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Alkyl Group Transmetalation Reactions in Electrolytic Solutions Studied by Multinuclear NMR

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Advantageous electrolytic solutions for rechargeable magnesium batteries are obtained by dissolving in THF the reaction products of $EtAlCl_2$ and Bu_2Mg, in various stoichiometric proportions. The components of these solutions are identified by multinuclear NMR (^{1}H, ^{13}C, ^{27}Al, and ^{25}Mg) and conductivity measurements for the closely related system where the organomagnesium species is Et_2Mg. The system with the highest electrochemical stability and relatively high ionic conductivity, denoted as a “2:1 complex”, is obtained from a 2:1 ratio of $EtAlCl_2$ and Et_2Mg and is shown to be composed of a chloride-bridged species, $Et_2ClAl-Cl-AlClEt_2^-$, and of $MgCl^+$, the result of transmetalation reactions.

Introduction

Magnesium is the metal with the highest energy density content after lithium, as an anode for batteries. However, despite the effort spent in the last five decades, no rechargeable magnesium battery has been developed. The major obstacle was the inability to develop an electrolytic solution from which magnesium can be plated and dissolved with high efficiency and that is also anodically stable. A battery based on magnesium is expected to be superior to many other battery systems, such as NiCd and lead-acid, and to be made of nonpoisonous materials.

In a search for electrolytic solutions that will realize our dream of developing rechargeable magnesium batteries, we synthesized ethereal solutions containing magnesium organochloro aluminate compounds of the formal general stoichiometry $Mg(AlCl_{4-n}R_n)_2$, $n = 1, 2$, $R = Et, Bu$, that are anodically stable and from which magnesium can be deposited highly reversibly. Of special interest is the compound of the general formula $Mg(AlCl_2BuEt)_2$ denoted in this paper “2:1 complex”. This compound is the reaction product between 1 equiv of dibutylmagnesium, Bu_2Mg, and 2 equiv of ethylaluminum dichloride, $EtAlCl_2$. Solutions of 2:1 complex in THF possess relatively high ionic conductivity and an electrochemical stability window in excess of 2.3 V; metallic magnesium can be reversibly plated from this solution with high current efficiency. In 1999 we presented, for the first time, a complete, practical, rechargeable magnesium battery, containing a magnesium anode, a solution of 2:1 complex in THF, and an intercalation cathode based on Mo_6S_8 (chevrel phase).[1] We realized that this compound is only one instance from a wide range of homologue compounds in which one can change both the reactant ratio and the identity of the halo-organo aluminum Lewis acid. Each product was found to possess different electrochemical properties, such as different electrochemical window, ionic conductivity, deposition overpotential, and deposition products. One of our most important challenges was to develop solutions that possess the highest electrochemical stability window possible, without compromising the other desirable properties. We speculated that the stronger the Lewis acidity of the acid (the halo-organo aluminum compound), the higher would be the stability of the complex salt solution toward oxidation. Indeed, the electrochemical stability window of a 0.25 M solution of 1:2 $Bu_2Mg + AlCl_xR_{3-x}$ ($x = 0-3$) in THF revealed a monotonic increase in the anodic stability as x increased from 0 to 3.[2] Unfortunately, the solution with the highest anodic stability exhibits relatively low magnesium deposition reversibility and high deposition overpotentials. Therefore, of this series of complexes, 2:1 complex was found to be the most advantageous case. As part of this study, we also explored the influence of changing the reactant ratio on the electrochemical properties. Figure 1 shows the specific conductivity of 0.25 M solutions of the reaction products of Bu_2Mg with $EtAlCl_2$ in THF at various reactant ratios. Surprisingly,

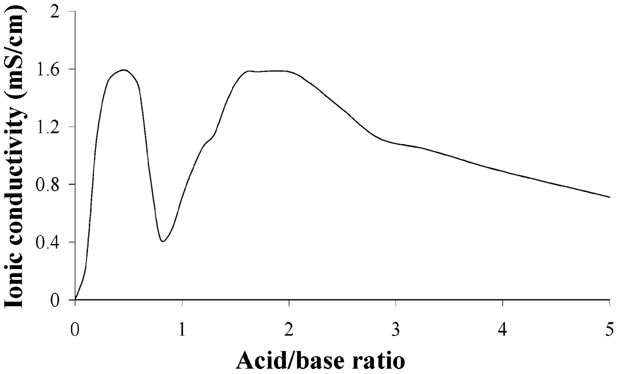

Figure 1. Specific conductivity of 0.25 M solutions of the reaction products of Bu_2Mg (“base”) with $EtAlCl_2$ (“acid”) in THF at various reactant ratios.

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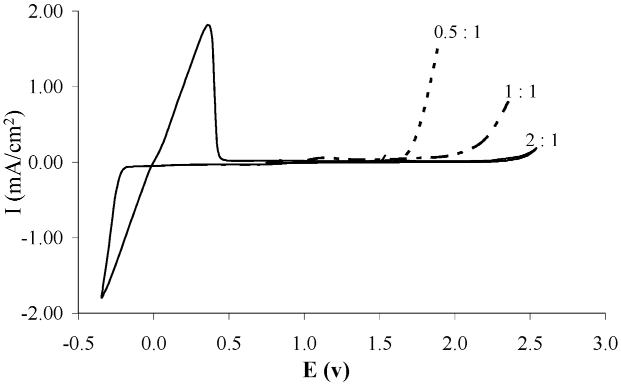

Figure 2. Typical cyclic voltammetry curve of the 2:1 complex on a Au electrode. Superimposed are the anodic parts of voltammograms from solutions with acid−base ratios of 1:1 and 0.5:1, respectively, demonstrating the increasing anodic stability window for solutions with higher acid content. Scan rate: 25 mV/s.

the curve presents a nonmonotonic behavior, with a clear minimum and two maxima at ca. 1:1, 1:2, and 2:1, respectively. We hypothesized that this behavior should be a result of the formation of distinct products at the different reactant ratios. Interestingly, the electrochemical stability of the various solutions is the highest close to the 1:2 ratio and becomes lower with an increasing content of Bu_2Mg (see Figure 2).

Attempts to determine the structure of the electrolyte by single-crystal XRD of a crystal grown from a 2:1 complex/THF solution revealed that the recrystallized material is not representative of the species in the solution.[3] Furthermore, controlled electrolysis in a setup for transference number determination, followed by elemental analysis of the migrating entities, did not resolve the question. We therefore decided to further investigate the system by a multinuclear NMR analysis of the various stages of the reaction.

Experimental Section

All chemical preparations and electrochemical measurements were carried out under pure argon atmosphere in M. Braun, Inc. gloveboxes (less than 1 ppm of water and oxygen).

Chemicals and Synthesis. A typical preparation of the 2:1 complex salt solution consists of the dropwise addition of 4.46 g of filtered 1 M dibutylmagnesium (Bu_2Mg) in hexane (Aldrich, 97%) to 9.11 g of a vigorously stirred, 1 M heptane solution of ethylaluminum dichloride ($EtAlCl_2$) (Aldrich, 97%). A mildly exothermic reaction takes place, yielding immediately a powdery white precipitate. The suspension thus formed is stirred at room temperature for an additional 48 h, after which it is vacuum-dried without separation or washing to yield an off-white solid containing a mixture of the initial reactants and their reaction products. Extra dry tetrahydrofuran (THF, Merck, Selectipure, >10 ppm water, as determined from a Karl Fischer titrator) is then added to this powder, usually to a nominal concentration of 0.25 M. Solutions prepared in this manner were clear and colorless.

A solution of diethylmagnesium (Et_2Mg) in hexane was prepared by the addition of a slight excess of dry, distilled 1,4-dioxane (Aldrich, 99.9%) to an ethylmagnesium chloride (EtMgCl) solution in THF (Aldrich, 97%), which caused the precipitation of $MgCl_2$·dioxane. The solution formed was decanted and filtered through a fine glass frit. A $MgCl_2$·2THF solution in THF was prepared by reacting an excess of pure magnesium foil (Merck, 99.95%) with a dry solution of $HgCl_2$ in THF.

Table 1. Oxidation Potential (in V) of THF Solutions[a]

	anion				
	$AlEt_4^-$	$AlEt_3Cl^-$	$AlEt_2Cl_2^-$	$AlEtCl_3^-$	$AlCl_4^-$
Mg^{2+}-containing solutions	1.7	1.9	2.2		
Mg^{2+}-free solutions		2.0	2.2	2.5	2.6

[a] Oxidation potential (anodic stability window) for various Et_xAlCl_{4-x} anions, in THF solutions with or without Mg^{2+} (in the latter, the cation is usually tetrabutylammonium), as determined from cyclic voltammetry in 0.25 M solutions of the anion, at 25 mV/s on gold electrodes.

Triethylaluminum (Et_3Al, Aldrich, 97%), diethylaluminum chloride (Et_2AlCl, Aldrich, 97%), $AlCl_3$ (Aldrich, 99.99%), and ethylaluminum dichloride ($EtAlCl_2$, Aldrich, 97%) were used as received. Tetrabutylammonium chloride (TBACl, Fluka, 97%) was dried in a vacuum oven at 75 °C for 24 h.

Magnesium-free organo-halo aluminate solutions, namely, $TBA^+AlEt_xCl^-_{4-x}$ (x = 0−3) in THF were synthesized in a similar manner by the reaction of equimolar amounts of tetrabutylammonium chloride with $AlEt_xCl_{3-x}$ (x between 0 and 3).

Electrochemistry. The electrochemical stability of the solutions was determined by their cyclic voltammetry in a one-compartment, three-electrode cell, using an EG&G, Inc. 273 potentiostat. The electrochemical cells consisted of magnesium metal counter and reference electrodes and either gold or platinum working electrodes. The scan rate used was 25 mV/s, and the anodic limit of the electrochemical window was determined at the deflection point, where the I vs E curve showed a rapid increase in the positive currents, usually, at ca. 5.0 $\mu A/cm^2$ above the background currents. Specific conductivities were measured for 0.25 M solutions with a digital conductometer (at 1 kHz) at 25 ± 0.5 °C.

NMR. NMR spectra were performed on a 14.1 T spectrometer at 600.1 (^1H), 150.9 (^{13}C), 156.3 (^{27}Al), and 36.7 (^{25}Mg) MHz. Solutions of 0.25−0.5 M in THF with respect to aluminum were run in 8 mm NMR tubes without a deuterium lock. ^{13}C and ^1H chemical shifts were referenced to the downfield THF signal (δ 68.17 and 3.68, respectively). ^{27}Al and ^{25}Mg chemical shifts are reported relative to external references: a solution of $AlCl_3$ in D_2O with a drop of concentrated HCl [$Al(D_2O)_6^{+3}$], and a saturated solution of $MgSO_4$ in D_2O, respectively. All the experiments were performed at room temperature (25 ± 2 °C).

Results

Figure 2 shows a typical cyclic voltammetry (CV) curve, obtained with an inert (Pt) electrode in a 2:1 complex/THF solution. A magnesium deposition process occurs at ca. −260 mV, forming a nucleation hysteresis loop at the reverse, anodic sweep. The reduction and reoxidation charge balance is ca. 97%. In the double-layer region of the anodic scan, very low currents are recorded, until a rapid increase in the current is evident, marking the anodic stability limit of the system, which, in this case, is 2.3 V. Superimposed are the positive vertexes of a series of voltammograms with solutions of the same nominal concentration (0.25 M), but with different acid:base ratios, as indicated in Figure 2. This picture demonstrates the trend in the electrochemical stability of the various solutions; the anodic stability limits are summarized in Table 1. The first row relates

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(3) Aurbach, D.; Gizbar, H.; Schechter, A.; Chusid, O.; Gottlieb, H. E.; Gofer, Y.; Goldberg, I. *J. Electrochem. Soc.* **2002**, 149**,** A115.

Table 2. NMR Data[a]

		^1H		^{13}C			
		CH_3[b]	CH_2[b]	CH_3	CH_2	^{27}Al	^{25}Mg
		Reaction Sequence					
1	$EtAlCl_2$ dimer	1.09	0.13	8.25	1.0 (300)	122 (800)	
2	$AlCl_3{\cdot}L_2$					64 (300)	
3	$Et_2ClAl-Cl-AlClEt_2^-$	0.99	−0.12	9.02	1.5 (50)	155 (2400)	
4	$MgCl^+$						4.1 (130)
5	$MgCl_2$						5.2 (180)
6	$Et_3Al{\cdot}L$	1.01	−0.19	9.78	0.2 (35)	178 (2200)	
7	Et_4Al^-	0.97	−0.48[c]	12.52	2.09[d]	155.4 (15)	
8	$EtMg^+ + MgCl_2$	0.97	−0.85	*e*	−2.50		2.5 (470)
		Model Compounds					
9	$Et_2AlCl{\cdot}L$	1.08	0.00	8.36	0.7 (105)	156 (1700)	
10	EtMgCl	1.08	−0.85	12.84	−3.07		55 (3800)
11	$MgCl_2$						8.7 (270)
12	$AlCl_3{\cdot}L_2$					63 (400)	

[a] Data refer to TMS solutions. Numbers indicate chemical shifts in ppm (for reference compounds, see Experimental Section) and, in parentheses, line widths in Hz when relevant, corrected for the extra broadening introduced in the data processing step. Presumably, L = THF (the magnesium species are, probably, also complexed with THF to coordination number 6). [b] $^3J_{HH} = 8$ Hz. [c] $^2J_{HAl} = 7.1$ Hz. [d] $^1J_{CAl} = 73.2$ Hz. [e] The signal is probably hidden under the other methyl peak at δ 12.52.

to solutions containing $Mg(AlCl_{4-n}Et_n)_2$, as indicated. The second row relates to similar solutions with tetrabutylammonium cations instead of Mg^{2+}.

To elucidate the chemical identity of the species in the various THF solutions obtained from the reaction between the organoaluminum acid ($EtAlCl_2$) and the R_2Mg base, we decided to perform an NMR analysis, at various acid/base ratios. Maximum information was obtained by running spectra for each of the nuclei: ^1H, ^{13}C, ^{25}Mg, and ^{27}Al. The two latter nuclei are quadrupolar ($I = 5/2$ for both) and hence often produce quite broad lines.[4−6] However, the ^{27}Al isotope is present in 100% natural abundance and has a relatively high magnetogyric ratio (similar to ^{13}C); with our experimental conditions, we could acquire a good-quality spectrum with a high S/N ratio within 15 min. In contrast, spectra of ^{25}Mg are much more difficult to obtain due to lower natural abundance (only 10%) and magnetogyric ratio (less than a quarter of that of ^{27}Al). Nonetheless, we were able to obtain good spectra in overnight runs. Due to the relative high concentration of the solutes, ^1H and ^{13}C signals were readily detectable even in the presence of the large THF peaks.

Preliminary experiments indicated that the presence of different types of alkyl substituents (ethyl and butyl, and the latter is actually a mixture of *n*- and *s*-butyl[3]) results in very complex NMR spectra. We therefore decided to conduct this study with Et_2Mg instead of Bu_2Mg. As expected, the ^{27}Al spectra were virtually identical, while the ^1H and ^{13}C traces were much easier to interpret (vide infra).

Using Et_2Mg as the Mg base in these studies is further justified by the fact that the conductivity of the $Et_2Mg-AlCl_2Et$ solutions, as a function of the acid−base ratio, is very similar to that of the solutions based on Bu_2Mg, as shown in Figure 3. Furthermore, electrochemical measurements proved that the 1:2 adduct in this all-ethyl system possesses the same key characteristics as 2:1 complex: Mg can be deposited electrochemically in high current efficiency and very high reversibility. The chevrel-phase cathodes can be intercalated reversibly with magnesium in the all-ethyl systems, and just like the "regular" 2:1 complex, they possess an electrochemical stability window wider than 2.2 V vs Mg.

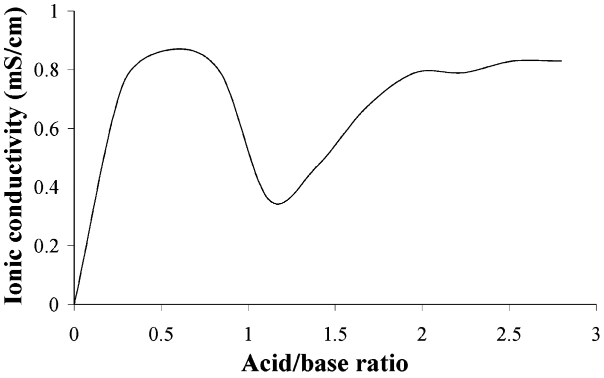

Figure 3. Specific conductivity of 0.25 M solutions of the reaction products of Et_2Mg ("base") with $EtAlCl_2$ ("acid") in THF, at various reactant ratios.

Scheme 1[a]

$$2EtAlCl_2.L + Et_2Mg.L_4 \rightarrow Et_2ClAl–Cl–AlClEt_2^- + MgCl^+.L_5 + L \quad \text{(eq. 1)}$$

$$EtAlCl_2.L + Et_2Mg.L_4 \rightarrow Et_3Al.L + MgCl_2.L_4 \quad \text{(eq. 2)}$$

$$EtAlCl_2.L + 2Et_2Mg.L_4 \rightarrow Et_4Al^- + EtMg^+.L_5 + MgCl_2.L_4 \quad \text{(eq. 3)}$$

[a] Presumably, L = THF (we have assumed that the magnesium species are all hexacoordinated).

The extensive NMR data that we have obtained are summarized in Table 2 and are fully consistent with the reaction sequence described in Scheme 1. This model is based on the following facts.

(1) When 0.5 equiv of Et_2Mg is added to the starting $EtAlCl_2$ (achieving an acid:base ratio of 2:1; see eq 1 in Scheme 1), a single Al-containing product is formed, with one ^{27}Al NMR peak. ^{27}Al chemical shifts are largely determined by the degree of coordination of the metal; in this case, δ 155 (Figure 4, bottom trace, and item 3, Table 2) is compatible with a tetracoordinated species.[4−6] The ^1H and ^{13}C spectra show only one type of ethyl group, and the chemical shifts of the methylene suggest that the Et is connected to an Al and not to a Mg atom (the methylene nuclei in MgEtCl appear at higher fields;

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(4) Benn, R.; Lehmkuhl, H.; Mehler, K.; Rufinska, A. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 534−536.

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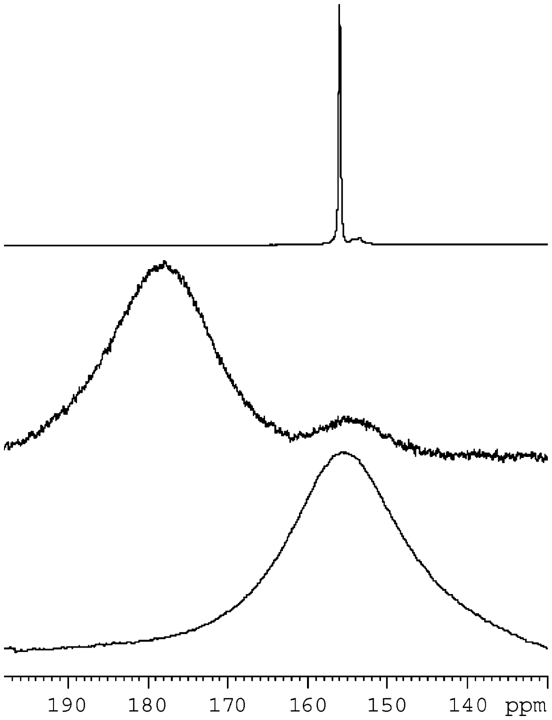

Figure 4. ^{27}Al NMR spectra at three stages in the addition of Et_2Mg to $EtAlCl_2$ (see text). Bottom, middle, and top traces correspond roughly to eqs 1, 2, and 3, respectively, in Scheme 1.

see items 8 and 10 in Table 2; cf. also item 9), so that transmetalation reactions have taken place. In view of the relatively high ionic conductivity of this solution (see Figure 3), we suggest that both the Al and Mg species carry a charge. We therefore propose a chloride-bridged dimeric aluminum anion and the $MgCl^+$ cation (both species have been described in the literature; see refs 7 and 8). A ^{25}Mg NMR spectrum gave a signal for the latter species that is consistent with a hexacoordinated magnesium atom (item 4, Table 2).

(2) Addition of more Et_2Mg to the previous sample results in the appearance of a second Al peak, at the expense of the first one, and when another half an equivalent is added (acid:base ratio of 1:1; see eq 2 in Scheme 1), this new peak predominates (see Figure 4, middle trace). This new, dominant species also has a tetracoordinated Al (δ 178) and, again, equivalent Al-bound ethyl groups. At intermediate proportions, where both species are seen, the integral ratios in the ^1H and ^{27}Al spectra are consistent with the assumption that we proceed from a diethylated to a triethylated Al species. ^{25}Mg NMR yielded a single, relatively sharp peak at ca. 5.2 ppm, similar to the spectrum obtained for a synthesized anhydrous $MgCl_2$ solution (prepared by the reaction of metallic magnesium with a $HgCl_2$ solution in THF), cf. items 5 and 11, Table 2. We attribute this signal to the hexacoordinated $MgCl_2{\cdot}4THF$.

(3) When a further equivalent of Et_2Mg is added (to a final acid:base ratio of 0.5:1), the ^{27}Al NMR spectrum changes drastically (Figure 4, top trace). Again, a single signal is dominant, but it is very sharp, indicating a much longer T_2 relaxation time. This suggests that the Al atom has tetrahedral (or higher) symmetry. Since the chemical shift is still in the range for tetracoordinated Al, we propose that a tetraethylaluminate anion (Et_4Al^-) has been formed. This is confirmed by the ^1H and ^{13}C spectra, in which the splitting of both types of protons and the CH_2 carbon to the ^{27}Al nucleus (into six lines of equal intensity) is clearly visible (Figure 5). A second type of ethyl group, integrating to one-fourth of the intensity of the first in the ^1H spectrum, is also observed. The ^1H and ^{13}C chemical shifts of the second ethyl group are similar to those measured for EtMgCl in THF (cf. items 7 and 9). The ^{25}Mg NMR spectrum of the 0.5:1 acid–base solution features a single, relatively broad, peak (δ 2.5, $W_{1/2}$ 470 Hz, item 8). This can be rationalized by postulating fast ligand exchange, on the NMR time scale, between $MgCl_2{\cdot}4THF$ and $EtMg^+{\cdot}5THF$.

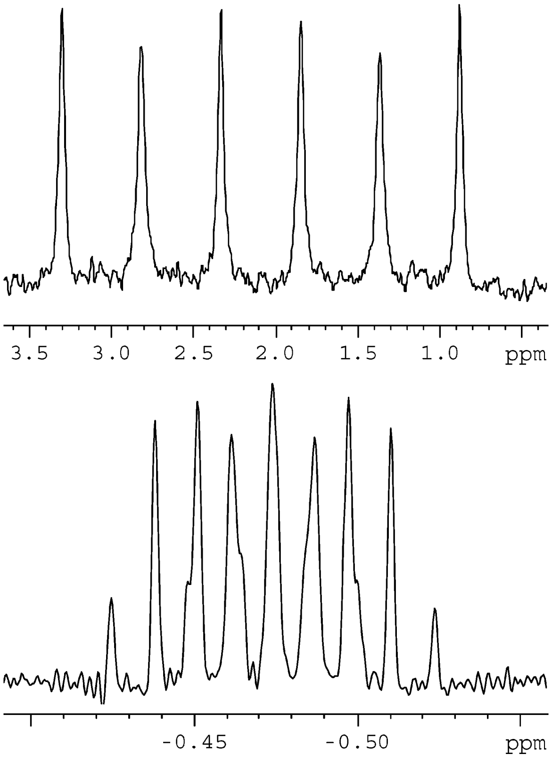

Figure 5. NMR spectra for the CH_2 moieties of Et_4Al^-, showing coupling interactions to ^{27}Al ($I = 5/2$). Top trace: $^{13}C\{^1H\}$ spectrum (150.9 MHz), $^1J_{CAl} = 73.2$ Hz. Bottom trace: ^1H spectrum (600.1 MHz), $^2J_{HAl} = 7.1$ Hz; the signal is further split into a quartet by the adjacent methyl protons, $^3J_{HH} = 7.9$ Hz. The resolution of the ^1H spectrum was enhanced with a Lorentzian to Gaussian conversion.

(4) As explained above, the equivalent reaction sequence with Bu_2Mg instead of Et_2Mg gives complex ^1H and ^{13}C NMR spectra. However, the ^{27}Al spectra of the solutions containing $MgBu_2$–$AlCl_2Et$ products are virtually identical to those of the solutions with all ethyl groups, as discussed above. The main difference occurs at the last stage. Several different lines can be detected, which are considerably sharpened by ^1H decoupling (from ca. 45 to 10–15 Hz), revealing the presence of at least 12 species, in different amounts (Figure 6). We can infer that the many possible combinations of four alkyl groups, every one of which can be Et, *n*-Bu, or *s*-Bu, is

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(8) Sobota, P.; Pluzinsky, T.; Utko, J.; Lis, T. *Inorg. Chem.* **1988**, *28*, 2217–2219.

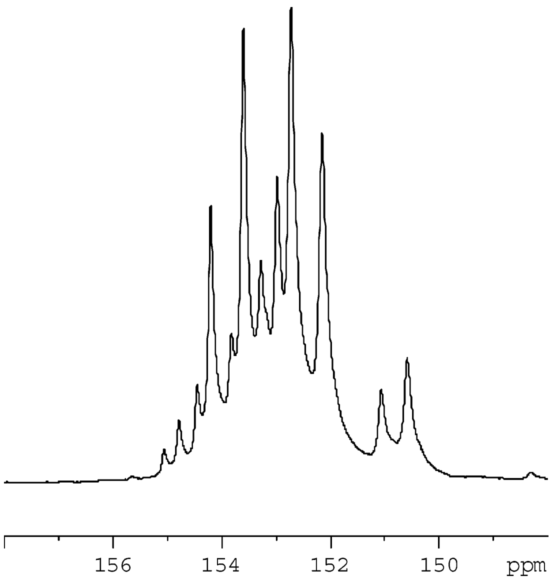

Figure 6. $^{27}Al\{^1H\}$ NMR spectra for R_4Al^-; R = Et, *n*-Bu, or *s*-Bu; see text.

Scheme 2

$$(EtAlCl_2)_2 + 3L \rightleftarrows Et_2AlCl.L + AlCl_3.L_2 \qquad \text{(eq. 4)}$$

responsible for the multiplicity of signals, and that the alkyl group exchange is slow on the NMR time scale.

(5) The spectrum of the starting acid ($EtAlCl_2$) in THF solution is more complex than we expected. There are three major Al peaks, one of which appears at δ 122 (item 1, Table 2). A similar signal is reported in the spectrum of neat $EtAlCl_2$ and attributed to a dimeric species.[9] A second peak (δ 155) is strongly reminiscent of $Et_2AlCl{\cdot}L$ (items 3 and 9, Table 2); corresponding peaks are also seen in the ^1H and ^{13}C spectra. It seems that the nature of the extra ligand—either THF or the bridging chloride of the dimer in the reaction sequence, see point 1, above—is of secondary importance in defining the chemical shifts of the Et_2Al fragment. Simple stoichiometry implies that the third species should have no alkyl substituents (indeed, only two sets of peaks are present in the ^1H and ^{13}C spectra) and that it should be present in the same amount as $Et_2AlCl{\cdot}L$, as is roughly the case (the exact proportions of the three species are dependent on the preparation of the sample). A possible candidate would be $AlCl_3$, and indeed, a spectrum of the commercial trichloride in THF gives an essentially identical signal (cf. items 6 and 12, Table 2). The ^{27}Al chemical shift of this compound (δ 64) indicates pentacoordination,[4−6] presumably with two molecules of the THF solvent (see Table 1). In fact, a similar signal in the ^{27}Al NMR spectrum of $AlCl_3$ in THF has been attributed to precisely this species.[10] We propose, therefore, that $EtAlCl_2$ in THF solution exists in the equilibrium described in Scheme 2.

Discussion

The model described above, while based on the NMR data, is also consistent with the chemical and electrochemical properties of the various solutions. The solution containing the 1:1 reactant ratio possesses the lowest specific ionic conductivity. As proposed, the main constituents of this solution are indeed the neutral species, R_3Al and $MgCl_2$. In contrast, for a 1:2 acid−base ratio, the major components are charged ions. In the case of the important 2:1 acid−base ratio, which forms the best electrolyte solutions for rechargeable Mg batteries, there is clear evidence of a charged tetracoordinated aluminum species containing both chlorine and alkyl ligands.

The above NMR results are also consistent with the decreasing anodic stability of the solutions with an increase in the Bu_2Mg concentration. Normally, the anodic stability of an electrolyte solution is determined by the vulnerability of the salt anion to electro-oxidation (unless it is the solvent or the electrode that oxidize). As can be learned from the reaction paths in Scheme 1, Bu_2Mg reacts with the aluminum compound by exchanging ligands in such a way that the magnesium atom takes as many chloride ions as possible, while the aluminum becomes enriched with organic ligands. This reaction path is not surprising, as the aluminum compound has a greater Lewis acid character, and thus its affinity to electron-donating ligands is superior to that of magnesium. The reactions above yield aluminum core species, surrounded by varying number of alkyl and chloride ligands. It is reasonable to expect that the more organic ligands the aluminum is bonded to, the more susceptible it should be toward oxidation, as the weakest bond in these compounds is the one between carbon and aluminum. However, in the presence of electron-withdrawing ligands such as Cl, the C−Al bond becomes less electron-rich, and thus stronger. This trend was shown previously in the ^1H and ^{13}C NMR spectra of a series of complex salts with various numbers of chlorines as ligands.[1] In the case of the solutions obtained from a reactant ratio of 1:1, the anodic stability trend is maintained, suggesting that although the solution is less conductive, and the concentration of Al-based anions is low, the stability is dominated by the oxidation of R_3Al, which, as expected, occurs at lower potentials than with anions that contain Cl^-.

In a complementary series of experiments we measured the electrochemical anodic stability window of a homologous series of organo-halo aluminum compounds, without the addition of organomagnesium compounds. The electrochemical oxidation potentials for these materials are tabulated in Table 1. These experiments confirmed the ever-increasing trend of the electrochemical oxidation susceptibility for aluminum compounds possessing more organic ligands. Moreover, the electrochemical stability of these solutions was very close to that observed with the above organomagnesium reactants, confirming that the anodic stability is solely dominated by the stability of the organo-halo aluminum compound as long as the salt-anion is not more electro-oxidation stable than the solvent, i.e., THF (as is the case for $AlCl_4^-$). The electrochemical stability window of these solutions is dominated by the weakest Al−C bond, and not, as previously thought, by C−Mg bonds, as in Grignard solutions.

With respect to magnesium species in the various solutions, the main components change from a charged

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magnesium species, which does not contain a Mg−C bond, in 2:1 complex, through $MgCl_2$ to $RMg^+ + MgCl_2$ in the 1:2 acid−base ratio sample. The existence of naked Mg^{2+} ions in THF solution is unlikely, since the polarity (and the donor number) of THF is expected to be too low for salt dissolution and dissociation. [e.g., $Mg(ClO_4)_2$ and $Mg(CF_3SO_2)$ are insoluble in THF].

Despite the existence of the above species as major components in the solution from which electrochemical magnesium deposition occurs, it is not clear if these are also the electroactive ones. It is definitely conceivable that in the electrochemical deposition and dissolution of magnesium from 2:1 complex solutions, other undetected species play a major role. The detection limit is no better than 3% in the case of ^1H and ^{13}C NMR and much worse for ^{25}Mg and ^{27}Al. These solutions may exist in complicated dynamic equilibria that involve many different species, some of which are below the detection limit of the NMR. It is possible that the organomagnesium species that is crucial in enabling reversible electrochemical deposition of magnesium from 2:1 complex solutions is below the detection limit or exists only as a short-lived intermediate. What may strongly support the latter assumption is the fact that in general, as the base−acid ratio in these solutions is higher, the kinetics of Mg deposition and dissolution are faster (e.g., the addition of small amounts of Bu_2Mg to 2:1 complex solutions considerably decreases the Mg nucleating overpotential and increases the possible rates of Mg deposition and dissolution). On the other hand, as was mentioned above, there is a clear correlation between the anodic stability window, the solution's ionic conductivity, and the detected organoaluminum species. Furthermore, recent electroanalytical measurements confirmed that even inorganic magnesium species, such as $MgCl_2$ and $MgCl_4^{2-}$, could deposit magnesium. Hence, although one cannot be confident regarding the electrochemical active species in deposition, there is more evidence that these are the very ones unraveled in this study.

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