Preparation of $W_2[\mu\text{-}CPh(CPh)CPh](\mu\text{-}CPh)(NMe_2)_4$. A small Schlenk tube was charged with 0.610 g (1.0 mmol) of $W_2Cl_2(NMe_2)_4$ and 0.370 g (1.0 mmol) of $Li_2(CPh)_4$. Adding 5 mL of THF at 0 °C yielded a yellow solution, which turned black a few moments later. The solution was stirred for an additional 6 h. After the solvent was removed in vacuo, the black residue was extracted with 2 × 10 mL of toluene and filtered through a fine frit. The volume of the deep red solution was concentrated to ca. 2 mL and the flask stored at −20 °C. After 24 h, black crystals were collected (400 mg, 45%). Reducing the volume to half of the amount and storing of the solution for an additional 48 h at −20 °C yielded a second crop of black crystals (140 mg, 15%). Anal. Calcd for $C_{36}H_{44}N_4W_2$: C, 48.02; H, 4.92; N, 6.22. Found: C, 47.77; H, 4.66; N, 5.82. Mp: 203 °C. ^1H NMR (toluene-d_8, 22 °C) δ: 7.96 (dd, 2 H), 7.80 (dd, 2 H), 7.58 (t, 2 H), 7.22 (t, 2 H), 7.13 (t, 1 H), 7.02 (t, 1 H), 6.99 (t, 4 H), 6.70 (t, 2 H), 6.50 (dd, 4 H), 2.89 (s, 24 H). $^{13}C\{^1H\}$ NMR δ: 335.5 ($^1J_{^{183}W-^{13}C}$ = 146 Hz (μ-CPh)), 172.9 ($^1J_{^{183}W-^{13}C}$ = 40 Hz (μ-CPh)), 157.2, 144.2, 140.2, 130.8, 130.5, 128.6, 128.3, 128.0, 127.9, 127.1, 126.5, 124.8, 123.8, 48.1 (NCH_3).

Crystallographic Studies. General operating procedures and listings of programs have been given.[5] A suitable crystal was located, transferred to the goniostat using inert atmosphere handling techniques, and cooled to −171 °C for characterization and data collection. A summary of crystal data is given in Table III.

A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with symmetry and systematic absences corresponding to the unique monoclinic space group $P2_1/c$. Subsequent solution and refinement of the structure confirmed this choice.

Data were collected in the usual manner by using a continuous θ–2θ scan with fixed backgrounds. Data were reduced to a unique set of intensities and associated σ's in the usual manner. The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques. A difference Fourier synthesis revealed the location of some, but not all, hydrogen atoms. All hydrogen atom positions were therefore calculated using idealized geometries and d(C–H) = 0.95 Å. These calculated positions were fixed for the final cycles of refinement.

A final difference Fourier was featureless, with several peaks of 1.1–1.5 e/Å^3 located at the metal site, and all other peaks less than 0.6 e/Å^3.

No absorption correction was performed.

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Supplementary Material Available: A listing of anisotropic thermal parameters, VERSORT and stereo drawings giving the atom number scheme, and a complete listing of bond distances and bond angles (10 pages). Ordering information is given on any current masthead page.

OM910639Z

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[5] Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* 1984, *23*, 1021.

Synthesis of Magnesium Hydride by the Reaction of Phenylsilane and Dibutylmagnesium

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Summary: The reaction of phenylsilane with dibutylmagnesium in ethereal or hydrocarbon solvents in the presence of appropriate ligands, usually tetrahydrofuran (THF) or *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) leads to precipitation of magnesium hydride MgH_2L_x.

Magnesium hydride has generated some interest as a reducing agent for aldehydes and ketones,[1] as a hydride source in the synthesis of silane,[2] and as a potential material for use in hydrogen storage devices.[3] The hydride is usually synthesized by catalytic hydrogenation of magnesium or by reduction of $MgMe_2$ with $LiAlH_4$.[3a,4] We now report that MgH_2 can be simply prepared by the reaction of phenylsilane with dibutylmagnesium. Magnesium hydride precipitates from the reaction mixture either as a solvated hydride (from tetrahydrofuran (THF)/heptane or ethylene glycol dimethyl ether (DME)/heptane) or as a *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) adduct (from TMEDA/heptane/solutions).[5]

Experimental Section

All experiments were performed under nitrogen in a Vacuum Atmospheres drybox at room temperature or under argon using Schlenk techniques at room temperature or below. *Magnesium hydride is a highly pyrophoric, air-sensitive solid and should be handled with extreme caution.* All solvents were dried and distilled before use. Dibutylmagnesium (consisting of a 1:1 mixture of *n*-butyl/*sec*-butyl) was purchased from Alfa as a 1.07 M solution in heptane. Phenylsilane was obtained from Petrarch/Hüls America and distilled before use. TMEDA (Aldrich) was dried over CaH_2 and distilled. Proton NMR spectra were recorded on a General Electric QE-300 spectrometer; FT-IR spectra were obtained in Nujol and in THF on KBr using a Nicolet 60-SX spectrometer. GC/MS analysis was performed using a Varian 3700 gas chromatograph coupled with a VG micromass 16 mass

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[1] (a) Ashby, E. C.; Lin, J. J.; Goel, A. B. *J. Org. Chem.* 1978, *43*, 1557. (b) Carfagna, C.; Musco, A.; Pontellini, R.; Terzoni, G. *J. Mol. Catal.* 1989, *57*, 23. (c) Musco, A.; Pontellini, R.; Terzoni, G. *Inorg. Chim. Acta* 1990, *172*, 1.

[2] (a) Bogdanović, B. German Patent 3247362, 1984. (b) Marlett, E.; McKinney, B. G. U. S. Patent 7725419, 1988. (c) Porcham, W. German Patent 3409172, 1985.

[3] (a) Bogdanović, B.; Liao, S.-T.; Schwickardi, M.; Sikorsky, P.; Spliethoff, B. *Angew. Chem., Int. Ed. Engl.* 1980, *19*, 818. (b) Bogdanović, B. *Acc. Chem. Res.* 1988, *21*, 261. (c) Reilly, J. J.; Wiswall, R. H. *Inorg. Chem.* 1967, *6*, 220. (d) Reilly, J. J.; Wiswall, R. H. *Inorg. Chem.* 1968, *7*, 2254. (e) Wiswall, R. H. *Top. Appl. Phys.* 1978, *29*, 209.

[4] (a) Ashby, E. C.; Goel, A. B. *J. Chem. Soc., Chem. Commun.* 1977, 169. (b) Ashby, E. C.; Goel, A. B. *J. Org. Chem.* 1977, *42*, 3480. (c) Goel, A. B.; Ashby, E. C. *Inorg. Chim. Acta* 1984, *87*, 61. (d) See also: McCaffrey, J. G.; Parnis, J. M.; Ozin, G. A.; Breckenridge, W. H. *J. Phys. Chem.* 1985, *89*, 4945.

[5] Earlier workers reported formation of Mg(H)OEt from the reaction of SiH_4 with $MgEt_2$ in Et_2O: Bauer, R. Z. *Naturforsch., Teil B* 1962, *17*, 201.

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spectrometer. GC analysis was performed using a Hewlett-Packard 5890 Series II gas chromatograph; yields were determined by integration of products relative to an internal *n*-decane standard. Elemental analyses were performed by Mikroanalytisches Labor Pascher, Remagen-Bandorf, Germany.

Synthesis of $MgH_2(THF)_{0.23}$ (1a). A solution of 8.0 mL (8.6 mmol) of 1.07 M $MgBu_2$ in heptane in 40 mL of THF was stirred at 25 °C, and 2.10 g (19.4 mmol) of $PhSiH_3$ was slowly added over a 30-min period. The mixture was stirred for ~17 h, during which time it turned from clear to cloudy grey. The precipitated solid was filtered, washed twice with hexane to remove any residual silanes, and dried in vacuo, leaving 0.321 g (90%) of white THF-solvated MgH_2 powder. MgH_2 prepared in this way can sometimes vary in color from white to brown and was found to be insoluble in all common solvents. IR (cm^{-1}): 1400–800 (br), 800–450 (br). Anal. Calcd for $C_{0.92}H_{3.84}O_{0.23}Mg$ ($MgH_2 \cdot 0.23THF$): C, 25.76; H, 9.01; Mg, 56.65. Found: C, 26.65; H, 8.51; Mg, 54.6.

Synthesis of $MgH_2(DME)_{0.33}$ (1b). To a stirred solution of 6.07 g (56.1 mmol) of $PhSiH_3$ in 60 mL of DME at 25 °C was slowly added 24.2 mL (26.0 mmol) of 1.07 M $MgBu_2$ in heptane over a 30-min period. After being stirred overnight at room temperature, the reaction mixture was cloudy grey. The precipitated solids were filtered, washed with hexane, and dried in vacuo, leaving 0.998 g (71.9%) of a white powder formulated as $MgH_2(DME)_{0.33}$. IR (cm^{-1}): 1400–780 (br) (some resolved peaks in broad band at 1105, 1065, 990, 910, 840), 770–450 (br). Anal. Calcd for $C_{1.32}H_{5.3}O_{0.66}Mg$ ($MgH_2 \cdot 0.33DME$): C, 28.28; H, 9.53; Mg, 43.35. Found: C, 28.73; H, 8.14; Mg, 43.3.

Synthesis of $MgH_2(TMEDA)_{0.50}$ (1c). A solution of 16.0 mL (17.1 mmol) of 1.07 M $MgBu_2$ in heptane and 80 mL of TMEDA was stirred and cooled to −41 °C. To this was added 4.21 g (38.9 mmol) of $PhSiH_3$. An orange-brown solution resulted. After a couple of hours, a cloudy brown mixture was produced; this was stirred at −41 °C for 1 h and warmed to room temperature. After stirring for 17 h, filtering, washing, and drying, 0.566 g (39.2 %) of grey powder formulated as $MgH_2(TMEDA)_{0.50}$ was isolated. This hydride is somewhat soluble in THF, producing grey-red solutions. IR (cm^{-1}): 1400–780 (br). ^1H NMR (THF-d_8): 2.1–2.7 (br), 2.31 (s, CH_2N), 2.16 (s, MeN) ppm. Anal. Calcd. for $C_3H_{10}NMg$: C, 42.68; H, 10.08; Mg, 28.79. Found: C, 42.25; H, 10.01; Mg, 28.20.

Determination of Active Hydride in MgH_2 Samples. A simple method to estimate the amount of ligand and active hydride in MgH_2L_x samples is based on the quantitative reaction of MgH_2 with pyridine.[6] Magnesium hydride reacts readily with pyridine producing 1,2-dihydro-1-pyridylmagnesium and 1,4-dihydro-1-pyridylmagnesium complexes which exchange with free pyridine in solution. At the same time, the 1,2-dihydro-1-pyridylmagnesium kinetic products slowly convert to the thermodynamically stable 1,4-dihydro-1-pyridylmagnesium complexes, leaving only solvated bis(1,4-dihydro-1-pyridyl)magnesium at equilibrium. These reactions ultimately depend on the reactivity of MgH_2 but are usually equilibrated within 24 h.

To estimate the amount of hydride in MgH_2L_x or $MgH_{2-x}Bu_x$, a small sample of hydride is added to a 5-mm NMR tube containing pyridine-d_5, producing a red color. A proton NMR taken at this point should show a roughly 2:1 ratio of the protons from the 1,2-dihydro-1-pyridylmagnesium complex (3.95 ppm) and the 1,4-dihydro-1-pyridylmagnesium complex (3.77 ppm), respectively. During equilibration, these hydride signals decrease while the signals assigned to the two and six (ortho) and the four (para) positions in pyridine increase due to H/D exchange. After 24 h, the exchange in the NMR sample has reached equilibrium.[7] By use of the three and five (meta) signals as reference, the intensities of the NMR signals due to H/D exchange on pyridine are measured and added with the integrated area of the residual 3.77 ppm signal. This total represents the total H derived by MgH_2 reduction of pyridine. The amount x in MgH_2L_x can be determined from measuring the amount of L that appears in the NMR spectrum vs the "total H" from MgH_2. This was done for **1a**–**c**. Combining these results with those obtained from elemental analyses, we arrive at the following active H^-/Mg ratios for **1a**–**c**; active H^-/Mg Calcd: for **1a**–**c**, 2.0/1.0. Found: **1a**, 1.8/1.0; **1b**, 1.9/1.0; **1c**, 1.0/1.0.[8] The amount of residual butyl groups in $MgH_{2-y}Bu_y$ can be determined similarly using the proton resonances on the carbons bound to Mg to determine the amount y. ^1H NMR (pyridine-d_5): 0.05–0.15 (t, $MgCH_2$ (*n*-butyl)), 0.26–0.40 (m, MgCH (*sec*-butyl)) ppm.

Reduction of Chlorosilanes by MgH_2L_x. A solution of 0.230 g (0.908 mmol) of Ph_2SiCl_2 and of 0.122 g (0.857 mmol) of *n*-decane (GC standard) in 5 mL of THF was stirred at 25 °C. A small aliquot was removed for GC analysis. A sample of 0.020 g (0.451 mmol) of $MgH_2(THF)_{0.25}$ (synthesized in a manner similar to **1a**) was added to the solution. A cloudy white precipitate formed after 5 min. After stirring an additional 17 h at room temperature, the salts were precipitated by the addition of 5 mL of hexane. The mixture was centrifuged, and GC analysis of the clear solution showed the presence of the reduction products Ph_2SiH_2 (49%) and $Ph_2Si(H)Cl$ (4%) along with unreacted Ph_2SiCl_2 (40%). Similar reaction of 0.115 g (0.454 mmol) of Ph_2SiCl_2 with 0.023 g (0.519 mmol) of $MgH_2(THF)_{0.25}$ in the presence of 0.61 g of *n*-decane produced Ph_2SiH_2 (63%) and unreacted Ph_2SiCl_2 (1.9%).

The reduction of Ph_3SiCl was accomplished in a manner similar to that described for Ph_2SiCl_2. Reaction of 0.269 g (0.912 mmol) of Ph_3SiCl and 0.020 g (0.451 mmol) of $MgH_2(THF)_{0.25}$, with 0.133 g of *n*-decane as a GC standard, produced Ph_3SiH (44%) along with unreacted Ph_3SiCl (19%). By use of an excess of $MgH_2(THF)_{0.25}$, reaction of 0.267 g (0.906 mmol) of Ph_3SiCl with 0.026 g (0.586 mmol) of $MgH_2(THF)_{0.25}$ and 0.136 g of *n*-decane gave only Ph_3SiH (57%). No Ph_3SiCl was detected.

Reaction of Ph_2SiH_2 with $MgBu_2$. To a solution of 2.50 g (2.70 mmol) of Ph_2SiH_2 in 15 mL of hexane/THF (2:1) was added 1.28 mL of 1.07 M $MgBu_2$ in heptane at room temperature. A slight golden tint developed. After being stirred for 24 h, the cloudy golden solution was filtered, and the residual solution was quenched with water, extracted with hexane, and dried over $MgSO_4$. GC/MS analysis showed only Ph_2SiH_2 (79%) and $Ph_2Si(H)Bu$ (21%). The reaction of Et_3SiH and Et_2SiH_2 under similar conditions produced no products containing Si–Bu by GC/MS.

Reaction of $PhSiH_3$ with $ZnEt_2$. The reaction was performed in a manner similar to that used in the preparation of **1a** using 12.63 g (116.7 mmol) of $PhSiH_3$ and 6.530 g (52.9 mmol) of 1.0 M $ZnEt_2$ in hexanes (in place of $MgBu_2$) in 40 mL of THF. After 24 h the solution was cloudy dark grey. The grey solids were filtered, and the solution was quenched with water, extracted with hexane, dried over $MgSO_4$, and subjected to GC/MS analysis. The isolated grey solid (0.056 g, 1.6%) was identified as Zn metal by X-ray analysis. GC/MS analysis showed no Si–Et-containing products. Similar results were obtained when the reaction was performed in hexane at 25 °C.

Reaction of $PhSiH_3$ with $AlMe_3$. This reaction was carried out in a manner similar to that used in the preparation of **1a** using 2.017 g of $PhSiH_3$ (18.6 mmol) and 3.13 mL (6.3 mmol) of 2.0 M $AlMe_3$ in hexanes in 40 mL of THF. The resulting clear solution was stirred for 24 h at 25 °C. After being stirred, the solution was still clear. The volatiles were removed in vacuo, leaving 0.20 g of a slightly yellow solution. Proton NMR analysis (pyridine-d_5) showed a single sharp resonance at −0.37 ppm which was identified as $AlMe_3$. The reaction of $PhSiH_3$ and $AlMe_3$ in hexane at 25 °C gave similar results.

Results and Discussion

The reaction of phenylsilane with dibutylmagnesium leads to clean precipitation of solvated MgH_2L_x, **1**. Only

$$2PhSiH_3 + MgBu_2 \xrightarrow{L} MgH_2L_x + 2PhSiH_2Bu$$

1a: L = THF, x = 0.23
1b: L = DME, x = 0.33
1c: L = TMEDA, x = 0.50

the isomers $PhSiH_2Bu^s$ and $PhSiH_2Bu^n$ are observed in 1:1 ratios as sole products in filtrate residues by GC/MS.

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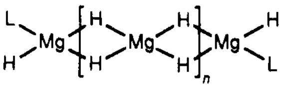
[6] (a) De Koning, A. J.; Boersma, J.; Van der Kerk, G. J. M. *J. Organomet. Chem.* **1980**, *186*, 159, 173. (b) De Koning, A. J.; Budzelaar, P. H. M.; Boersma, J.; Van der Kerk, G. J. M. *J. Organomet. Chem.* **1980**, *199*, 153. (c) De Koning, A. J.; Budzelaar, P. H. M.; Van Aarssen, B. G. K.; Boersma, J.; Van der Kerk, G. J. M. *J. Organomet. Chem.* **1981**, *217*, C1.

[7] Some samples such as $MgH_2(DME)_{0.33}$ require 2–3 days due to the low reactivity of the hydride.

[8] Mg^{2+} can also be determined by titration; see refs 4b and 4c.

The precipitation can be carried out at room temperature or low temperature in ethereal solvents such as THF or DME, mixtures of THF and hexane or heptane, mixtures of hexane or heptane with excess TMEDA, or in neat TMEDA. Magnesium hydride synthesized using this method is free of halide or impurities derived from the use of reducing agents such as $LiAlH_4$.[9] This preparation of MgH_2 is simple to perform and should be useful to the synthetic chemist needing a quick and convenient way to obtain magnesium hydride. The amount of ligand L incorporated into MgH_2 does vary from preparation to preparation; in samples of $MgH_2(THF)_x$, we have observed $x = 0.08$–0.25. The active hydride to ligand ratio can be easily determined by ^1H NMR in pyridine-d_5 (see Experimental Section). In our hands, **1a** was found to be the best source of active hydride (active $H^-/Mg = 1.8/1.0$) and the easiest to prepare; **1c** was found to contain a lower H^-/Mg ratio (1.0/1.0). If no coordinating ligand is added, a hydride $MgH_{2-y}Bu_y$ is obtained containing varying amounts of residual butyl groups. Other ligands such as NEt_3, 1,2-bis(dimethylphosphino)ethane (DMPE), and 18-crown-6 can be used in the preparation of MgH_2L_x.[10]

The powders obtained by this method are very air-sensitive and extremely pyrophoric when dried under vacuum. If the hydrides are left wet with solvent after filtration, they are not pyrophoric. X-ray analysis of the powders shows no intensities due to local ordering; thus we believe our MgH_2L_x probably exists as distributions of polymeric $[MgH_2L_x]_n$ capped by the added ligand as shown:[11]



None of the MgH_2L_x synthesized melts up to 360 °C. At around 148–190 °C, some samples showed some discoloration due either to loss of ligand or possibly to reaction with N_2 to form magnesium nitride. No rapid decomposition or formation of Mg metal was observed.

Different reactivities are observed depending on the ligand L. With respect to reducing pyridine-d_5, the order of activity was determined to be $MgH_2(TMEDA)_{0.50} > MgH_2(THF)_{0.23} \gg MgH_2(DME)_{0.33}$. Samples of $MgH_2(TMEDA)_x$ (reactions done in neat TMEDA at −41 °C or +25 °C) dissolve in THF producing dark brown solutions. This provides an easy method to obtain tetrahydrofuran-soluble MgH_2.[12] Infrared analyses of these solutions show broad bands between 1300 and 1000 cm^{-1} assignable to Mg–H, in agreement with the results of Bogdanovic′ and co-workers.[2,13] Centrifugation of these samples results in brown solutions from which MgH_2 precipitates with time.[14] No assignable Mg–H signal is observed in the proton NMR of solutions of $MgH_2(TMEDA)_{0.50}$ in THF-d_8.[15]

The reaction of Ph_2SiH_2 with $MgBu_2$ in THF/hexane leads to some precipitation of MgH_2; GC/MS analysis of filtrate residues shows Ph_2SiH_2 and $Ph_2Si(H)Bu$ in a 79/21 ratio. Triethylsilane and diethylsilane give no observable reaction with $MgBu_2$. We believe that the formation of MgH_2L_x involves simple nucleophilic substitution on silicon and is analogous to the reactions of organolithium reagents with organosilicon hydrides.[16] Thus, the more electrophilic arylsilanes such as $PhSiH_3$ and Ph_2SiH_2 will lead to MgH_2 formation.

Chlorosilanes such as Ph_2SiCl_2 and Ph_3SiCl can be reduced to the corresponding hydrides by using excess $MgH_2(THF)_x$. When less $MgH_2(THF)_x$ is used (molar ratio $MgH_2/Ph_2SiCl_2 = 1/2$), mostly Ph_2SiH_2 and unreacted Ph_2SiCl_2 are found along with a small amount of the partial reduction product $Ph_2Si(H)Cl$. The Si–Si bond of disilanes $(Me_3Si)_2$ or $(PhMe_2Si)_2$ was not cleaved by MgH_2L_x (L = TMEDA, THF); no Si–Mg species were observed.[17]

We have attempted to extend this method to AlH_3 and ZnH_2. No reaction occurred between $PhSiH_3$ and $AlMe_3$ in THF or hexane at room temperature. With $ZnEt_2$ we observed no formation of $PhSiH_2Et$ or $PhSiHEt_2$; however, we did obtain small amounts of Zn metal in the reaction. Thus, the use of $PhSiH_3$ may only be specific for MgH_2.

Acknowledgment. We thank C. P. Adams, R. Zubyk, E. W. Matthews, C. Foris, T. Pawlowski, and J. Wyre for expert technical assistance. The helpful comments of Prof. D. Seyferth and Prof. M. J. Fink are greatly appreciated.

Registry No. $PhSiH_3$, 694-53-1; $MgBu_2$, 1191-47-5; Ph_2SiCl_2, 80-10-4; Ph_2SiH_2, 775-12-2; $Ph_2Si(H)Cl$, 1631-83-0; Ph_3SiCl, 76-86-8; Ph_3SiH, 789-25-3; $ZnEt_2$, 557-20-0; $AlMe_3$, 75-24-1; $Ph_2Si(H)Bu$, 17964-31-7; Zn, 7440-66-6.

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[9] We do observe some silicon impurities in the range of 0.4–3.0% (determined by XPS analysis) in samples of $MgH_2(THF)_x$ and $MgH_2(TMEDA)_y$, presumably due to incomplete washing of the MgH_2 powder. **1b** was found experimentally to have 2.5% Si by XPS. No surface nitrogen was found on **1a** or **1b**.

[10] Active hydride/ligand ratios were found to be: L = NEt_3, $H^-/L = 1.0/0.055$; L = DMPE, $H^-/L = 1.0/0.085$; L = 18-crown-6, $H^-/L = 1.0/0.11$.

[11] Such a linear structure has been proposed previously for MgH_2: Ashby, E. C.; Lin, J. J.; Goel, A. B. *J. Org. Chem.* 1978, 43, 1557.

[12] Bogdanović, B.; Bons, P.; Schwickardi, M.; Seevogel, K. *Chem. Ber.* **1991**, *124*, 1041.

[13] The spectral features of the Mg–H region are partially obscured by THF (as noted in ref 12), and by absorptions of TMEDA. The IR spectrum of $MgD_2(TMEDA)_{0.5}$ is not obscured and shows broad absorbances from 1000–700 cm^{-1} with identifiable features at 900 (br), 954 (s), 755 (br), 710 (br), and 703 (s) presumable due to Mg–H.

[14] We still observe erratic signals in the IR spectra of centrifuged samples of soluble $MgH_2(TMEDA)_{0.5}$ in THF, presumably due to scattering of the beam by small suspended particles of insoluble material.

[15] We do observe resonances at 2.16 and 2.31 ppm for free TMEDA along with a broad signal at 2.1–2.7 ppm, which was first thought to be due to Mg–H. However, the same signal is seen in solutions of $MgD_2(TMEDA)_{0.5}$ in THF-d_8. We now believe that the broad signal may be due to TMEDA complexed on the surface of small insoluble MgH_2 particles. The broad signal does not change with temperature (−30 to +33 °C).

[16] (a) Gilman, H., Massie, S. P. *J. Am. Chem. Soc.* **1946**, *68*, 1128. (b) Meals, R. N. *J. Am. Chem. Soc.* **1946**, *68*, 1880. (c) Gilman, H.; Melvin, H. W. *J. Am. Chem. Soc.* **1949**, *71*, 4050. (d) Nebergall, W. H. *J. Am. Chem. Soc.* **1950**, *72*, 4702.

[17] See: Corriu, R. J. P.; Guerin, C. *J. Chem. Soc., Chem. Commun.* **1980**, 168.