Reversible Oxidative Insertion of a C=C Bond into Magnesium(I) Dimers: Generation of Highly Active 1,2-Dimagnesioethane Compounds

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The oxidative insertion of 1,1-diphenylethylene into the Mg-Mg bond of two magnesium(I) dimers, $[(^{Ar}Nacnac)Mg-]_2$ (Ar = $C_6H_2Me_3$-2,4,6 (Mes); $C_6H_3Et_2$-2,6; R = Et (Dep)), yielding 1,2-dimagnesioethane products, $[\{(^{Ar}Nacnac)Mg\}_2(\mu-CH_2CPh_2)]$, is described. These reactions are readily reversible at room temperature, proceeding *via* reductive elimination of the olefin. Thus, the reactions represent the first examples of room temperature reversible redox processes for s-block metal complexes. The 1,2-dimagnesioethane products are highly activated magnesium alkyls, and show unprecedented, uncatalyzed reactivity towards, H_2, CO and ethylene. Computational studies have investigated the mechanisms of all presented reaction types.

Over the last decade or so, the chemistry of compounds containing p-block elements in low oxidation states has been revolutionized by the realization that such species can exhibit novel "transition metal-like" properties and reactivity patterns. This is perhaps best illustrated by the fact that main group compounds are increasingly being exploited in catalytically relevant small molecule (e.g. H_2, CO, ethylene etc.) activation processes, previously thought to be the domain of the d-block metals.[1] Because such activations typically involve irreversible oxidation of the p-block center (yielding thermodynamically stable products), it has proved difficult to incorporate them into competent catalytic cycles that involve both oxidative addition and reductive elimination events.[2] With that said, recent years have seen the emergence of a number of p-block mediated small molecule activations that are reversible under mild conditions, thus giving hope for the eventual development of large scale redox catalysis based on cheap, environmentally benign main group elements. Of most relevance to this study are single and dual site cycloadditions of olefins to low oxidation state p-block compounds (e.g. ditetrelynes, RE^IE^IR, E = Ge or Sn; tetrelylenes, $:E^{II}R_2$, E = Si or Sn), many of which are cleanly reversible at room temperature.[3]

In contrast to the p-block, the chemistry of stable low oxidation state s-block compounds is largely confined to that of magnesium(I) dimers, first developed in 2007.[4] Since that time, these compounds have proved invaluable as selective, moderately strong reducing agents in both organic and inorganic synthesis.[5] Not surprisingly, there have been no reports of such reductions being reversible, though if such redox processes involving magnesium(I) dimers could be developed, the potential for incorporating these systems into catalytic cycles is obvious. Here we report such a process, namely the oxidative insertion of an activated olefin into the Mg−Mg bonds of magnesium(I) dimers. Remarkably, these reactions are rapidly and cleanly reversible at ambient temperature. Preliminary studies of the reactivity of the highly active 1,2-dimagnesioethane products of these insertions towards H_2, CO and ethylene are also described.

As magnesium(I) dimers have proved versatile reagents for the selective reduction of a variety of unsaturated organic molecules,[5] it was considered that this chemistry might well extend to olefin substrates. To this end, toluene solutions of the magnesium(I) dimers, [(^{Ar}Nacnac)Mg−]$_2$ (Ar = $C_6H_2Me_3$-2,4,6 (Mes);[6] $C_6H_3R_2$-2,6; R = Et (Dep),[7] R = Pr^i (Dip)[4]) were treated with excess 1,1-diphenylethylene (DPE). Reactions with the two less hindered magnesium(I) dimers led to deep red-orange solutions, and the isolation of deep-red crystalline 1,2-dimagnesioethane insertion products, **1** and **2**, in high yield, upon work-up (Scheme 1). The bulkier dimer, [(^{Dip}Nacnac)Mg−]$_2$, displayed negligible reactivity towards the alkene, presumably due to steric reasons. It is of note that the least hindered dimer, [(^{Mes}Nacnac)Mg−]$_2$, was treated with a variety of less activated olefins, and these led either to no reaction occurring (for styrene, *tert*-butylethylene and tetraphenylethylene) or an intractable product mixture (for *trans*-stilbene).
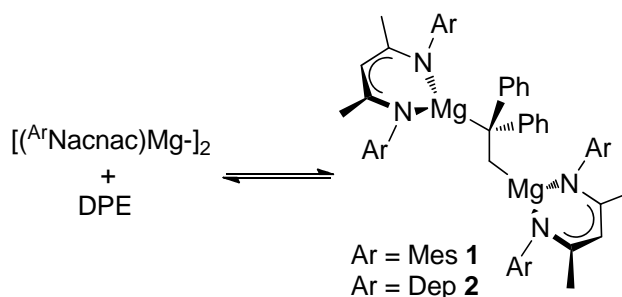
Scheme 1. Synthesis of compounds **1** and **2** (DPE = 1,1-diphenylethylene).

The proposed formulation of **1** was confirmed by an X-ray crystal structure analysis, while crystals of **2** suitable for this technique remain elusive. The molecular structure of **1** (Figure 2) reveals that the alkene moiety has inserted into the Mg−Mg bond of [(^{Mes}Nacnac)Mg−]$_2$, cleaving it and yielding the 1,2-dimagmesioethane complex.[8,9] Consistent with this is the long Mg···Mg non-bonding separation in the compound (4.326(2) Å, *cf.* 2.808(1) Å in [(^{Mes}Nacnac)Mg−]$_2$[6]), and its C(1)-C(2) distance (1.562(4) Å) which is reminiscent of a single bond. Although such oxidative additions of metal-metal bonds across

alkenes are rare, non-reversible examples involving Ge-Ge[2(e)] and Al-Al[10] bonds have been reported from the p-block. The Mg-C bonds in **1** (Mg(1)-C(2) 2.135(3) Å, Mg(2)-C(1) 2.150(3) Å) are in the normal range for magnesium alkyls,[11] while the carbon centres associated with those bonds have heavily distorted tetrahedral geometries (e.g. Mg(1)-C(2)-C(1) 77.8(2)°, Mg(2)-C(1)-C(2) 99.9(2)°). This is not surprising considering the likely highly polarized nature of the $^{\delta+}$Mg-C$^{\delta-}$ bonds, and the presence of other relatively close Mg-C intermolecular interactions in the compound (e.g. Mg(1)···C(1) 2.363(3) Å, Mg(2)···C(4) 2.567(3) Å).
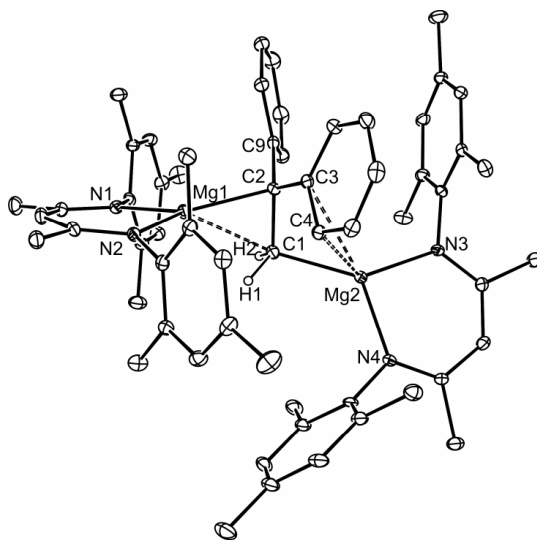
Figure 1. Molecular structure of **1** (20% ellipsoids. Hydrogen atoms, except olefinic protons, omitted for clarity).

The ^{1}H NMR spectra of pure crystalline samples of compounds **1** and **2**, dissolved in C_6D_6, exhibit spectral patterns consistent with their proposed structures (e.g. MgCH_2 resonances δ: 0.38 ppm **1**, 0.25 ppm **2**, *cf.* δ 5.36 ppm DPE CH_2 resonance). However, these spectra also consistently displayed signals associated with the presence of significant amounts of the DPE and magnesium(I) dimer reactants. At 298 K the ratio of products:reactants is approximately 80:20 for **1**, and 40:60 for the bulkier insertion product **2**. In both cases, increasing the temperature of the solution led to a decrease in this ratio, while

decreasing the temperature led to an increase in the proportion of product present. This strongly suggests that the reactants and products are in equilibrium with each other, which is further evidenced by the fact that adding excess DPE to the solutions shifts the equilibria towards the 1,2-dimagnesioethane products. It is worth noting that attempts were also made to investigate the effect that substitution of DPE phenyl groups with electron donating (*para*-methoxy) or withdrawing (3,5-bis(trifluoromethyl)) substitutents would have on the equilibria. However, reaction of both substituted DPEs with [(^{Mes}Nacnac)Mg−]$_2$ led to unidentifiable product mixtures.

The equilibria mentioned above are extraordinary in that they indicate that the oxidative insertion of DPE into the Mg-Mg bond of magnesium(I) dimers is cleanly reversible at room temperature, proceeding *via* reductive elimination of the alkene from magnesium(II) alkyls, **1** and **2**. Moreover, variable temperature ^{1}H NMR studies of solutions of **1** revealed that the equilibration process is rapid, even at low temperatures, which implies a low kinetic barrier to the forward and reverse reactions. A van't Hoff analysis of the variable temperature NMR data afforded values of ΔH = -13.7(1.4) kcal/mol and ΔG^{298} = -3.2(0.3) kcal/mol, for the reaction that gave **1** (see SI). These values show the reaction to be weakly exergonic, and are largely consistent with the equilibrium mixture of reactants and products observed for this reaction.

In order to gain an understanding of the bonding involved in **1** and **2**, DFT calculations (B3PW91) were performed on compound **1** in the gas phase (i.e. **1'**). The geometry of this compound optimized to be close to that of the experimental compound, and as expected, its Mg-C bonds were found to be heavily polarized (charges: Mg(1) +1.6, Mg(2) +1.5, C(1) -1.2, C(2) -0.5; N.B. atom labels as in Fig. 1) with concomitantly low bond orders (WBI: Mg(1)-C(2) 0.11, Mg(2)-C(1) 0.26, C(1)-C(2) 1.01). Moreover, as suggested from the crystal structure of **1**, there is a weak interaction (WBI: 0.07) between Mg(1) and the carbon center, C(1), that has a close contact with it. It is also noteworthy that an inspection of the

HOMO (Fig. 2) reveals a significant degree of electronic delocalization over the doubly reduced DPE moiety and its bonds to the two magnesium centers.
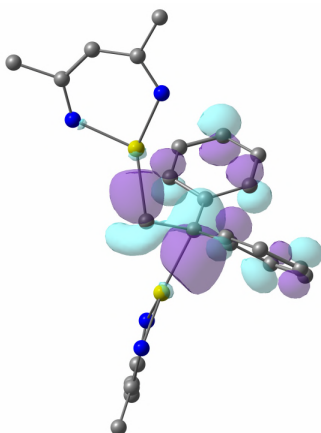

Figure 2. HOMO of **1'** (mesityl groups omitted for clarity).

An analysis of the reaction profile that gave **1'** showed that it is almost thermo-neutral (ΔH = -1.8 kcal/mol), and that it is apparently barrierless, as no transition state could be located for it (see Fig. 3, left). These results are consistent with the experimentally observed reaction equilibrium involving **1**, and the fact that this reaction mixture rapidly reaches equilibrium, even at low temperature. That the experimental reaction is slightly more favorable (ΔH = -13.7(1.4) kcal/mol) is possibly due to solvent effects.

Although the exact mechanism for the insertion of DPE into magnesium(I) dimers could not be determined, it seemed possible that **1** and **2** could act as masked sources of monomeric magnesium(I) fragments, [(^{Ar}Nacnac)Mg·], in a similar fashion to that recently proposed for a related amidinato calcium stilbene complex, [{(Amid)Ca}$_2$(μ-C$_2$H$_2$Ph$_2$)] (Amid = [(DipN)$_2$CBu^t]$^-$).[12] If that were the case, compounds **1** and **2** could potentially react with small molecules that are unreactive towards magnesium(I) dimers, [(^{Ar}Nacnac)Mg$-$]$_2$. Alternatively, given the high charge density on the doubly reduced C-C cores of **1** and **2**, those compounds could behave as "activated" Mg alkyls that can react with molecules that other magnesium alkyls are not known to, at least in the absence of catalysts.

To test these proposals, benzene or toluene solutions of **1** and/or **2** were stirred under atmospheres of either H_2, CO or ethylene at ambient temperature. The reaction with H_2 cleanly gave an approximately 50:50 mixture of the known magnesium hydrides, $[(^{Ar}Nacnac)Mg(\mu-H)]_n$,[7,13] and the magnesium alkyls, **3** (Scheme 2).[14] To discount the possibility that the reaction proceeded *via* initial formation of $[(^{Ar}Nacnac)Mg(\mu-H)]_n$ and free DPE, followed by hydromagnesiation of DPE by half the generated magnesium hydride complex, a control experiment involving treating $[(^{Dep}Nacnac)Mg(\mu-H)]_2$ with one equivalent of DPE was carried out. However, no reaction was observed at ambient temperature, suggesting the activations of H_2 that gave **3**, did not involve them acting as masked $[(^{Ar}Nacnac)Mg\cdot]$ sources. The reaction of **2** with excess CO afforded a high isolated yield of the unusual cyclobutenediolate complex, **4**, *via* a coupling of two CO molecules with the DPE dianion (see SI for crystallographic details of **4**).[15] Reaction of **1** with ethylene proceeded *via* insertion of the olefin into the Mg-CPh$_2$ bond of the 1,2-dimagnesioethane complex to give $[(^{Mes}Nacnac)Mg(\mu-C_2H_4CPh_2CH_2)Mg(^{Mes}Nacnac)]$. This compound is, however, unstable at room temperature in solution, and was therefore treated with DMAP to form the stable adduct complex, **5**. All of these reactions are exceptional, considering that, as far as we are aware, magnesium alkyls are not known to react with H_2 or CO at room temperature, and carbomagnesiations of ethylene only proceed in the presence of transition metal catalysts.[16]
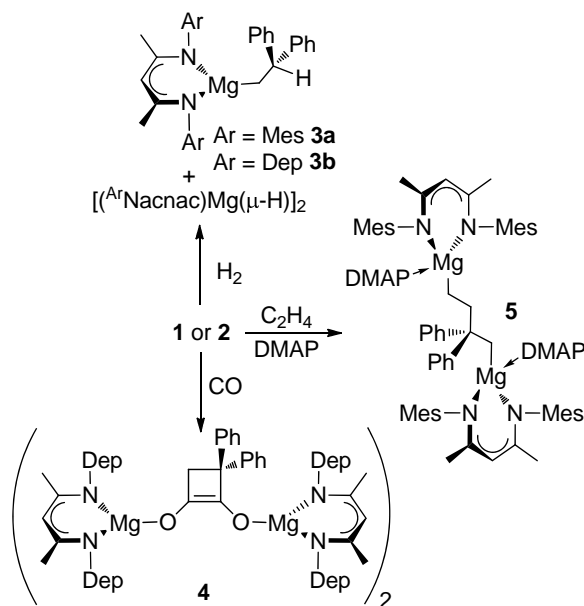
Scheme 2. Synthesis of compounds **3**-**5** (DMAP = 4-dimethylaminopyridine).

So as to gain a greater understanding of the mechanisms of formation of **3**-**5**, profiles of the reactions between **1'** and the three gaseous substrates were calculated (B3PW91). In all cases, radical reaction pathways were considered, but were dismissed as improbable, based on the results of preliminary calculations (see ESI). The reaction involving H_2 progresses *via* a σ-bond methathesis-like activation of the substrate by the expectedly more reactive Mg-CPh_2 bond of **1'** (Fig. 3). Indeed, the experimental reaction of **1** or **2** with D_2 led only to $[(^{Ar}Nacnac)Mg\{CH_2C(D)Ph_2\}]$ **3-D** and $[(^{Ar}Nacnac)Mg(\mu\text{-}D)]_n$, with no H/D "scrambling" observed at any stage. Furthermore, the reason that **3a** does not undergo β-hydride elimination reactions at room temperature, yielding free DPE and a second equivalent of $[(^{Mes}Nacnac)Mg(\mu\text{-}H)]_n$, was shown by calculations to be due to the high energy barrier (35.3 kcal/mol) to that reaction. The reaction of ethylene with **1'** was calculated to proceed *via* a relatively low energy four-membered transition state ($\Delta H^{\ddagger}$ = 16.3 kcal/mol) involving the Mg-CPh_2 bond of **1'**, similar to the transition state in the H_2 activation reaction. This then

leads to the insertion product [(^{Mes}Nacnac)Mg(μ-C$_2$H$_4$CPh$_2$CH$_2$)Mg(^{Mes}Nacnac)], which is favored by 7.9 kcal/mol, relative to **1'** (see SI for more details).
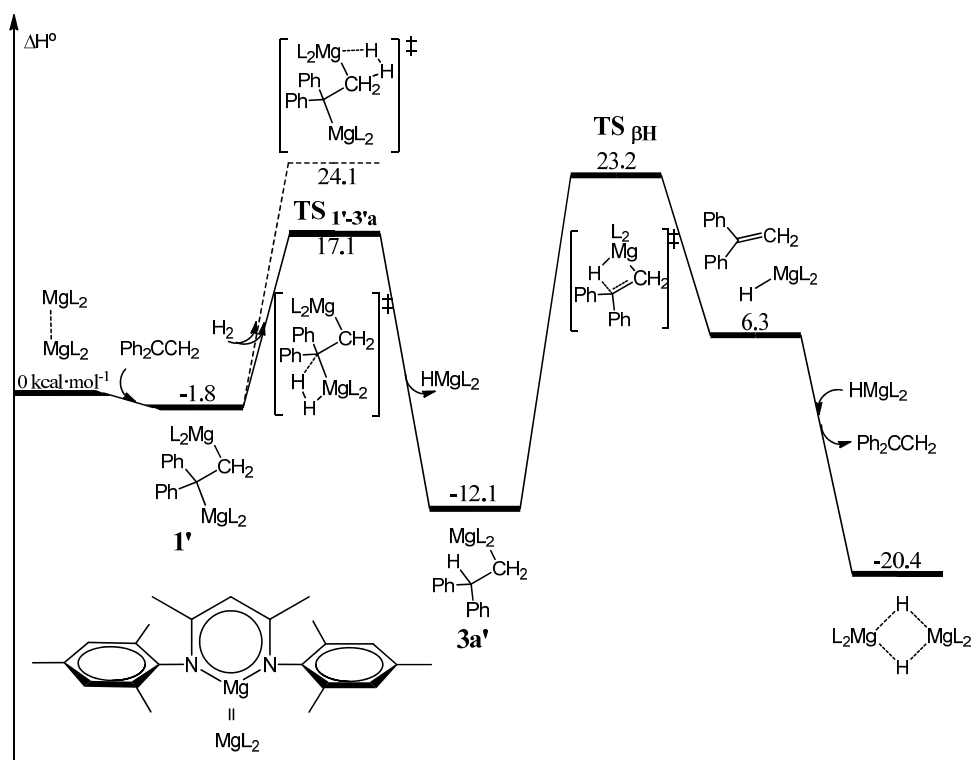
Figure 3. Reaction profile for the formation of **1'** and **3a'**.

Similar to the previous two reactions, the first transition state in the reaction of **1'** with CO is low in energy, and incorporates a four-membered ring involving the Mg-CPh$_2$ bond (Fig. 4). The CO fragment subsequently inserts into that bond, and the carbenic center (see HOMO of Fig. 4) of that insertion product, **Inta**, is attacked by a second molecule of CO, leading to a ketene-like intermediate, **Intb**. This then undergoes an intramolecular C-C bond forming reaction, and a series of magnesium migration reactions to give the calculated cyclobutendiolate complex, **4'**. The formation of **4'** is somewhat similar to recently reported preparations of magnesium diolate complexes from reactions of magnesium hydrides and CO.[17]
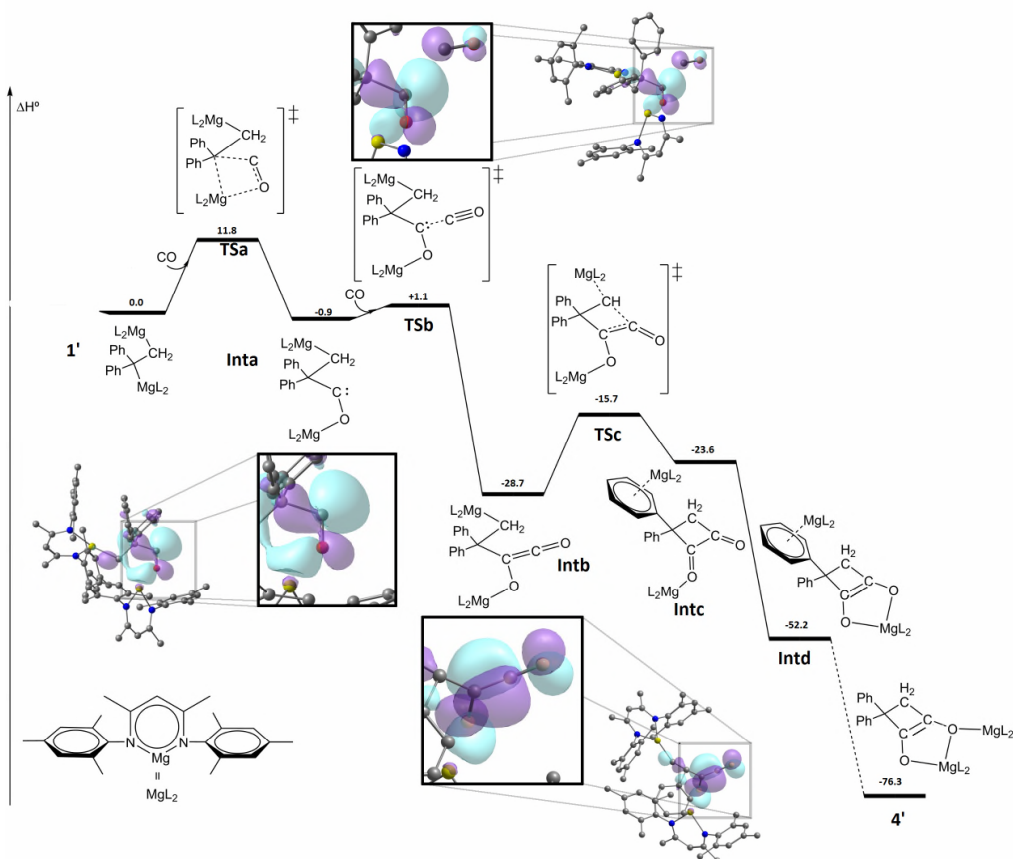
Figure 4. Reaction profile for the formation of **4'**.

In summary, the oxidative insertion of 1,1-diphenylethylene into Mg-Mg bonds of magnesium(I) dimers has been described. These reactions are readily reversible at room temperature, proceeding *via* reductive elimination of the olefin. The reactions represent the first examples of room temperature reversible redox processes for an s-block metal complex, and give hope for the eventual incorporation of magnesium(I) dimers into catalytic cycles based on oxidative addition/reductive elimination events. The 1,2-dimagnesioethane products of these reactions are highly activated magnesium alkyls, and show unprecedented uncatalysed reactivity towards, H_2, CO and ethylene.

Supporting Information Available. Details of the synthesis and characterizing data for all new compounds. Full details and references for the crystallographic and computational data. Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Table of Contents Graphic

Mes = mesityl