**Metal–Metal Bonds**

DOI: 10.1002/anie.201404284

# Synthesis of a Dimeric Magnesium(I) Compound by an $Mg^I/Mg^{II}$ Redox Reaction**

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***Abstract:*** *The synthesis of dimeric magnesium(I) compounds of the general type RMgMgR (R = monoanionic substituent) is still a challenging synthetic task and limited to few examples with sterically demanding ligands with delocalized CN-frameworks that all have been accessed by Na or K metal reduction of magnesium(II) halide precursors. Here we report on the synthesis of a novel diiminophosphinato magnesium(I) compound that has been synthesized by a facile redox reaction using a known magnesium(I) complex. The synthetic strategy may be applicable to other ligand systems and can help expand the class of low oxidation state magnesium complexes even if reductions with Na or K are unsuccessful. The new dimeric magnesium(I) complex has been structurally characterized and undergoes a C–C coupling reaction with tert-butylisocyanate.*

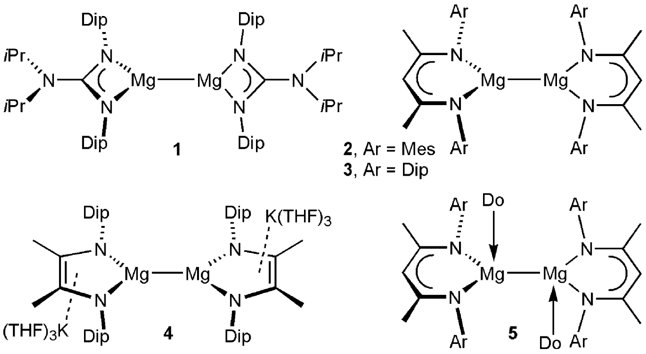
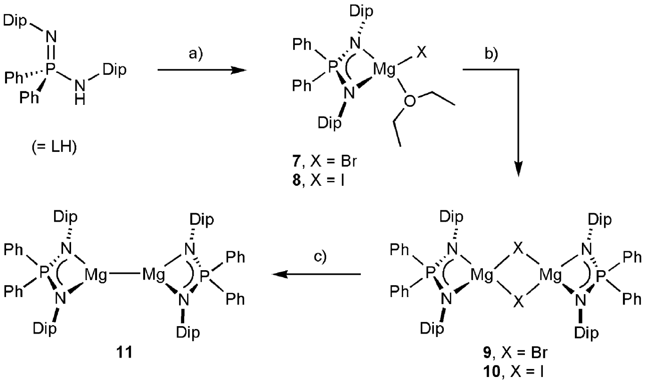


***Figure 1.*** Well-defined dimeric magnesium(I) compounds; Dip = 2,6-$iPr_2C_6H_3$, Mes = 2,4,6-$Me_3C_6H_2$, Do = neutral donor ligands.

Stable dimeric magnesium(I) compounds with Mg–Mg single bonds[1] are known since 2007[2] and represent coordination compounds of the $Mg_2^{2+}$ cation with anionic, N,N′-chelating ligands (for example, see compounds **1**–**5**, Figure 1). These mainly encompass a series of β-diketiminate derivatives such as **2** and **3**,[1–3] and their respective vicinal 1,2-donor adducts **5** (Do = THF, dioxane, substituted pyridines) with in some cases significantly lengthened Mg–Mg bonds,[4] and one example with a sterically demanding guanidinate (**1**)[2] or diazabutadienediide (**4**)[5] ligand, respectively. The complexes contain long, deformable Mg–Mg σ bonds with diffuse electron density[6] that are generally high in s-character.[1] These stable low oxidation state s-block compounds are highly reducing and have been employed as valuable selective, stoichiometric, soluble and safe reducing agents for a series of transformations of organic[2,3,7] and inorganic/organometallic[8] molecules, often as a superior alternative to other strong s-block metal reducing agents such as Na, K, and $KC_8$. Related Zn-Zn-bonded complexes[9] are known since 2004[10] and until now, more than 20 dimeric zinc(I) complexes have been reported and the $Zn_2^{2+}$ ion so far tolerates a more diverse range of ligands in its coordination sphere, including transition metal fragments.[9]

We have recently employed the new diiminophosphinate ligand $Ph_2P(NDip)_2^-$ ($L^-$; Dip = 2,6-$iPr_2C_6H_3$) to stabilize the novel dimeric zinc(I) complex $[(LZn)_2]$ (**6**) and investigated its reactivity towards some organic substrates including the activation of alkyl halides.[11] Here we report on the extension to low oxidation state magnesium chemistry. Reacting the aminoiminophosphorane LH with MeMgX (X = Br or I) in diethyl ether afforded good isolated yields of the heteroleptic diiminophosphinato magnesium(II) halide etherate complexes $[LMgX(OEt_2)]$ (**7**, X = Br; **8**, X = I) (Scheme 1), as has previously been carried out for related NH-based ligand precursors such as guanidines and β-diketimines.[2,3] The ether donor molecules can be removed by repeatedly dissolving the complexes in toluene and removing the solvent under reduced pressure at elevated temperature to yield $[(LMgX)_2]$ (**9**, X = Br; **10**, X = I) (Scheme 1). The complexes **8**–**10** were structurally characterized[12] and show the expected geometrical features with distorted tetrahedral $Mg^{II}$ centers.



***Scheme 1.*** Synthesis of complexes **7**–**11**; a) MeMgX (X = Br, I), $Et_2O$; b) toluene, Δ, reduced pressure; c) 1.1–1.2 equiv $[\{(^{Mes}nacnac)Mg\}_2]$ (**2**), toluene or benzene, 75–85 °C, 70–95 min.

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[**] We are grateful to the Australian Research Council for support and a fellowship. Part of this research was undertaken on the MX1 and MX2 beamlines at the Australian Synchrotron, Victoria, Australia.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201404284.

The spectroscopic data of **7**–**10** is in agreement with their composition and comparable to related $Zn^{II}$ complexes of that ligand.[11]

Reductions of **7**–**10**, respectively, with sodium or potassium metal did not yield novel reduced magnesium complexes and only alkali metal complexes such as [LK][11] could be isolated. The reduction of $[(LZnX)_2]$ precursors to $[(LZn)_2]$ (**6**) was previously achieved using the dimeric magnesium(I) reagents **2** and **3**, and could not be carried out using Na, K, or $KC_8$.[11] The reduction potential for the magnesium(I) dimers is expected to be larger than that of directly related zinc(I) dimers.[1] Reacting $[(LMgBr)_2]$ (**9**) with one equivalent of $[\{(^{Mes}nacnac)Mg\}_2]$ (**2**) in deuterated benzene at elevated temperatures shows that the starting materials get largely consumed and the reaction gives rise to a main new product with a sharp $^{31}P\{^1H\}$ NMR resonance at 5.9 ppm (see for example Figure S1 in the Supporting Information),[12] and the crystalline by-product $[\{(^{Mes}nacnac)MgBr\}_2]$ precipitates from the reaction mixture upon cooling. A trace conversion to the former species was already detected by $^{31}P\{^1H\}$ NMR spectroscopy at room temperature. On a preparative scale, the reaction was performed at around 80 °C in approximately 90 min. Work-up and recrystallization from *n*-pentane or *n*-hexane afforded the new dimeric magnesium(I) complex $[(LMg)_2]$ (**11**) in up to 60 % isolated yield as colorless crystals (Scheme 1). No significant formation of this species was detected from reductions using **7**–**10**, respectively, with Na or K metal. Also, the sterically more demanding magnesium(I) dimer $[\{(^{Dip}nacnac)Mg\}_2]$ (**3**)[2] could not be employed for the synthesis of **11**.

Complex $[(LMg)_2]$ (**11**) crystallizes from a range of hydrocarbon solvents with a full molecule and some solvent in the asymmetric unit in the orthorhombic crystal system. The molecule shows two four-membered MgNPN rings for the diiminophosphinate ligand chelating one Mg center and a central, unsupported Mg–Mg bond (Figure 2). The approximate parallel, almost co-planar arrangement[13] of the two least-square MgNPN-planes (16.1° angle between the planes; c.f. 54.2–56.3° for **6**) in the crystal structure of **11** has been found to allow facile co-crystallization with small amounts of magnesium(II) complexes featuring bridging anionic ligands such as the starting materials $[(LMgX)_2]$ (**9**, X = Br; **10**, X = I) which was also verified by NMR spectroscopic analysis of those crystalline materials. Consequently, relatively large electron density peaks in the $Mg_2$ core of the complex from small percentages of $[(LMgX)_2]$ impurities were found in most cases.[12,14] Suitable crystals were obtained using an excess of $[\{(^{Mes}nacnac)Mg\}_2]$ (**2**) followed by recrystallization from cyclohexane. The Mg–Mg bond length of 2.8445(9) Å in **11**·$C_6H_{12}$ compares well with previously characterized examples featuring three-coordinated Mg centers and monoanionic N,N′-chelating ligands (ca. 2.81–2.88 Å)[1] such as **1**–**3**. The Mg–N distances are similar to those found for the guanidinate derivative **1**.[2] It is worth to note that a "high-oxidation-state" ligand with $\sigma^4,\lambda^5$ phosphorane ($P^V$) center stabilizes the highly reducing $Mg_2^{2+}$ ion. Complex **11** is sufficiently thermally stable; visible decomposition of **11** does not occur below ca. 170 °C and it appears to be more thermally stable compared with $[(LZn)_2]$ (**6**),[11] both in hydrocarbon solution and in the solid state. The $^1H$ NMR spectrum of **11** shows one doublet and one septet for the protons of the isopropyl groups, as has been found for $[(LZn)_2]$ (**6**),[11] and no resonance that could be assigned to bridging hydride moieties (c.f. related ligand-stabilized magnesium(II) hydride complexes).[3,4,15]

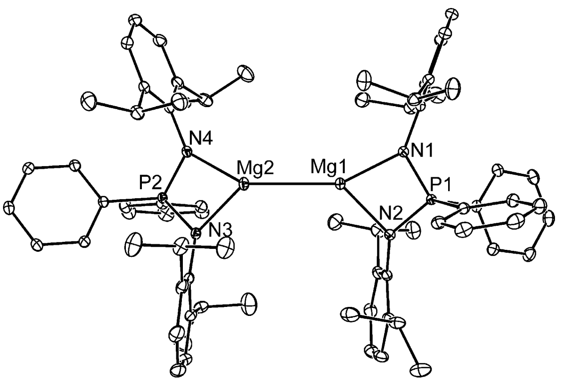
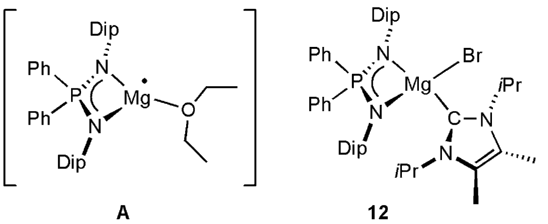


***Figure 2.*** Molecular structure of $[(LMg)_2]\cdot C_6H_{12}$ (**11**·$C_6H_{12}$) (30 % probability thermal ellipsoids). Hydrogen atoms and solvent molecule omitted for clarity. Selected bond lengths [Å] and angles [°]: Mg(1)–Mg(2) 2.8445(9), Mg(1)–N(1) 2.0769(15), Mg(1)–N(2) 2.0903(15), Mg(2)–N(3) 2.0935(15), Mg(2)–N(4) 2.0652(15), Mg(1)···P(1) ca. 2.710, P(1)–N(1) 1.6161(14), P(1)–N(2) 1.6031(14), P(2)–N(3) 1.6093(14), P(2)–N(4) 1.6195(14); N(2)-P(1)-N(1) 99.97(8), C(7)-P(1)-C(1) 100.61(8), N(1)-Mg(1)-N(2) 72.55(6).

The reduction of the etherate complexes $[LMgX(OEt_2)]$ (**7**, X = Br; **8**, X = I) with half an equivalent of $[\{(^{Mes}nacnac)Mg\}_2]$ (**2**) proceeds rapidly at room temperature to give a mixture of numerous products that contains significant amounts of $[(LMg)_2]$ (**11**) by NMR spectroscopy. A similar product mixture was obtained when reagent additions were performed under controlled conditions at low temperature with slow warming to ambient temperature. Upon addition of $[\{(^{Mes}nacnac)Mg\}_2]$ (**2**) during the reduction attempt with $[LMgBr(OEt_2)]$ (**7**) at room temperature, a rapid color change via red-brown, dark brown and finally to the precipitation of black, activated magnesium occurred. These observations are reminiscent of the recent generation of metastable brown "$Mg^IBr$" solutions[16] that disproportionate even at low temperatures. Accordingly, a metastable monomeric magnesium(I) complex such as **A** (Figure 3) might be formed as a "short-lived" reactive intermediate that is responsible for the formation of a product mixture including **11**. To synthesize a potentially longer-lived monomeric magnesium(I) compound, we prepared the N-hetero-



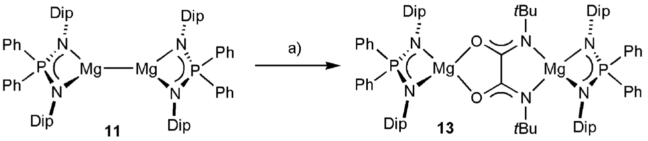
**A** **12**

***Figure 3.*** Proposed intermediate **A** and NHC-adduct **12**.

cyclic carbene adduct[17] [LMgBr(NHC)] (**12**; NHC = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene; see Figure 3) from [(LMgBr)$_2$] (**9**) and NHC.[12] The reduction of **12** with half an equivalent of [{($^{Mes}$nacnac)Mg}$_2$] (**2**), however, did not proceed as judged by NMR spectroscopy, even at 80 °C, likely for steric reasons.

We believe that the success of the almost completely advanced reduction of **9** (or **10**) to **11** using [{($^{Mes}$nacnac)Mg}$_2$] (**2**) is mainly due to kinetic and steric reasons, and a consequence of the more flexible properties of the diiminophosphinate ligand[11] compared with CN-based ligands. The thermodynamics of the formal $Br_2$ exchange in the $Mg^I/Mg^{II}$ system between two bulky, monoanionic N,N′-chelating ligand–magnesium moieties (i.e. between **2** and **11**) are expected to be negligible.[18]

The magnesium(I) compound [(LMg)$_2$] (**11**) shows similar chemical behavior compared with previously reported Mg-Mg-bonded complexes.[1] For example, the addition of benzophenone to a solution of **11** results in the formation of a characteristic deep purple-blue solution of a coordinated ketyl radical, c.f. the crystalline complex [($^{Dip}$nacnac)Mg-(DMAP)OC($^{\cdot}$)$Ph_2$].[7c,19] Treating the dimer **11** with two equivalents of *tert*-butyl isocyanate yields the colorless C-C-coupled product [(LMg)$_2$(*t*BuNCO)$_2$] (**13**) with a bridging *N*,*N*′-di-*tert*-butyloxamide fragment with *N*,*N*′ and *O*,*O*′ coordination modes to the $Mg^{2+}$ centers (Scheme 2). The complex was structurally characterized,[12] and the $^1$H, $^{13}$C{$^1$H} and $^{31}$P{$^1$H} NMR spectra show two diiminophosphinate ligand environments, and one *tert*-butyl environment in $^1$H and $^{13}$C{$^1$H} NMR spectra that support the retention of the overall solid-state structure in solution. The same coupled *tert*-butyloxamide fragments have previously been obtained from both [{($^{Mes}$nacnac)Mg}$_2$] (**2**)[3] and [{($^{Dip}$nacnac)Mg}$_2$] (**3**)[7d] reactions with *t*BuNCO, and the overall complex geometry found in **13** has previously been observed for the ($^{Mes}$nacnac)Mg product, though not the ($^{Dip}$nacnac)Mg product, which features the bridging oxamide with *N*,*O* and *O*,*O*′ coordination modes to the two $Mg^{2+}$ centers. This may be suggestive of a closer overall steric demand of an LMg unit with an ($^{Mes}$nacnac)Mg fragment, compared with the bulkier ($^{Dip}$nacnac)Mg moiety. Steric considerations have been found crucial for the chemistry of dimeric magnesium(I) complexes, a fine steric balance is often required for some reactions, and less protected complexes generally allow a higher reactivity.[1]



*Scheme 2.* Synthesis of **13**; a) 2 equiv *t*BuNCO, toluene.

In summary, we have shown that facile reductions of diiminophosphinato magnesium(II) halide complexes to the new dimeric magnesium(I) complex [(LMg)$_2$] (**11**) occur when a β-diketiminate magnesium(I) dimer is used as the reducing agent, but not commonly employed alkali metals. The $Mg^I/Mg^{II}$ redox system may allow further access to novel low oxidation state magnesium species. The novel magnesium(I) dimer **11** presented in here is stabilized by a high oxidation state P-centered ligand, is thermally stable and can undergo substrate reduction as demonstrated by a C-C-bond forming reaction.

Received: April 14, 2014
Published online: July 22, 2014

**Keywords:** magnesium · metal–metal bonds · N-ligands · reductions · subvalent compounds

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[13] Dimeric magnesium(I) compounds have been found with orthogonal, co-planar and intermediate ligand–metal heterocyclic planes, and the rotation around the Mg–Mg bond has been calculated to be very low in energy if steric effects are not taken into consideration, see Refs. [1] and [4].

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[18] It is worth to note that at elevated temperatures, the reaction occurs in solution and is not driven by the precipitation of [{($^{Mes}$nacnac)MgBr}$_2$]. Also, no entropic advantage to the driving force is expected for either the product or the starting materials side. If thermodynamic reasons are responsible for the conversion, than this could suggest that the diiminophosphinate is a significantly softer ligand than the employed β-diketiminate.

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