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Photochemically Activated Dimagnesium(I) Compounds: Reagents for the Reduction and Selective C–H Bond Activation of Inert Arenes

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Abstract: The photochemical activation of dimagnesium(I) compounds, and subsequent high yielding, regioselective reactions with inert arenes are reported. Irradiating benzene of [{(^{Ar}Nacnac)Mg}₂] solutions $(^{Ar}Nacnac = [HC (MeCNAr)_2]^-$; Ar = 2,6-diisopropylphenyl (Dip) or 2,4,6tricyclohexylphenyl (TCHP)) with blue or UV light, leads to double reduction of benzene and formation of the "Birch-like" cyclohexadienediyl bridged compounds, $[{(^{Ar}Nacnac)Mg}_2(\mu C_6H_6$]. Irradiation of $[{(^{Dip}Nacnac)Mg}_2]$ in toluene, and each of the three isomers of xylene, promoted completely regio- and chemo-selective C-H bond activations, and formation of $[(^{Dip}Nacnac)Mg(Ar')]$ (Ar' = meta-tolyl; 2,3-, 3,5- or 2,5dimethylphenyl), and $[\{(^{Dip}Nacnac)Mg(\mu-H)\}_2]$. Fluorobendefluorinated by photoactivated zene was cleanly $[{(^{Dip}Nacnac)Mg}_2],$ leading biphenyl to and $[\{(^{Dip}Nacnac)Mg(\mu-F)\}_2]$. Computational studies suggest all reactions proceed via photochemically generated magnesium-(I) radicals, which reduce the arene substrate, before C-H or *C*–*F* bond activation processes occur.

he activation and subsequent functionalization of otherwise inert C–H fragments in simple arenes and alkanes has become central to the value-adding, atom economical syntheses of more complex molecules such as pharmaceuticals and natural products.^[1] Despite rapid progress in this field over recent decades, achieving selectivity in the activation of substrates with many C–H bonds remains a significant challenge, especially where site directing functional groups are absent. Moreover, the low reactivity of weakly polarized C–H bonds often requires harsh conditions for their activation, which in turn can affect product selectivity.^[2]

There is no doubt that synthetic transformations requiring the activation of inert C–H bonds have relied heavily on the use of 4d and 5d metal complexes as catalysts.^[1,2] However,

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given the often high cost and toxicity of these metals, there is increasing interest in finding less toxic alternatives incorporating earth abundant metals from the 3d row,^[3] in addition to reactive main group compounds that can effect the C-H functionalization of organic molecules in the absence of catalysts.^[4] With respect to the latter, remarkable advances have come from the groups of Mulvey, Knochel, Hevia and others, who have developed a variety of "normal" oxidation state main group heterobimetallic systems, for example, turbo-Grignard reagents and turbo-Hauser bases, for the synergistic and selective deprotonation(s) of numerous unsaturated substrates.^[5] In the past several years, low oxidation state p-block compounds have entered this arena, most notably from the groups of Harder,^[6] Crimmin,^[7] Aldridge and Goicoechea,^[8] and Yamashita,^[9,10] who have used either neutral or anionic nucleophilic aluminum(I) reagents for the activation of C-H bonds in benzene, toluene and xylenes, both in the presence or absence of catalysts. These reactions proceed via formal oxidative addition of the C-H bond to an Al^I center, and deliver varying degrees of product selectivity, depending on the Al^I reagent and substrate employed.

In 2007, we developed the first examples of stable magnesium(I) compounds,^[11] and have since systematically investigated β-diketiminate coordinated examples, $[{(^{Ar}Nacnac)Mg}_2]$ $(^{Ar}Nacnac = [HC(MeCNAr)_2]^-, Ar =$ bulky aryl), as selective reducing agents in both organic and inorganic synthetic methodologies,^[12] including the cleavage of weak C-H bonds (e.g. in 1,3-cyclohexadiene).^[13] Although magnesium(I) compounds do not react with inert arenes under normal conditions, Crimmin and co-workers have shown that they can functionalize a C-H bond of benzene (bond dissociation energy $BDE = 113 \text{ kcal mol}^{-1}$) in the presence of a Pd⁰ catalyst (Scheme 1).^[14] Similarly, Harder and co-workers recently proposed that magnesium(I) radicals, generated in situ by the alkali metal reduction of βdiketiminato magnesium(II) iodide complexes, doubly reduce benzene (reduction potential = -3.42 V vs. SCE) to give the "Birch-like" reduction products 1 and 2.^[15] They also showed that heating a toluene solution of the bulkier of these, 2, at 120°C for 3 days, afforded magnesium hydride and phenyl products. Thus, overall, the reactions represent the formal activation of a benzene C-H bond.

We are increasingly interested in activating magnesium(I) compounds (e.g. by Lewis base Mg–Mg bond elongation/ polarization) toward reactions with normally unreactive substrates (e.g. CO, H_2 and ethylene).^[16] Here we show, for the first time, that dimagnesium(I) compounds can also be photoactivated by irradiation with blue or UV light, and can subsequently cleanly doubly reduce or activate C–H bonds of benzene, toluene and xylenes, with complete regioselectivity



Scheme 1. Reported C-H bond activations involving dimagnesium(I) compounds and magnesium(I) radicals (Mes=mesityl, Dip=2,6-diisopropylphenyl; Dipep=2,6-diisopentylphenyl).

at room temperature. Computational studies suggest the reactions proceed via magnesium(I) radicals (arising from photolytic cleavage or elongation of Mg–Mg bonds), which reduce the arene substrate to "Birch-like" reduction intermediates (cf. 1 and $2^{[15]}$), before yielding the ultimate C–H activated product. The outcomes of related reductions of substituted benzenes (PhX, X=F, OMe or NMe₂) are also reported.

The photochemical activation of d- and p-block metalmetal bonded compounds is well established, and is of considerable value to synthetic chemists.^[17,18] In contrast, photochemical activations of stable s-block metal-metal bonded systems are unknown. In order to correct this paucity, β -diketiminato dimagnesium(I) compounds were chosen as photochemical precursor candidates in this study. At the outset, benzene solutions of two magnesium(I) compounds $[{(^{Ar}Nacnac)Mg}_2]$ (Ar = Dip^[19] or 2.4,6-tricyclohexylphenyl (TCHP)^[16b]), in 5 mm NMR tubes, were irradiated with either UV light ($\lambda = 370$ nm, 43W LED lamp) or blue light ($\lambda =$ 456 nm, 50W LED lamp) at 20°C for 48 h. This led to the near quantitative double reduction of benzene, and formation of the known and new "Birch-like" products 1 and 3 (Scheme 2).^[20] When the course of these reactions was followed by NMR spectroscopy, it was found that those involving higher energy UV light were moderately faster. For example, after 320 min irradiation, the formation of **3** is 90 % complete with UV light, and 74% complete with blue light. Moreover, the formation of 1 is considerably slower than that of 3 (90% conversion under UV light occurs after ca. 720 min and 320 min, respectively; see Figures S23 and S24). This is believed to be a result of the significantly elongated, and presumably more readily cleaved, Mg-Mg bond in the bulkier



Scheme 2. The use of photoactivated dimagnesium(I) compounds in the selective synthesis of cyclohexadienediyl bridged complexes 1 and 3; and in the regioselective synthesis of the magnesium aryls 4–7 (TCHP=2,4,6-tricyclohexylphenyl).

system (3.021(1) Å vs. 2.8457(8) Å), which we propose leads to the more facile generation of transient magnesium(I) radical intermediates, [(^{Ar}Nacnac)Mg[•]], and subsequent arene reduction. It is noteworthy that irradiation of benzene solutions of less bulky, and less kinetically protected, magnesium(I) compounds, [{(^{Ar}Nacnac)Mg₂] (Ar = mesityl^[21] or 2,6-xylyl^[22]), did not lead to reduction of benzene, but instead to disproportionation to [Mg(^{Ar}Nacnac)₂] and magnesium metal.^[23] Moreover, heating solutions of **1** at 60 °C for 12 h led to clean conversion of the compound to magnesium phenyl and hydride products in a similar fashion to the higher temperature thermolysis of bulkier **2**.^[15]

The NMR spectroscopic data for orange micro-crystalline **1** are identical to those reported by Harder and co-workers,^[15] who prepared the compound in low yield, as part of a product mixture, as described above. Similar to that compound, and **2**, the solution state ¹H NMR spectrum of **3** displays a singlet resonance at $\delta = 3.82$ ppm (cf. $\delta = 3.75$ ppm for **1**; $\delta = 3.78$ ppm for **2**^[15]) for the [C₆H₆]²⁻ dianion. This indicates a fluxional process involving rapid Mg–C bond breaking and re-forming on the NMR timescale. The X-ray crystal structure of orange **3** was determined, and its molecular structure is depicted in Figure 1. This shows it to be closely related to the cyclohexadienediyl bridged structure of **2**.

Given the facility by which benzene could be reduced by photo-activated magnesium(I) compounds, attention turned to irradiation of solutions of $[{(^{Dip}Nacnac)Mg}_2]$ in toluene, or one of the three isomers of xylene. Blue light was chosen for these irradiations, so as to allow the reactions to be carried out on preparative scales in glass walled Schlenk flasks. With that said, UV irradiation of arene solutions of $[{(^{Dip}Nacnac)Mg}_2]$ in thin walled 5 mm NMR tubes gave similar reaction outcomes. That is, the blue light irradiations (24–96 h at 20 °C) led to the near quantitative formal C–H activations of the arenes, to give ca. 50:50 mixtures of the magnesium(II) hydride, $[{(^{Dip}Nacnac)Mg(\mu-H)}_2]$, which is stable to irradi-



Figure 1. Molecular structure of **3** (25% thermal ellipsoids; hydrogen atoms omitted; TCHP substituents shown as wire-frame for sake of clarity).^[28] Selected bond lengths [Å] and angles [°]: Mg1–C6 2.360(3), Mg1–C3 2.373(3), Mg2–C1 2.391(3), Mg2–C2 2.553(3), Mg2–C4 2.391-(3), Mg2–C5 2.622(3), C1–C2 1.386(4), C4–C5 1.380(4); C6-Mg1-C3 70.31(9), C1-Mg2-C4 69.78(9), C2-Mg2-C5 65.24(9).

ation, and one of the magnesium aryl complexes 4-7 (Scheme 2). All of these reactions were completely selective for the depicted isomers, as determined by ¹H NMR spectroscopic analyses of the total reaction mixtures, and each of the products could be isolated from the reaction mixtures as colorless crystalline solids (see Figure 2 for molecular structures).^[24] It is noteworthy that when the reactions were monitored over time by ¹H NMR spectroscopy, no intermediates were observed in the formation of the magnesium xylyl complexes, though in the first few hours of the reaction that gave the magnesium tolyl, 4, resonances corresponding to that compound and a reaction intermediate were present. The signals for the intermediate remained until all of the magnesium(I) starting material was consumed (after ca. 14 h), then decreased in intensity at the expense of signals for the final product 4. It is believed the intermediate is a "Birch-like" reduction product similar to 1-3, which is further evidenced by the results of calculations (see below). Quenching of 4-7 with I_2 gave mono(iodo)-arenes with complete selectivity for the formation of the regio-isomer that corresponds to that of the magnesium aryl starting material.

The very high yielding nature and regioselectivity of the reactions that gave 4-7 is remarkable. These outcomes can be compared to the Al¹ and Mg¹ induced arene C-H activations mentioned in the introduction. Those reactions typically require forcing conditions or transition metal catalysts to proceed, they often give rise to two or more isomers, and these isomers can include benzylic products arising from competing C-H activations of toluene or xylene methyl groups. In the current study, the metallations of toluene and meta-xylene were found to occur selectively at a C-position meta to a methyl group (yielding 4 and 6), as is often the case with the major isomer of product mixtures resulting from Al^I (and Mg^{II[5f]}) induced arene metallations.^[7-9] Although the formation of 5 also involves metallation at a site meta to one methyl group, there are no instances of a main group reagent selectively metallating ortho-xylene to give a 1-metallo-2,3dimethylphenyl product (as is 5). That being the case, Crimmin and co-workers have reported that a Pd⁰ catalyzed alumination of ortho-xylene yields the ortho-aluminated product as the minor isomer.^[7a]

Some initial investigations of the chemoselectivity and functional group tolerance of photoactivated arene magnesiations have been carried out using fluorobenzene, anisole and *N*,*N*'-dimethylaminoaniline as substrates. The magnesium(I) compound [{(^{Dip}Nacnac)Mg}₂] does not react with any of these in solution at room temperature.^[25] However, blue light irradiation of a solution of [{(^{Dip}Nacnac)Mg}₂] in fluorobenzene led to the chemo-selective activation of its strong, and normally inert, C-F bond, leading to the essentially quantitative formation of biphenyl and the known compound, $[{(^{Dip}Nacnac)Mg(\mu-F)}_2]$, after 6 hours. Computational studies suggest this reaction involves a radical defluorination mechanism (see SI for further details). Reactions of photoactivated $[\{(^{Dip}Nacnac)Mg\}_2]$ in the presence of anisole or N,N'-dimethylaminoaniline were not as clean as those involving fluorobenezne, and likewise, did not yield any C-H activated products. Instead C_{Ph}-O or

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Figure 2. The molecular structures of a) 4, b) 5, c) 6, and d) 7.^[28]

 C_{Ph} -N bond cleavages occurred, affording crystallographically characterized [{($^{Dip}Nacnac$)Mg(μ -OMe)}₂] and [{($^{Dip}Nacnac$)Mg(μ -NMe₂)}₂], respectively (see SI for further details). The only other identifiable products of these reactions were [{($^{Dip}Nacnac$)MgPh] or biphenyl. It is of note that Aldridge and co-workers recently reported that the related reaction of an Al¹ anion with anisole led to O-C_{Me} cleavage, as opposed to the C_{Ph}-O cleavage seen here.^[8a]

As hinted at above, we propose that the mechanisms of formation of **4–7** involve an initial homolytic cleavage of the weak Mg–Mg bond of [{ $(^{Dip}Nacnac)Mg$ }₂], under photolytic conditions, thus generating transient [$(^{Dip}Nacnac)Mg'$] radicals, which subsequently react with the arene substrate.^[26] Whilst unknown for s-block compounds, related photolytically induced, and cleanly reversible, M–M bond cleavages have precedent for low oxidation state d-^[17] and p-block systems (e.g. cleavage of distannynes ArSn=SnAr to give (ArSn:)· radicals^[27]). The fact that photolysis of [{ $(^{Dip}Nacnac)Mg$ }₂] (or [{ $(^{TCHP}Nacnac)Mg$ }₂]) in cyclohexane

gave no observable reaction, and no spectroscopically observable paramagnetic species at 20 °C, suggests that if homolytic Mg–Mg bond cleavage is indeed occurring, the cleavage is cleanly reversible, the generated Mg^I radicals are short lived, and they do not react with cyclohexane.

In order to further explore the mechanisms of the experimentally observed arene reductions and C–H bond activations, the profiles of gas phase reactions between $[\{(^{Dip}Nacnac)Mg\}_2]$ and benzene or toluene were calculated (Figure 3, B3PW91 functional). The route to **1** can proceed via two thermodynamically similar radical pathways. In the first case, irradiation allows access to the high energy triplet state **Int1**, the two SOMOs of which predominantly exhibit σ and σ^* Mg···Mg "bond" character. The weak Mg···Mg interaction of **Int1** then cleaves to give two doublet radicals, **Int2**, the high s-character SOMO of which is located on the Mg center. Two molecules of **Int2** then reduce benzene to give the experimentally observed complex **1**. The other route to **1** involves elongation of the Mg–Mg bond of

GDCh



Figure 3. Computed enthalpy profile for the reaction of $[{(^{Dip}Nacnac)Mg}_2]$ with benzene (top) and toluene (bottom). Energies are presented as kcal mol⁻¹.

[{(^{Dip}Nacnac)Mg}₂] upon irradiation, and complexation of benzene to the excited species to give triplet complex **Int1 a**. The SOMO of this is benzene centered, while the SOMO-1 is associated with the elongated Mg···Mg σ -bond (SOMO-SOMO-1 energy gap = 0.83 eV). In the experimental setting, compound **1** does not isomerize to **Int3** at room temperature (with or without irradiation), which suggests a relatively high kinetic barrier to this process. However, heating **1** at 60 °C for 12 h cleanly gives [(^{Dip}Nacnac)MgPh] and [{(^{Dip}Nacnac)Mg(μ -H)}₂], consistent with the calculated 34.2 kcal mol⁻¹ barrier from **Int3** to those products.

In contrast to the reduction of benzene, the double reduction of the bulkier substrate toluene (yielding Int5, cf. 1), is only accessible via doublet Int2, and not the toluene analogue of Int1a. The kinetic barrier from Int5 to 4 and $[(^{Dip}Nacnac)MgH]$ is low enough (20.5 kcalmol⁻¹) for the reaction to proceed at room temperature with irradiation, but high enough for Int5 to be spectroscopically observed as an experimental transient. It is noteworthy that the kinetic barrier to the formation of the isomeric para-tolyl product, [(^{Dip}Nacnac)Mg(p-tolyl)], is significantly higher (25.2 kcal mol⁻¹, see SI for details), which helps explain why this was not experimentally detected. Given that Harder and coworkers observed the formation of 1 via reaction of benzene with alkali metal generated magnesium(I) radicals, the proposed involvement of photochemically generated magnesium(I) radicals in the formation of **1** and **4** (and **5–7**) here, seems altogether feasible.

In summary, reactions resulting from the first photochemical activations of s-block metalbonded metal compounds are reported. When solutions of dimagnesium(I) compounds in normally inert arene solvents are irradiated with blue or UV light at room temperature, arene activation products are returned in high yield. Benzene is doubly reduced to give "Birch-like" cyclohexadienediyl bridged dimagnesium compounds, whereas toluene and the three isomers of xylene undergo completely regio- and chemo-selective C-H bond activations, vielding magnesium aryl and magnesium hydride products. Fluorobenzene is defluorinated,

leading to biphenyl and a magnesium fluoride complex. The results of computational studies suggest all reactions proceed via photochemically generated magnesium(I) radicals. Given that the selective activation of inert arenes is of enormous synthetic importance, and typically requires late transition metal catalysts to proceed, there is considerable scope to fully develop the chemistry of photoactivated magnesium(I) compounds, and their application to organic synthesis. We are currently exploring this possibility, in addition to further probing the mechanism by which dimagnesium(I) compounds are photoactivated.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: arene reduction \cdot C–H activation \cdot DFT calculations \cdot magnesium(I) \cdot photochemistry

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