstracted from the corresponding HF calculation. All the molecules have C_1 symmetry except for **11** (C_{2h}) and **1a** (C_i).

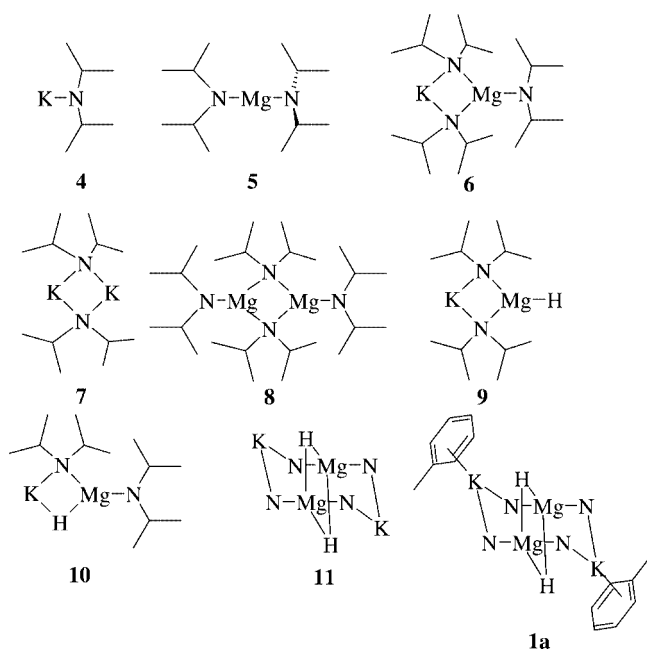
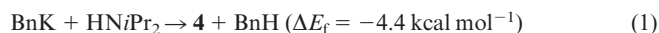


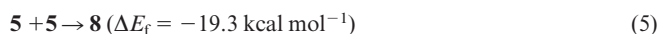
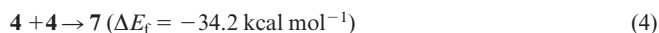
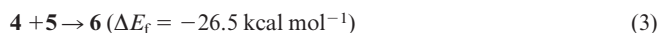
Figure 4. Schematic diagram of **1a** (modelled version of the experimental complex **1**) and other key complexes which were modelled by DFT calculations

In Stage I, KNiPr_2 (**4**) and $\text{Mg}(\text{NiPr}_2)_2$ (**5**) are assumed to be the initial products along with toluene and butane [Equations (1) and (2)]. To aid calculational simplicity, the metallo products were modelled as monomers. For the potassium amide **4** the K–N bond length was found to be 2.438 Å and the N centre was distorted trigonal planar with KNC angles of 123.0° and a CNC angle of 114°. For the magnesium amide **5** the Mg–N bond length is 1.935 Å, whilst the diisopropylamide ligands lie essentially perpendicular to each other. The N–Mg–N bond angle is near-perfect linear (179.6°). The combined calculated energy for the formation of the monometallic amides from the monomeric alkyl reagents was found to be $-44.0 \text{ kcal mol}^{-1}$. The formation of **4** is a much less exothermic process than the formation of **5**. This can be partially attributed to the fact that for the formation of **4**, only one new metal–N bond is

being formed whereas for **5**, two new metal–N bonds are formed. However, even if the energy of formation value for the latter process [Equation (2)] is halved, to account for the formation of only one new metal–N bond, the energy derived from the monoamination of Bu_2Mg ($19.8 \text{ kcal mol}^{-1}$) is significantly higher than for the amination of BnK ($4.4 \text{ kcal mol}^{-1}$). Intuitively, it would be expected that an alkylpotassium reagent would react more exothermally than an alkylmagnesium; however, in the case of the BnK model, the K centre is stabilised by coordination to the π -system of the benzyl fragment.

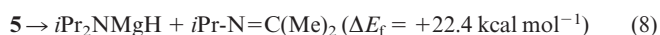
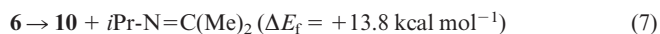
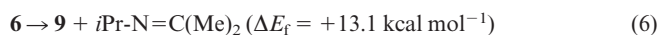


In Stage II, the mixed metal tris(amido) species **6** is formed [Equation (3)]. Largely as a consequence of forming two new (one K–N and one Mg–N) bonds, **6** was calculated to be $26.5 \text{ kcal mol}^{-1}$ more stable than its monometallic components. The optimised structure indicates asymmetric K–N bonds (2.690 and 2.737 Å) whilst the Mg–N_{bridging} bonds are more uniform in length (2.097 and 2.100 Å). As expected from coordination number considerations, the Mg–N_{terminal} bond length is shorter and calculated to be 2.000 Å. A general elongation of approximately 0.2 Å is observed in all of the M–N_{bridging} bonds in comparison with the terminal ones in the respective monometallic species. Another possibility at this stage would be the formation of the monometallic dimers **7** and **8** [Equation (4) and (5) respectively]. The energies for the formation of **7** and **8** are $-34.2 \text{ kcal mol}^{-1}$ and $-19.3 \text{ kcal mol}^{-1}$ respectively. The energy of formation of **6** is intermediate between these two values, hence either outcome could be considered as a viable possibility.

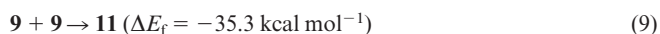


In Stage III, a hydride anion is transferred from a β -carbon of a diisopropylamide unit to the magnesium centre with the elimination of the imine $\text{iPr-N}=\text{C}(\text{Me})_2$, which, as previously noted, was detected in the experimental study. Two possible pathways for this elimination have been investigated, one where the hydride elimination occurs via a terminal amide group, giving **9** [Equation (6)], and one where the hydride elimination occurs via a bridging amide group, giving **10** [Equation (7)]. In an effort to determine which pathway hydride transfer favours, the optimised geometries of both intermediates were calculated. Since a C–H and a Mg–N bond are broken while a Mg–H and a C–N bond are formed, it would be expected that the reaction would be endothermic. This was indeed found to be the case [this

is in agreement with the experimental work, as **1** can only be prepared if the tris(amido) intermediate **6** is heated strongly] with the formation of **9** having a calculated energy of +13.1 kcal mol⁻¹, while the corresponding value for **10** is +13.8 kcal mol⁻¹ (i.e. +0.7 kcal mol⁻¹ higher in energy). Hence, hydride transfer is most likely to occur via the terminal amide. As a further comparison, it was observed that the β -hydride elimination reaction from the terminal amide of magnesium bis(diisopropylamide) (**5**) — a known experimentally observed process^[5] [Equation (8)] — was found to be considerably higher in energy (+22.4 kcal mol⁻¹).^[38] Therefore it appears that on synergistically combining the two metal amides, β -hydride elimination occurs more readily for either **9** or **10** than for when the diisopropylamide moiety resides on the Mg centre in the monometallic Mg(NiPr₂)₂. Intermediate **9** has a greater degree of symmetry than **6**, due to the absence of the terminal, sterically demanding diisopropylamido group. Focusing on the planar, four-membered [Mg-(μ -N)₂-K] ring in **9**, the Mg–N bonds span 2.087 Å, whilst the K–N bond lengths are symmetrical (unlike those previously mentioned for **6**) and have a length of 2.714 Å. The former bonds are slightly shorter, whilst the latter are longer than the calculated values in **6** due to the presence of the terminal Mg–H bond (length, 1.743 Å).



In Stage IV, it has been assumed that two equivalents of **9** (since the formation of **9** was slightly preferred over **10**) combine to produce the dimeric inverse crown **11** [Equation (9)]. The calculated energy of dimerisation is –35.3 kcal mol⁻¹. This can be rationalised in terms of the formation of new Mg–H bonds and also in the formation of a less sterically demanding larger eight-membered ring.



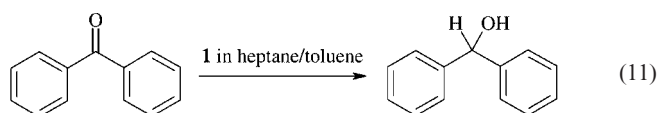
In Stage V, one toluene molecule coordinates to each K centre and, as expected, this process is exothermic resulting in the calculated structure corresponding to **1a** [Equation (10)]. The data from the calculated structure were found to closely resemble the crystal data. For instance, the K–N bonds from the X-ray crystallographic data were found to be 2.7754(16) Å whilst the theoretical value is 2.777 Å. Good agreement was also found in the Mg–N bond lengths [2.0595(15) Å vs. theoretical value of 2.103 Å], the N–K–N bond angle [119.55(6)° vs. theoretical value of 122.30°] and the N–Mg–N bond angle [126.55(9)° vs. theoretical value of 128.40°]. As expected the docking of the toluene molecules is exothermic (–1.45 kcal mol⁻¹ per coordinating toluene molecule). However, the energy gain

calculated by this study is much lower than would have been predicted considering the strength of the K–arene interaction which is evident from the crystal data. This is related to the substantial difference between the K–arene bond lengths for the calculated structure and those found experimentally [shortest K...C_{tol} approach 3.730 Å vs. 3.107(3) Å from the X-ray data].



Reduction of Benzophenone

Preliminary studies have shown that a heptane/toluene solution of **1** has the ability to act as a reducing agent. As mentioned previously, Sanchez and Scott^[5] report that, like **1**, Mg(NiPr₂)₂ can reduce benzophenone to benzhydrol [Equation (11)].



A 1:4 molar ratio of benzophenone to an in situ solution of **1** was chosen, in accordance with the work of Ashby et al.^[4] On work up of the reaction mixture using standard protocols, a ¹H NMR spectrum of the crude product was obtained. The spectrum indicated that, as well as the reduction product benzhydrol, some unchanged benzophenone was present (26% by NMR spectroscopy). The spectrum of the crude product also indicated the presence of the imine *i*Pr–N=C(Me)₂ produced as a secondary product of the β -hydride elimination. The yield of benzhydrol (74%) is similar to that obtained using monometallic Mg(NiPr₂)₂^[5] as the reducing agent (73%).

To provide further evidence that the reduction is taking place as a consequence of β -hydride elimination, 2,2,6,6-tetramethylpiperidine (TMP) — an amide in which it is impossible for β -hydride elimination to take place — was utilised instead of diisopropylamide. Previously, BuK, Bu₂Mg and TMPH in a 1:1:3 mixture in toluene has been used to prepare the hexapotassium-hexamagnesium twenty-four membered inverse crown [K₆Mg₆(TMP)₁₂(C₆H₄CH₃)₆], where the 6+ charge of the “host” heterobimetallic cationic ring is balanced by the encapsulation of six monodeprotonated “guest” arene molecules.^[39] For the experiment outlined here, BuK was exchanged for BnK. The reaction was carried out in an analogous fashion to that shown for the benzophenone reduction using **1** in the Exp. Sect. As for the reaction reported earlier, a dramatic colour change occurred upon addition of the ketone. Similarly, when quenched with water, a white suspension of NaOH and Mg(OH)₂ was produced. After work up, a ¹H NMR spectrum of the crude reaction mixture was obtained. While this spectrum contained a large number of resonances it was

clear that benzhydrol was not present although some unchanged benzophenone remained. As found in the study by Sanchez and Scott,^[5] it proved impossible to identify the other products present, presumably due to their intractable polymeric nature. This evidence coupled with both the X-ray data and the detection of $i\text{Pr-N}=\text{C}(\text{Me})_2$ by ^1H NMR spectroscopy, unequivocally proves that the reduction must be taking place as a consequence of a β -hydride elimination pathway.

Experimental Section

The synthesis of **1** was carried out under a protective atmosphere of argon using standard Schlenk techniques. Hexane and toluene were dried by heating to reflux over sodium benzophenone ketyl and distilled under nitrogen prior to use. Diisopropylamine was dried by heating to reflux over calcium hydride, distilled under nitrogen and stored over 4 Å molecular sieve. n,s -Dibutylmagnesium in the form of a 1 M solution in heptane was purchased from Aldrich Chemicals and standardised immediately prior to use using salicylaldehyde phenylhydrazone.^[40] Benzylpotassium was prepared according to literature methods.^[41] Benzophenone was used as received from Aldrich Chemicals. The melting point was determined in a sealed argon-filled capillary tube and is uncorrected. NMR spectroscopic experiments were carried out on a Bruker DPX 400 MHz spectrometer.

[K₂Mg₂(NiPr₂)₄(μ-H)₂(toluene)] (1): A flame-dried, argon-filled Schlenk tube was charged with benzylpotassium (0.65 g, 5 mmol). This orange/red solid was subsequently suspended in toluene (10 mL). n,s -Dibutylmagnesium in heptane (5 mL, 5 mmol) was added, followed by diisopropylamine (2.1 mL, 15 mmol) to give an orange solution. The solution was heated to reflux for 35 minutes and an orange to red colour change was observed. The solution was then concentrated by removal of some solvent in vacuo and then placed in a freezer operating at -28°C . After 48 hours, colourless needle-like crystals were deposited from the solution. Due to their high solubility, the crystals proved difficult to isolate in high yields (first batch = 0.26 g, 15%). m.p. $>280^\circ\text{C}$. $\text{C}_{38}\text{H}_{74}\text{K}_2\text{Mg}_2\text{N}_4$ (713.8): calcd. C 63.9, H 10.4, N 7.8; found C 64.7, H 10.3, N 7.6. ^1H NMR (400.13 MHz, C_6D_6 , 300 K): δ = 1.29 [d, 48 H, $\text{CH}(\text{CH}_3)_2$], 2.11 (s, 6 H, $\text{C}_6\text{H}_5\text{CH}_3$), 3.35 [sept, 8 H, $\text{CH}(\text{CH}_3)_2$], 3.78 (s, 2 H, MgH), 6.94 (d, 4 H, $o\text{-tol}$), 7.05 (t, 2 H, $p\text{-tol}$), 7.15 (m, 4 H, $m\text{-tol}$) ppm. ^{13}C NMR (100.62 MHz, C_6D_6 , 300 K): δ = 21.75 ($\text{C}_6\text{H}_5\text{CH}_3$), 27.29 [$\text{CH}(\text{CH}_3)_2$], 49.50 [$\text{CH}(\text{CH}_3)_2$], 126.03 ($p\text{-tol}$), 129.67 ($o\text{-tol}$), 138.00 ($ipso\text{-tol}$) ppm. The $m\text{-tol}$ resonance is obscured by the solvent C_6D_6 resonance at δ = 128 ppm.

X-ray Crystal Structure Determination of 1: The X-ray structural analysis was carried out at 123 K on a Nonius Kappa CCD diffractometer (Mo- K_α , λ = 0.71073 Å, graphite monochromator, standard techniques). Crystal data: $\text{C}_{38}\text{H}_{74}\text{K}_2\text{Mg}_2\text{N}_4$, mol. wt. 713.83, orthorhombic, space group $Pnmm$, a = 9.9080(2) Å, b = 12.5553(3) Å, c = 17.4310(4) Å, U = 2168.38(8) Å³, Z = 2, D_c = 1.093 g cm⁻³. A total of 5567 reflections were collected out to θ_{max} = 29.16°, of which 3018 were unique (R_{int} = 0.0204). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with all non-H atoms anisotropic and using SHELX-97.^[42] The bridging hydride H-atoms were refined isotropically but all other H-atoms were placed in calculated positions. Final R values: R_1 = 0.0508, wR_2 = 0.1422, GOF = 1.043.

CCDC-213617 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Reduction of Benzophenone: A flame-dried, argon-filled Schlenk tube was charged with benzylpotassium (0.65 g, 5 mmol). This orange/red solid was subsequently suspended in toluene (10 mL). n,s -Dibutylmagnesium in heptane (5 mL, 5 mmol) was added, followed by diisopropylamine (2.1 mL, 15 mmol) to give an orange solution. The solution was heated to reflux for 35 minutes and an orange to red colour change was observed. Benzophenone (0.2275 g, 1.25 mmol) was added, immediately producing a deep purple coloured oil. This mixture was allowed to stir for thirty minutes before being quenched with distilled water (5 mL). The resulting white suspension was washed with three aliquots of diethyl ether (10 mL). The organic phase was dried over anhydrous MgSO_4 . All volatiles were removed in vacuo and the reduction product — benzhydrol, Ph_2CHOH — was recrystallised from petroleum ether 60–80 (0.11 g, 48% not optimised: yield obtained from NMR analysis relative to recovered benzophenone was 74%). The purity of the product was confirmed by ^1H NMR spectroscopy. ^1H NMR (400.13 MHz, CDCl_3 , 300 K): δ = 2.20 (d, 1 H, OH), 5.87 (d, 1 H, CH), 7.25–7.41 (overlapping multiplets, 10 H, Ph) ppm. As well as obtaining the yield with respect to benzophenone from the ^1H NMR spectrum of the crude product, the presence of $i\text{Pr-N}=\text{C}(\text{Me})_2$, the by-product from the formation of **1**,^[43] was also noted: δ = 1.12 (d, 6 H, CH_3), 1.85 (s, 3 H, $\text{H}_3\text{C}'\text{-C}=\text{N}$), 1.99 (s, 3 H, $\text{H}_3\text{C-C}=\text{N}$), 3.62 (sept, 1 H, CH) ppm.

Acknowledgments

The authors gratefully acknowledge the financial support of the UK EPSRC through grant award GR/R81183/01.

- [1] First preparation of LiAlH_4 : [1a] A. E. Finholt, A. C. Bond, Jr., H. I. Schlesinger, *J. Am. Chem. Soc.* **1947**, 69, 1199–1203. First use of LiAlH_4 as a reducing agent: [1b] R. F. Nystrom, W. G. Brown, *J. Am. Chem. Soc.* **1947**, 69, 1197–1199. Selected recent uses of aluminium-containing hydride reagents in reduction reactions: [1c] J. T. Kuethe, A. Wong, J. Wu, I. W. Davies, P. G. Dormer, C. J. Welch, M. C. Hillier, D. L. Hughes, P. J. Reider, *J. Org. Chem.* **2002**, 67, 5993–6000. [1d] M. Harding, R. Hodgson, A. Nelson, *J. Chem. Soc., Perkin Trans. 1* **2002**, 2403–2413. [1e] F. Benedetti, F. Berti, S. Norbedo, *J. Org. Chem.* **2002**, 67, 8635–8643. [1f] S. Kim, R. Kavali, *Tetrahedron Lett.* **2002**, 43, 7189–7191. [1g] P. Sairam, R. Puranik, B. S. Rao, P. V. Swamy, S. Chandra, *Carbohydrate Res.* **2003**, 338, 303–306.
- [2] 48 Compounds in the Cambridge crystallographic database contain an Al–H–Al unit within their molecular structure. For selected examples of homometallic species see: [2a] W. Uhl, J. Molter, B. Neumuller, F. Schmock, *Z. Anorg. Allg. Chem.* **2001**, 627, 909–917. [2b] U. Fookan, M. A. Khan, R. J. Wehmschulte, *Inorg. Chem.* **2001**, 40, 1316–1322. [2c] U. Dumiichen, T. Gelbrich, J. Sieler, *J. Anorg. Allg. Chem.* **2001**, 627, 1915–1920. [2d] W. Uhl, F. Breher, A. Lutzen, W. Saak, *Angew. Chem. Int. Ed.* **2000**, 39, 406–409; *Angew. Chem.* **2000**, 112, 414–416. [2e] N. Kuhn, S. Fuchs, M. Steimann, *Z. Anorg. Allg. Chem.* **2000**, 626, 1387–1392. [2f] G. S. Hair, S. L. Battle, A. Decken, A. H. Cowley, R. A. Jones, *Inorg. Chem.* **2000**, 39, 27–31. [2g] W. Uhl, F. Breher, *Angew. Chem. Int. Ed.* **1999**, 38,

- 1477–1479; *Angew. Chem.* **1999**, *111*, 1578–1580. ^[2h] J. F. Janik, R. L. Wells, A. L. Rheingold, I. A. Guzei, *Polyhedron* **1998**, *17*, 4101–4108. ^[2i] H. Nöth, A. Schlegel, J. Knizek, I. Krossing, H. Schwenk, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2640–2643; *Angew. Chem.* **1997**, *109*, 2754–2758. ^[2j] P. C. Andrews, M. G. Gardiner, C. L. Raston, V.-A. Tolhurst, *Inorg. Chim. Acta* **1997**, *259*, 249–255. ^[2k] R. J. Wehmschulte, W. J. Grigsby, B. Schiemenz, R. A. Bartlett, P. P. Power, *Inorg. Chem.* **1996**, *35*, 6694–6702. ^[2l] I. B. Gorrell, P. B. Hitchcock, J. D. Smith, *J. Chem. Soc., Chem. Commun.* **1993**, 189–190. ^[2m] W. Uhl, *Z. Anorg. Allg. Chem.* **1989**, *570*, 37–53. ^[2n] G. Perego, M. Cesari, G. del Piero, A. Balducci, E. Cernia, *J. Organomet. Chem.* **1975**, *87*, 33–41. For selected examples of heterometallic species see: ^[2o] C. Eaborn, S. M. El-Hamruni, M. S. Hill, P. B. Hitchcock, M. Hopman, A. Le Gouic, J. D. Smith, *J. Organomet. Chem.* **2000**, *597*, 3–9. ^[2p] N. Etkin, A. J. Hoskin, D. W. Stephan, *J. Am. Chem. Soc.* **1997**, *119*, 11420–11424. ^[2q] V. K. Belsky, Yu. K. Gun'ko, B. M. Bulychev, G. L. Soloveichik, *J. Organomet. Chem.* **1991**, *420*, 43–52. ^[2r] G. S. Girolami, C. G. Howard, G. Wilkinson, H. M. Dawes, M. Thornton-Pett, M. Motevalli, M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.* **1985**, 921–929. ^[2s] E. B. Lobkovskii, G. L. Soloveichik, A. I. Sizov, B. M. Bulychev, *J. Organomet. Chem.* **1985**, *280*, 53–66.
- ^[3] D. J. Gallagher, K. W. Henderson, A. R. Kennedy, C. T. O'Hara, R. E. Mulvey, R. B. Rowlings, *Chem. Commun.* **2002**, 376–377.
- ^[4] ^[4a] E. C. Ashby, A. B. Goel, *J. Chem. Soc., Chem. Commun.* **1977**, 169. ^[4b] E. C. Ashby, A. B. Goel, *J. Org. Chem.* **1977**, *42*, 3480–3485. ^[4c] A. B. Goel, E. C. Ashby, *J. Organomet. Chem.* **1981**, *214*, C1–C6. ^[4d] E. C. Ashby, A. B. Goel, *Inorg. Chem.* **1979**, *18*, 1306–1311. ^[4e] E. C. Ashby, A. B. Goel, J. J. Lin, *J. Org. Chem.* **1978**, *43*, 1564–1566. ^[4f] E. C. Ashby, A. B. Goel, J. J. Lin, *Tetrahedron Lett.* **1977**, *36*, 3133–3136. ^[4g] R. G. Be-ach, E. C. Ashby, *Inorg. Chem.* **1971**, *10*, 906–910.
- ^[5] ^[5a] R. Sanchez, W. Scott, *Tetrahedron Lett.* **1988**, *29*, 139–142. ^[5b] R. Sanchez, G. Vest, W. Scott, P. S. Engel, *J. Org. Chem.* **1989**, *54*, 4026–4027.
- ^[6] W. Clegg, S. Kleditzsch, R. E. Mulvey, P. O'Shaughnessy, *J. Organomet. Chem.* **1998**, *558*, 193–196.
- ^[7] R. E. Mulvey, *Chem. Commun.* **2001**, 1049–1056.
- ^[8] A. R. Kennedy, R. E. Mulvey, R. B. Rowlings, *Angew. Chem. Int. Ed.* **1998**, *37*, 3180–3183; *Angew. Chem. Int. Ed.* **1998**, *110*, 3321–3323.
- ^[9] D. R. Armstrong, A. R. Kennedy, R. E. Mulvey, R. B. Rowlings, *Angew. Chem. Int. Ed.* **1999**, *38*, 131–133. *Angew. Chem. Int. Ed.* **1999**, *111*, 231–233.
- ^[10] W. Clegg, K. W. Henderson, A. R. Kennedy, R. E. Mulvey, C. T. O'Hara, R. B. Rowlings, D. M. Tooke, *Angew. Chem. Int. Ed.* **2001**, *40*, 3902–3905; *Angew. Chem.* **2001**, *113*, 4020–4023.
- ^[11] ^[11a] G. W. Gokel, L. J. Barbour, S. L. De Wall, E. S. Meadows, *Coord. Chem. Rev.* **2001**, *222*, 127–154. ^[11b] E. S. Meadows, S. L. De Wall, L. J. Barbour, G. W. Gokel, *J. Am. Chem. Soc.* **2001**, *123*, 3092–3107. ^[11c] G. C. Forbes, A. R. Kennedy, R. E. Mulvey, B. A. Roberts, R. B. Rowlings, *Organometallics* **2002**, *21*, 5115–5121.
- ^[12] S. Hashimoto, M. Hagiri, N. Matsubara, S. Tobita, *Phys. Chem. Chem. Phys.* **2001**, *3*, 5043–5051.
- ^[13] ^[13a] D. A. Dougherty, *Science* **1996**, *271*, 163–168. ^[13b] D. Sun, V. L. Davidson, *Biochemistry* **2001**, *40*, 12285–12291. ^[13c] J. Wouters, *Protein Sci.* **1998**, *2472*–2475. ^[13d] G. W. Gokel, S. L. De Wall, E. S. Meadows, *Eur. J. Org. Chem.* **2000**, 2967–2978.
- ^[14] A. R. Kennedy, J. G. MacLellan, R. E. Mulvey, *Angew. Chem. Int. Ed.* **2001**, *40*, 3245–3247; *Angew. Chem.* **2001**, *113*, 3345–3347.
- ^[15] For the first inverse crown to be prepared from a benzyl-alkali metal reagent see: G. C. Forbes, F. R. Kenley, A. R. Kennedy, R. E. Mulvey, C. T. O'Hara, J. A. Parkinson, *Chem. Commun.* **2003**, 1140–1141.
- ^[16] E. Hevia, F. R. Kenley, A. R. Kennedy, R. E. Mulvey, R. B. Rowlings, *preceding paper in this issue*.
- ^[17] S. D. Droulin, D. Amoroso, G. P. A. Yap, D. E. Fogg, *Organometallics* **2002**, *21*, 1042–1049.
- ^[18] S. I. Troyanov, V. Varga, K. Mach, *J. Chem. Soc., Chem. Commun.* **1993**, 1174–1175.
- ^[19] M. Horáček, I. Czařová, J. Čejka, J. Karban, L. Petrusová, K. Mach, *J. Organomet. Chem.* **1999**, *577*, 103–112.
- ^[20] H. Lee, T. Hascall, P. J. Desrosiers, G. Parkin, *J. Am. Chem. Soc.* **1998**, *120*, 5830–5831.
- ^[21] Z. Hou, Y. Zhang, O. Tardif, Y. Wakatsuki, *J. Am. Chem. Soc.* **2001**, *123*, 9216–9217.
- ^[22] Values quoted are for six coordinate cations and were obtained from: R. D. Shannon, *Acta Crystallogr., Sect. A* **1976**, *32*, 751–767.
- ^[23] F. H. Allen, O. Kennard, *Chem. Des. Autom. News* **1993**, *8*, 31. CSD Version 5.24, April 2003 update.
- ^[24] Due to the large range of metal-arene distances found in the crystal structures, and the ambiguity of whether the contact is a meaningful interaction or simply the random presence of a molecule of solvent of crystallisation, the inclusion or exclusion of molecules here is subjective. ^[24a] S. Chadwick, U. Englisch, K. Ruhlandt-Senge, *Organometallics* **1997**, *16*, 5792–5803. ^[24b] L. Rösch, G. Altnau, C. Kruger, Y. H. Tsay, *Z. Naturforsch., Teil B* **1983**, *38*, 34–41. ^[24c] R. Wochele, W. Schwarz, K. W. Klinkhammer, K. Locke, J. Weidlein, *Z. Anorg. Allg. Chem.* **2000**, *626*, 1963–1973. ^[24d] K. W. Klinkhammer, *Chem. Eur. J.* **1997**, *3*, 1418–1431.
- ^[25] ^[25a] C. J. Schaverien, J. B. van Mechelen, *Organometallics* **1991**, *10*, 1704–1709. ^[25b] E. Leiner, O. Hampe, M. Scheer, *Eur. J. Inorg. Chem.* **2002**, 584–590. ^[25c] M. A. Beswick, N. Choi, A. D. Hopkins, M. McPartlin, M. A. Paver, D. S. Wright, *Chem. Commun.* **1998**, 261–262. ^[25d] M. Unverzagt, H.-J. Winkler, M. Brock, M. Hofmann, P. v. R. Schleyer, W. Massa, A. Berndt, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 853–855; *Angew. Chem.* **1997**, *36*, 879–882. ^[25e] S. Chitsaz, B. Neumüller, *Organometallics* **2001**, *20*, 2338–2343. ^[25f] P. B. Hitchcock, M. F. Lappert, G. A. Lawless, B. Royo, *J. Chem. Soc., Chem. Commun.* **1993**, 554–555. ^[25g] C. Kayser, R. Fischer, J. Baumgartner, C. Marchner, *Organometallics* **2002**, *21*, 1023–1030. ^[25h] H.-J. Gosink, F. Nief, L. Ricard, F. Mathey, *Inorg. Chem.* **1995**, *34*, 1306–1307. ^[25i] I. Korobkov, G. Aharonian, S. Gambarotta, G. P. A. Yap, *Organometallics* **2002**, *21*, 4899–4901. ^[25j] G. Bai, H. W. Roesky, M. Noltemeyer, H.-G. Schmidt, *J. Chem. Soc., Dalton Trans.* **2002**, 2437–2440. ^[25k] G. Bai, H. W. Roesky, M. Noltemeyer, H.-G. Schmidt, *Organometallics* **2002**, *21*, 2789–2792.
- ^[26] Gaussian 98 (Revision A.9); M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, P. Salvador, J. J. Dannenberg, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh PA, 2001.
- ^[27] R. Ditchfield, W. J. Hehre, J. A. Pople, *J. Chem. Phys.* **1971**, *54*, 724–728.
- ^[28] W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* **1972**, *56*, 2257–2261.
- ^[29] P. C. Hariharan, J. A. Pople, *Mol. Phys.* **1974**, *27*, 209–212.
- ^[30] M. S. Gordon, *Chem. Phys. Lett.* **1980**, *76*, 163–168.
- ^[31] P. C. Hariharan, J. A. Pople, *Theo. Chim. Acta* **1973**, *28*, 213–216.

- [32] W. Kohn, A. D. Becke, R. G. Parr, *J. Phys. Chem.* **1996**, *100*, 12974–12980.
- [33] A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098–3100.
- [34] C. T. Lee, W. T. Yang, R. G. Parr, *Phys. Rev. B* **1998**, *37*, 785–789.
- [35] A. D. McLean, G. S. Chandler, *J. Chem. Phys.* **1980**, *72*, 5639–5648.
- [36] R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 650–654.
- [37] The DFT total energies (in a.u.) including the zero point energy correction for calculated molecules are as follows: (**1a**) –3311.320228, (**4**) –891.646686, (**5**) –783.566645, (**6**) –1675.255643, (**7**) –1783.347845, (**8**) –1567.164098, (**9**) –1384.115447, (**10**) –1384.114410, (**11**) –2768.287148.
- [38] The β -hydride elimination from KNiPr_2 to give KH and $i\text{Pr-N}=\text{C}(\text{Me})_2$ was also modelled. The energy of the reaction was calculated to be $+20.9 \text{ kcal mol}^{-1}$.
- [39] P. C. Andrews, A. R. Kennedy, R. E. Mulvey, C. L. Raston, B. A. Roberts, R. B. Rowlings, *Angew. Chem. Int. Ed.* **2000**, *39*, 1960–1962; *Angew. Chem.* **2000**, *112*, 2036–2038.
- [40] B. E. Love, E. G. Jones, *J. Org. Chem.* **1999**, *64*, 3755–3756.
- [41] D. Hoffmann, W. Bauer, F. Hampel, N. J. R. van Eikema Hommes, P. v. R. Schleyer, P. Otto, U. Pieper, D. Stalke, D. S. Wright, R. Snaith, *J. Am. Chem. Soc.* **1994**, *116*, 528–536.
- [42] SHELXL-97; G. M. Sheldrick, University of Göttingen, Germany.
- [43] Synthetic procedure and NMR spectroscopic data for $i\text{Pr-N}=\text{C}(\text{Me})_2$: W. H. Bunnelle, P. R. Singam, B. A. Narayanan, C. W. Bradshaw, J. S. Liou, *Synthesis* **1997**, 439–442.

Received June 27, 2003