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A fundamental study on the $[(\mu\text{-Cl})_3\text{Mg}_2(\text{THF})_6]^+$ dimer electrolytes for rechargeable Mg batteries[†]

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Abstract

The long sought solvated $[\text{MgCl}]^+$ species in the Mg-dimer electrolytes was characterized by soft mass spectrometry. The presented study provides an insightful understanding on the electrolyte chemistry of rechargeable Mg batteries.

To address the global problems of escalating energy demand and increasing emissions of CO_2 , it is critical to develop effective approaches to convert renewable but intermittently available energy sources (*e.g.* solar and wind energy) into reliable energy forms. Battery systems with low cost, high energy density and long cycling lifetime have been suggested as viable technologies for storing sustainable energy.¹ Recently, rechargeable magnesium (Mg) batteries have been advocated as promising battery systems alternative to lithium or sodium based batteries for grid scale energy storage, powering portable devices, and transportation applications.^{1a,2} There are several technical advantages of Mg batteries over Li batteries and Na batteries. Mg is earth abundant and low-cost (*ca.* 24 times cheaper than Li). As an anode material, Mg is safe to use without dendrite formation (*vs.* Li, Li-ion or Na batteries) and has high volumetric capacity (3832 A h L^{-1} *vs.* 2062 A h L^{-1} for Li and 1165 A h L^{-1} for Na) due to its two-electron redox chemistry. Mg based electrolytes are environmentally benign. Furthermore, Mg has a sufficient high reduction potential (-2.37 V vs. SHE) amenable for assembling high energy density batteries with suitable cathode materials.

In 1990, Gregory *et al.* made a major breakthrough in electrochemical Mg deposition by using Al or B Lewis acid additives to enhance electrochemical performance of Grignard reagents and MgBu_2 electrolytes.³ Since then, there have been continuous efforts in

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developing Mg conductive electrolytes for rechargeable Mg batteries by Aurbach⁴ and others.⁵ We have put our efforts in developing advanced Mg electrolytes with improved oxidation stability and electrophile compatibility by avoiding the use of nucleophilic Mg sources such as Grignard reagents or dialkyl magnesium.⁶ Poor oxidation stability and/or undesired nucleophilicity of the reported electrolytes prepared from nucleophilic Mg sources are attributed to reactive alkyl or aryl anions in these reagents.^{4b,6} Based on a straightforward retrosynthesis analysis on the $[(\mu\text{-Cl})_3\text{Mg}_2(\text{THF})_6]^+$ dimer, a common recrystallized product of popular Mg–Cl complex electrolytes,^{4b,5a,c,7} we developed a facile approach (termed as mono-Cl abstraction, see Scheme 1) using MgCl_2 and an Al Lewis acid to produce high performance Mg-dimer containing electrolytes.⁶

The MgCl_2 –Al Lewis acid electrolytes are much cleaner compared to electrolytes made from nucleophilic Mg reagents in terms of composition because of the simple and clean Cl^- metathesis reaction without complication by nucleophilic alkyl or aryl species.^{5c,6} Therefore, these electrolytes provide a unique opportunity to understand the solution chemistry of the $[(\mu\text{-Cl})_3\text{Mg}_2(\text{THF})_6]^+$ dimer and further its electrochemical behaviors. Previously, we proposed a reaction mechanism for the formation of the Mg-dimer coordination complex from MgCl_2 and an Al Lewis acid by the mono-Cl abstraction approach (see Scheme 1). THF solvated MgCl_2 , *trans*- $\text{MgCl}_2(\text{THF})_4$, undergoes THF dissociation and subsequent mono- Cl^- abstraction by an Al Lewis acid (*e.g.* AlPh_3 in Scheme 1) to generate the reactive intermediate $[\text{MgCl}]^+$ cation, $[\text{MgCl}(\text{THF})_3]^+$. Coordination unsaturation of $[\text{MgCl}(\text{THF})_3]^+$ can promote a dimerization reaction with $\text{MgCl}_2(\text{THF})_3$ to result in the Mg-dimer cation.^{4b,6} Both $[(\mu\text{-Cl})_3\text{Mg}_2(\text{THF})_6]^+$ (ref. 5c) and $[\text{MgCl}(\text{THF})_5]^+$ (ref. 2b) have been proposed to be the active species responsible for electrochemical Mg cycling. However, there is no experimental evidence for the existence of THF solvated $[\text{MgCl}]^+$ in the solution of dimer electrolytes.^{4b} In this study, we report the first experimental evidence of a solution $[\text{MgCl}]^+$ species, $[\text{MgCl}(\text{THF})_3]^+$, in Mg-dimer electrolytes using subambient pressure ionization with nanoelectrospray mass spectrometry (SPIN-MS).⁸ In combination with additional results, the coordination chemistry of the Mg-dimer electrolytes is elucidated and electrochemical mechanisms involving Mg^{2+} and Cl^- transport for reversible Mg deposition and stripping of the Mg-dimer electrolytes have been proposed and discussed.

In an effort to further understand the chemical nature of the Mg-dimer electrolytes and elucidate the proposed reaction mechanism,^{4b,6} we attempted to detect the $[\text{MgCl}]^+$ monocation in our electrolyte solution. We first tried conventional electrospray ionization (ESI) MS, as the technique can resolve charged species based on values of the mass to charge ratio (m/z) and the corresponding isotopic patterns. However, no meaningful species were detected in the positive mode of ESI-MS with $[(\mu\text{-Cl})_3\text{Mg}_2(\text{THF})_6]\text{AlPh}_3\text{Cl}$ at different concentrations (from 0.05 mM up to 5 mM). Similar results were obtained using $[(\mu\text{-Cl})_3\text{Mg}_2(\text{THF})_6]\text{AlCl}_4$ and $[(\mu\text{-Cl})_3\text{Mg}_2(\text{THF})_6]\text{AlEtCl}_3$ as electrolytes.⁶ We rationalized that Mg–THF coordination interaction is too labile to survive under typical ESI-MS interface configuration which operates at an inlet temperature of 200 °C. So we started to seek a MS technique with a softer ESI source. We found that SPIN-MS⁸ is a unique MS interface technique with high ionization efficiency and a softer ion source which enables the

characterization of compounds with weak chemical bonds with high sensitivity. The SPIN source can be operated at a temperature below 80 °C and may provide a chance to detect positively charged THF solvated $[\text{MgCl}]^+$ species. To our delight, a $[\text{MgCl}]^+$ species with three THF coordination, $[\text{MgCl}(\text{THF})_3]^+$, was consistently identified at 275.13 m/z by SPIN-MS (Fig. 1) for $[(\mu\text{-Cl})_3\text{Mg}_2(\text{THF})_6]\text{AlPh}_3\text{Cl}$ THF solution. The match of the experimental and calculated isotope patterns further confirms its identity (Fig. 1). $[\text{MgCl}(\text{THF})_3]^+$ is either obtained directly from the solution or generated from $[\text{MgCl}(\text{THF})_5]^+$ during the ionization process. In the latter case, the results suggest that Mg–THF bonds in $[\text{MgCl}(\text{THF})_3]^+$ are stronger than the ones in $[\text{MgCl}(\text{THF})_5]^+$. However, no signal was observed for the dimer cation. Preliminary DFT calculations suggest that the $[\text{MgCl}]^+$ monomer is more dominant over the dimer cation in the equilibrium, which explains a lower possibility to observe the dimer cation. A recent study also suggests that the dimer is preferred in the solid state.⁹ Another possibility is the lack of sufficient stability of the dimer cation under the testing conditions. Consistently, the $[\text{MgCl}(\text{THF})_3]^+$ cation was also clearly identified in the $[(\mu\text{-Cl})_3\text{Mg}_2(\text{THF})_6]\text{AlEtCl}_3$ electrolyte (Fig. S5, ESI[†]). The SPIN-MS studies of the MgCl_2 THF solution without adding an Al Lewis acid did not show the monocation signal. To the best of our knowledge, the SPIN MS results are the first experimental evidence for the existence of the THF solvated $[\text{MgCl}]^+$ monocation in the solution of $[(\mu\text{-Cl})_3\text{Mg}_2(\text{THF})_6]^+$ dimer electrolytes. The identification of the $[\text{MgCl}(\text{THF})_3]^+$ monocation establishes the reaction nature of mono-Cl abstraction of solvated MgCl_2 by an Al Lewis acid as described above (see Scheme 1).

Raman spectroscopic studies of $[(\mu\text{-Cl})_3\text{Mg}_2(\text{THF})_6]\text{AlPh}_3\text{Cl}$ in solution were first attempted but no resolved spectrum was obtained due to strong fluorescence. The Raman spectrum of $[(\mu\text{-Cl})_3\text{Mg}_2(\text{THF})_6]\text{AlPh}_3\text{Cl}$ in the solid state confirmed the presence of the solvated MgCl_2 species, showing a diagnostic peak at 209 cm^{-1} (Fig. S1, ESI[†]). The weak peak at 252 cm^{-1} is assigned to $[(\mu\text{-Cl})_3\text{Mg}_2(\text{THF})_6]^+$ and two peaks at 618 and 653 cm^{-1} are attributed to phenyl ligand ring wagging of the AlPh_3Cl^- anion.^{4b} The SPIN mass, Raman spectroscopic results, and the established solid structure of $[(\mu\text{-Cl})_3\text{Mg}_2(\text{THF})_6]\text{AlPh}_3\text{Cl}$,⁶ provide a full experimental picture of the equilibrium between $[(\mu\text{-Cl})_3\text{Mg}_2(\text{THF})_6]^+$ and THF solvated $[\text{MgCl}]^+$ and MgCl_2 .

Cl^- is the primary ligand in supporting the coordination structures of solution Mg^{2+} species and defines their electronic structures, *i.e.* frontier HOMO and LUMO energies that are closely associated with redox potentials of electron transfer reactions. Studying Cl^- ligand behaviors can lead to further insights into the $[(\mu\text{-Cl})_3\text{Mg}_2(\text{THF})_6]^+$ dimer and species in equilibrium with it in terms of Cl^- and Mg^{2+} ion transport, and electrochemical Mg deposition and stripping. Aurbach *et al.* reported that external Cl^- anions can affect the chemical equilibrium of $[(\mu\text{-Cl})_3\text{Mg}_2(\text{THF})_6]^+$ and suggested that $[\text{MgCl}_4]^{2-}$ species are formed in the reaction of the APC electrolyte with Cl^- .¹⁰ However, the presence of MgPh_2 in the APC electrolyte^{6,10} can also react with external Cl^- due to the Schlenk equilibrium and complicate data interpretation. As our electrolytes are less complex than Aurbach's all phenyl complex (APC) electrolytes,^{4b,6,10} we anticipate that our electrolytes would provide

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new insights into the reactivities of the $[(\mu\text{-Cl})_3\text{Mg}_2(\text{THF})_6]^+$ dimer electrolyte with Cl^- . So we investigated the Cl^- effect on the $[(\mu\text{-Cl})_3\text{Mg}_2(\text{THF})_6]\text{AlPh}_3\text{Cl}$ electrolyte using various physical methods.

^{25}Mg NMR studies were carried out to monitor the effect of Cl^- on the ^{25}Mg chemical shift of $[(\mu\text{-Cl})_3\text{Mg}_2(\text{THF})_6]^+$. As shown in Fig. 2, $[(\mu\text{-Cl})_3\text{Mg}_2(\text{THF})_6]\text{AlPh}_3\text{Cl}$ exhibits a broad singlet at 5.3 ppm, consistent with an exchange process of the dimer with solvated $[\text{MgCl}_2]$ and $[\text{MgCl}]^+$ species. Upon addition of tetrabutylammonium chloride (TBACl) as the Cl^- source, the Mg resonance gradually shifts from 5.3 ppm to a lower field up to 11.9 ppm at 0.1M Cl^- (Fig. 2 and Fig. S2, ESI[†]). At the same time, the peak width of the Mg resonances broadens from 207.5 Hz to 419 Hz (see Fig. S2, ESI[†]), indicating a slower exchange process with increasing Cl^- concentration. The changes of the chemical shift and its peak width are consistent with the formation of new Mg species or a change of the chemical equilibrium of $[(\mu\text{-Cl})_3\text{Mg}_2(\text{THF})_6]^+$ upon addition of Cl^- . During the addition of Cl^- , there was no precipitate of MgCl_2 formed. The solution after adding Cl^- stayed clear for days. No obvious spectroscopic change was observed in the $^{27}\text{Al}\{^1\text{H}\}$ NMR spectrum after addition of Cl^- (Fig. S3, ESI[†]). To gain further understanding of the chemical equilibrium, the solution of $[(\mu\text{-Cl})_3\text{Mg}_2(\text{THF})_6]\text{AlPh}_3\text{Cl}$ and TBACl in a 1 : 1 ratio was examined by SPIN MS. It was found that the signal of $[\text{MgCl}(\text{THF})_3]^+$ at 275.2 m/z became significantly more intense than that of the $[(\mu\text{-Cl})_3\text{Mg}_2(\text{THF})_6]\text{AlPh}_3\text{Cl}$ sample without adding Cl^- (Fig. S4, ESI[†]). However, attempted SPIN-MS negative mode experiments did not identify new Mg species, either of $[\text{MgCl}_3(\text{THF})]^-$ or $[\text{MgCl}_4]^{2-}$.

Fig. 3 displays the cyclic voltammograms of $[(\mu\text{-Cl})_3\text{Mg}_2(\text{THF})_6]\text{-AlPh}_3\text{Cl}$ at various concentrations of TBACl. Upon increasing the Cl^- concentration to 0.02 M, the current intensities of Mg deposition and stripping initially increased, consistent with enhanced solution conductivity (Fig. S7, ESI[†]). However, when the Cl^- concentration was above 0.03 M, the current started to decrease. To clearly demonstrate the experimental observation, a plot of Mg deposition and stripping charge *versus* Cl^- concentration is shown in Fig. S7 (ESI[†]). Meanwhile, solution conductivity (0.96 mS cm^{-1} at 0.02 M Cl^-) started to decrease while there was no apparent relationship between solution conductivity and Cl^- concentration (Fig. S7, ESI[†]). The effect of Cl^- on the electrochemical behaviors of $[(\mu\text{-Cl})_3\text{Mg}_2(\text{THF})_6]\text{AlPh}_3\text{Cl}$ is different from what was observed for Aurbach's APC electrolyte.¹⁰ The difference is ascribed to the different solution constitutions of two electrolytes. Upon the addition of Cl^- , coulombic efficiencies for Mg cycling are retained *ca.* 100% and overpotential stays at *ca.* 0.29 V. The decrease of Mg cycling current at higher Cl^- concentrations is believed to be ascribed to the change of the chemical equilibrium of the electrolyte solution with Cl^- as indicated by the ^{25}Mg NMR spectroscopic studies. There are two possibilities: (a) if the $[(\mu\text{-Cl})_3\text{Mg}_2(\text{THF})_6]^+$ dimer is the active species for Mg deposition and stripping, then addition of Cl^- can shift the equilibrium to the mononuclear Mg species and lower the concentration of $[(\mu\text{-Cl})_3\text{Mg}_2(\text{THF})_6]^+$; (b) if the solvated $[\text{MgCl}]^+$ is the active species, the added Cl^- can complex with $[\text{MgCl}]^+$ to form solvated MgCl_2 to lower the concentration of the monomeric cation. If MgCl_2 had formed, it would have precipitated out of the solution as it is barely soluble in THF. One explanation is that the formed $[\text{MgCl}_2]$ could complex with the dimer cation to form a soluble trimmer cation,

$[\text{Mg}_3(\mu^3\text{-Cl})_2(\mu^2\text{-Cl})_3\text{THF}_6]^+$ (ref. 11) (see Scheme 2), consistent with the observed downshift of ^{25}Mg resonance. It is less likely that $[\text{MgCl}_2]$ can react with Cl^- to form $[\text{MgCl}_3]^-$ (ref. 12) and further $[\text{MgCl}_4]^{2-}$ dianions¹⁰ as these Mg anions would lead to high-field shift of the averaged Mg resonance. We are conducting comprehensive DFT calculations to gain insights into these possible reactions.

In terms of the solution nature of the dimer electrolyte and its reactivity with external Cl^- described above, comprehensive mechanisms have been proposed for Mg^{2+} and Cl^- transport and their involvement in Mg deposition and stripping of the dimer electrolyte in the operation of Mg batteries (Scheme 2). The proposed mechanism is an updated version of Aurbach's mechanism^{2b} by providing new aspects of the Mg electrolyte chemistry. For discussion purpose, $[\text{MgCl}(\text{THF})_3]^+$ and *cis*- $\text{MgCl}_2(\text{THF})_3$ will be used as primary species in equilibrium with $[(\mu\text{-Cl})_3\text{Mg}_2(\text{THF})_6]^+$ although they can undergo THF solvation to form $[\text{MgCl}(\text{THF})_5]^+$ and *trans*- $\text{MgCl}_2(\text{THF})_4$ (Scheme 1). Either the $[(\mu\text{-Cl})_3\text{Mg}_2(\text{THF})_6]^+$ or the $[\text{MgCl}(\text{THF})_3]^+$ monocation on the anodic electrode surface participates in the first electron transfer reaction to form a neutral $[\text{MgCl}]^0$ absorbed on the electrode. It should be noted that our preliminary DFT calculations suggest that the $[\text{MgCl}]^+$ cation is predominant in solution. Then the surface $[\text{MgCl}]^0$ species undergoes a second electron reduction to result in metallic Mg. It is believed that the intermediate of $[\text{MgCl}]^0$ is the key to the dendrite free deposition of Mg using $[(\mu\text{-Cl})_3\text{Mg}_2(\text{THF})_6]^+$ electrolytes and its formation is the rate determining step for Mg deposition, providing a kinetic control for the overall electron transfer reactions. However, there is no experimental evidence reported for the surface bound species. This principle can be applied to other anion-supported Mg electrolytes.^{5b,13} In the meantime, the released Cl^- will be trapped by $[\text{MgCl}]^+$ to form $[\text{MgCl}_2]^-$ species and subsequently $[\text{Mg}_3(\mu^3\text{-Cl})_2(\mu^2\text{-Cl})_3(\text{THF})_6]^+$ (Scheme 2). Alternatively, the solvated Mg^{2+} could directly react with $[\text{MgCl}_2]^-$ to regenerate $[\text{MgCl}]^+$ (Scheme S1, ESI[†]).

In summary, we have experimentally identified the long-sought solvated $[\text{MgCl}]^+$ species in the $[(\mu\text{-Cl})_3\text{Mg}_2(\text{THF})_6]^+$ electrolyte solution using the SPIN-MS technique, a unique tool to study weakly coordinating complexes. The identified $[\text{MgCl}]^+$ species confirmed the reaction nature of mono- Cl^- abstraction of solvated MgCl_2 with an Al Lewis acid and its role in forming the well-known $[(\mu\text{-Cl})_3\text{Mg}_2(\text{THF})_6]^+$ dimer. We suggest that both $[(\mu\text{-Cl})_3\text{Mg}_2(\text{THF})_6]^+$ and $[\text{MgCl}(\text{THF})_3]^+$ as monocations can be the active species responsible for Mg deposition. Synergistic operation mechanisms of co-existing solvated MgCl_2 and $[\text{MgCl}]^+$ were proposed for electrochemical Mg cycling and Mg^{2+} and Cl^- transport in the operation of Mg batteries. The present fundamental understanding of the coordination chemistry of the Mg–Cl complex electrolytes will inspire the synthetic design of next generation Mg electrolytes for rechargeable Mg batteries.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Notes and references

1. (a) Armand M, Tarascon JM. *Nature*. 2008; 451:652. [PubMed: 18256660] (b) Liu J, Zhang JG, Yang Z, Lemmon JP, Imhoff C, Graff GL, Li L, Hu J, Wang C, Xiao J, Xia G, Viswanathan VV, Baskaran S, Sprengle V, Li X, Shao Y, Schwenzer B. *Adv Funct Mater*. 2013; 23:929.(c) Yang Z, Zhang J, Kintner-Meyer MCW, Lu X, Choi D, Lemmon JP, Liu J. *Chem Rev*. 2011; 111:3577. [PubMed: 21375330] (d) Goodenough JB, Park KS. *J Am Chem Soc*. 2013; 135:1167. [PubMed: 23294028]
2. (a) Muldoon J, Bucur CB, Oliver AG, Sugimoto T, Matsui M, Kim HS, Allred GD, Zajicek J, Kotani Y. *Energy Environ Sci*. 2012; 5:5941.(b) Yoo HD, Shterenberg I, Gofer Y, Gershinsky G, Pour N, Aurbach D. *Energy Environ Sci*. 2013; 6:2265.(c) Kim H, Jeong G, Kim YU, Kim JH, Park CM, Sohn HJ. *Chem Soc Rev*. 2013; 42:9011. [PubMed: 23954955]
3. Gregory TD, Hoffman RJ, Winterton RC. *J Electrochem Soc*. 1990; 137:775.
4. (a) Aurbach D, Lu Z, Schechter A, Gofer Y, Gizbar H, Turgeman R, Cohen Y, Moshkovich M, Levi E. *Nature*. 2000; 407:724. [PubMed: 11048714] (b) Pour N, Gofer Y, Major DT, Aurbach D. *J Am Chem Soc*. 2011; 133:6270. [PubMed: 21456525]
5. (a) Guo Y, Zhang F, Yang J, Wang F, NuLi Y, Hirano S. *Energy Environ Sci*. 2012; 5:9100.(b) Mohtadi R, Matsui M, Arthur TS, Hwang SJ. *Angew Chem, Int Ed*. 2012; 51:9780.(c) Kim HS, Arthur TS, Allred GD, Zajicek J, Newman JG, Rodnyansky AE, Oliver AG, Boggess WC, Muldoon J. *Nat Commun*. 2011; 2:2.(d) Lv D, Xu T, Saha P, Datta MK, Gordin ML, Manivannan A, Kumta PN, Wang D. *J Electrochem Soc*. 2013; 160:A351.(e) Lv D, Tang D, Duan Y, Gordin ML, Dai F, Zhu P, Song J, Manivannan A, Wang D. *J Mater Chem A*. 2014; 2:15488.
6. Liu T, Shao Y, Li G, Gu M, Hu J, Xu S, Nie Z, Chen X, Wang C, Liu J. *J Mater Chem A*. 2014; 2:3430.
7. Sakamoto S, Imamoto T, Yamaguchi K. *Org Lett*. 2001; 3:1793. [PubMed: 11405713]
8. (a) Page JS, Tang K, Kelly RT, Smith RD. *Anal Chem*. 2008; 80:1800. [PubMed: 18237189] (b) Marginean I, Page JS, Tolmachev AV, Tang K, Smith RD. *Anal Chem*. 2010; 82:9344. [PubMed: 21028835] (c) Marginean I, Kronewitter SR, Moore RJ, Slys GW, Monroe ME, Anderson G, Tang K, Smith RD. *Anal Chem*. 2012; 84:9208. [PubMed: 23025344]
9. Wan LF, Prendergast D. *J Am Chem Soc*. 2014; 136:14456. [PubMed: 25243732]
10. Gofer Y, Chusid O, Gizbar H, Viestfrid Y, Gottlieb HE, Marks V, Aurbach D. *Electrochem Solid-State Lett*. 2006; 9:A257.
11. Barile CJ, Barile EC, Zavadil KR, Nuzzo RG, Gewirth AA. *J Phys Chem C*. 2014; 18:27623.
12. Liao C, Guo B, Jiang D-e, Custelcean R, Mahurin SM, Sun X-G, Dai S. *J Mater Chem A*. 2014; 2:581.
13. Shao Y, Liu T, Li G, Gu M, Nie Z, Engelhard M, Xiao J, Lv D, Wang C, Zhang J-G, Liu J. *Sci Rep*. 2013; 310.1038/srep03130

Fig. 1. The m/z isotopic distribution of the $[\text{MgCl}(\text{THF})_3]^+$ peak in the positive mode of SPIN MS of $[(\mu\text{-Cl})_3\text{Mg}_2(\text{THF})_6]\text{AlPh}_3\text{Cl}$. The inset shows the calculated isotopic pattern for $[\text{MgCl}(\text{THF})_3]^+$.

Fig. 2. ^{25}Mg NMR spectra of $[(\mu\text{-Cl})_3\text{Mg}_2(\text{THF})_6]\text{AlPh}_3\text{Cl}$, 0.1 M in THF (collected at 25 °C) in the presence of tetrabutylammonium chloride (TBACl) at different concentrations as indicated.

Fig. 3.

Cyclic voltammograms of $[(\mu\text{-Cl})_3\text{Mg}_2(\text{THF})_6]\text{AlPh}_3\text{Cl}$ (0.1M) at various concentrations of TBACl as indicated. For clearance, cyclic voltammograms with TBACl of 0.01, 0.03, 0.05, 0.07, 0.09 M are given in Fig. S6 in the ESI;[†] conditions: Pt working electrode, Mg reference electrode, glassy carbon counter electrode, 50 mV s⁻¹.

Scheme 1.

Scheme 2.