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Synthesis and Characterization of the New Tetrameric Magnesium Imide Compound $[(thf)MgNSiPh_3]_4$

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Reaction between di-*n*-butylmagnesium and the primary amine H_2NSiPh_3 affords the tetrameric magnesium imide $[(thf)MgNSiPh_3]_4$, representing the first example of a structurally characterized magnesium imide in which the group attached to the nitrogen is not aryl. The four Mg and N atoms are arranged in the form of a distorted heterocubane unit.

Introduction

Up to date, there are only very few known examples of molecular homoleptic magnesium imide compounds. The synthesis of the first compound of this class, namely $[(thf)MgNPh]_6$ (thf = tetrahydrofuran, Ph = C_6H_5), was reported in 1994.[1] This hexamer was shown to exhibit a slightly distorted hexagonal-prismatic framework of magnesium and nitrogen atoms, in which each N atom is coordinated by three Mg atoms and a phenyl group, and each Mg atom by three N atoms and the O atom of a thf. The compound can be used as a versatile starting reagent in a variety of reactions.[2,3] Very importantly, it has been shown to be an excellent imide transfer reagent.[2,4] In addition, reaction of $[(thf)MgNPh]_6$ with excess SO_2 leads to $\{(thf)Mg[O_2S(\mu\text{-}NPh)SO_2]\}_6$, which can be understood as insertion of twelve SO_2 molecules into the Mg–NPh bonds.[3] A few years later, the synthesis of the two naphthyl derivatives $[(thf)MgN(1\text{-naphthyl})]_6$ and $[(HMPA)MgN(1\text{-naphthyl})]_6$ (HMPA = hexamethylphosphoramide) with a similar framework followed.[2] Very recently, tetrameric species of the formula $[(D)MgN(2,4,6\text{-}Cl_3C_6H_2)]_4$ (D = 1,4-dioxane or tetrahydrofuran), have been synthesized.[5] In all these species the imido group consists of an aryl group directly bound to the nitrogen, and the imides were synthesized by reaction between dialkylmagnesium and the primary amine. Amides of the formula [R′MgN(H)R], where R and R′ are alkyl groups, have been shown to be unsusceptible to alkane (RH) elimination to give oligomeric magnesium imide compounds (because of their lower acidity).[4] Herein we report on the first synthesis and characterization of an example for a compound of the general formula $[(D)MgNR]_n$, in which R is *not* an aryl group, namely the species $[(thf)MgNSiPh_3]_4$.

Results and Discussion

The synthesis of the compound involves reaction of $Mg(n\text{-butyl})_2$ with one equivalent of H_2NSiPh_3 in a thf solution under reflux. The ^1H NMR spectrum of the reaction mixture after 17 h showed the disappearance of the *n*-butyl groups and of the N–H bonds. Crystalline product in 20–30 % yield precipitates from a thf solution layered with hexane at –19 °C. Figure 1 illustrates the structure of the product $[(thf)MgNSiPh_3]_4$ as determined by X-ray diffraction. The Mg–N bond lengths are 207.9(3), 208.9(3) and 210.1(3) pm. With 94.88(12)°, 95.11(12)° and 95.52(12)°, the N–Mg–N bond angles are slightly larger, and with 84.29(12)°, 84.63(12)° and 84.82(12)°, the Mg–N–Mg bond angles slightly smaller than the 90° angles of a cube. The four N–Si and Mg–O distances connecting the distorted heterocubane centre with the ligand shell were measured to be 168.4(3) and 201.0(3) pm long. The steric demand of the $SiPh_3$ groups is most likely responsible for the preference for a tetrameric rather than a hexameric assembly of the imide. From the space-filling model of the compound shown on the right side of Figure 1, one can see that the ligand shell covers the central heterocubane unit almost completely.

Quantum chemical calculations were employed to shed light on the possible general reaction pathway leading to the homoleptic imide species. These calculations were carried out for MgNPh rather than $MgNSiPh_3$, because of the large number of atoms in $MgNSiPh_3$. Figure 2 illustrates the standard Gibbs energies of several compounds relative to that of monomeric EtMgNHPh as calculated with B3LYP/TZVPP (see also Supporting Information).[6] Although no solvation effects were considered, these calcula-

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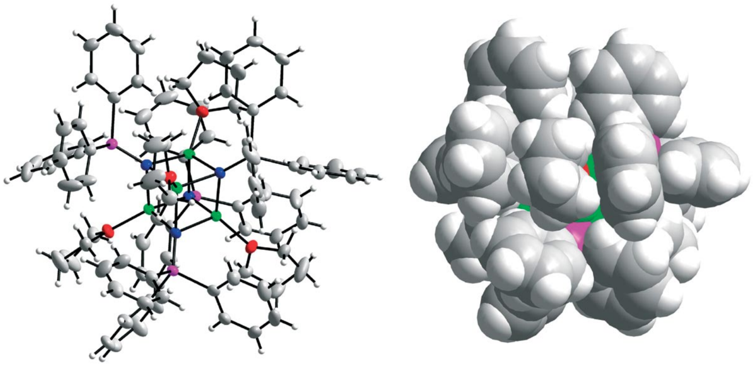

Figure 1. Structure of $[(thf)MgNSiPh_3]_4$ as derived from X-ray diffraction. Colour code: Mg green, N blue, Si purple, O red, C light grey, H white. Left side: ball-and-stick model, right side: space-filling model.

tions might provide valuable information about possible reaction pathways. Ethane elimination from monomeric EtMgNHPh to give MgNPh in its lowest energy singlet electronic state is associated with a ΔG^0 value of +194 kJ mol^{-1}, and this value increases to +249 kJ mol^{-1} if dimerization of the alkylmagnesium amide is taken into account. It should be mentioned that, according to B3LYP/TZVPP, monomeric MgNPh exhibits a triplet electronic ground state which is 46 kJ mol^{-1} lower in energy than the lowest energy singlet state (see Supporting Information). However, even if a barrier-free singlet–triplet conversion is assumed, and no other barrier opposes alkane elimination, the large ΔG^0 value seems to argue against any engagement of monomeric MgNPh in the reaction pathway. Moreover, for MgNH it has been shown that the singlet energy decreases relative to the triplet one at higher levels of theory [QCI or CCSD(T)], so that both states are thought to have similar energies within 5 kJ mol^{-1}.[7] It has been shown that solvation by thf molecules stabilizes the imide species significantly. Thus, HF/6-31G* calculations carried out previously for tetrameric and hexameric MgNPh returned average solvation energies normalized to a per monomer basis of –118 and –95 kJ mol^{-1}, respectively.[5] For the more sterically crowded tetrameric and hexameric MgN(2,4,6-$Cl_3C_6H_2$), the corresponding energies are –78 and –11 kJ mol^{-1}, respectively. However, the alkylmagnesium amide starting compounds are also significantly stabilized by solvent coordination,[8] and therefore the effect appears to be not large enough to compensate for the large positive ΔG^0 value for formation of the *monomeric* Mg imide. It is therefore more likely that dimeric imide is directly formed from dimeric alkylmagnesium amide and subsequently oligomerizes further.

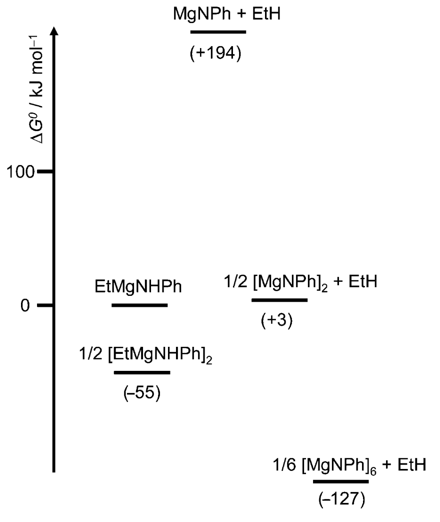

Figure 2. Calculated (B3LYP/TZVPP) standard Gibbs energies of several relevant species relative to that of monomeric ethylmagnesium(phenylamide).

Conclusions

We have reported on the first synthesis and characterization of the tetrameric magnesium imide $[(thf)MgNSiPh_3]_4$, enlarging the small number of homoleptic magnesium imide compounds which are known to date. The successful synthesis shows that these imides are not restricted to species featuring an aryl group directly attached to the nitrogen. The $SiPh_3$ and thf ligands cover almost completely the central slightly distorted cubic centre of $[(thf)MgNSiPh_3]_4$. The compound can now be used in a similar way to $[(thf)MgNPh]_6$ and $[(thf)MgN(naphthyl)]_6$ as an imide transfer reagent for the synthesis of transition-metal and main-group-element compounds featuring $NSiPh_3$ imido ligands.

Experimental Section

H_2NSiPh_3 (1.5 mmol) in thf (10 mL) was added dropwise to a thf (10 mL) solution of di-*n*-butylmagnesium (1.5 mmol) under reflux. After 17 h, the solvent was removed in vacuo to leave behind a white precipitate. White crystals of $[(thf)MgSiPh_3]_4$ were grown from a thf solution layered with hexane at –19 °C. Yield: 20–30%. ^1H NMR (400 MHz, [D$_8$]toluene): δ = 1.39 (quint, 4 H, CH_2, thf), 3.50 (m, 4 H, O–CH_2, thf), 7.10–7.14 (m, 9 H, *o*-H, *p*-H), 7.52–7.55 (m, 6 H, *m*-H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, [D$_8$]toluene): δ = 25.82 (CH_2, thf), 67.72 (O–CH_2, thf), 127.99 (*o*-C), 129.68 (*p*-C), 135.57 (*m*-C), 137.26 (*ipso*-C) ppm. Suitable crystals were taken directly out of the mother liquor, immersed in perfluorinated polyether oil and fixed on top of a glass capillary. Intensity data of a merohedrally twinned crystal were collected with a Nonius-Kappa CCD diffractometer having a low-temperature unit using graphite-monochromated Mo-K_α radiation. The temperature was set to 200 K. The data collected were processed with the standard Nonius software.[9] All calculations were performed by using the SHELXT-PLUS software package. Structures were solved by direct methods with the SHELXS-97 program and refined with the SHELXL-97 program.[10,11] Graphical handling of the structural data during solution and refinement was performed with XPMA.[12] Structural representations were generated by using Winray 32.[13] Atomic coordinates and anisotropic thermal parameters of non-hydrogen atoms were refined by full-matrix least-squares calculations. CCDC-662994 contains 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.

Supporting Information (see also the footnote on the first page of this article): Details of the quantum chemical calculations (illustration of the calculated structures and calculated coordinates).

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