

A Dimeric Magnesium(I) Compound as a Facile Two-Center/Two-Electron Reductant**

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For more than 100 years, magnesium compounds have proved indispensable tools for the organic and organometallic chemist. Of these, Grignard reagents are undoubtedly the most important and have been utilized in innumerable synthetic transformations.^[1] Some of these are thought to occur by mechanisms involving single electron transfer (SET) from the organomagnesium compound to a substrate, although the exact nature of these SET processes is not fully understood. Other magnesium reagents that can act as one-electron reductants include Mg/MgI₂ mixtures, which have been proposed to be in equilibrium with univalent magnesium, MgI[•], in organic solutions.^[2] Although this species has not been characterized in solution, elegant recent work by Schnöckel, Henke, and Köppe has led to the spectroscopic characterization of related MgCl[•] and Mg₂Cl₂[•] in a solid inert-gas matrix.^[3] In addition, the reactions of the MgCl₂[•] radical with several ketones have been studied in the gas phase by mass spectrometry, and SET products were identified.^[4]

In late 2007, the first “bottleable” magnesium(I) compounds, [LMgMgL] (L = [(ArN)₂CNiPr₂][−], Priso[−] (**1**) or [(ArNCMe)₂CH][−], nacnac[−] (**2**; Scheme 1); Ar = 2,6-*i*Pr₂C₆H₃), were reported.^[5,6] These contained Mg–Mg bonds that are kinetically protected from disproportionation processes by sterically bulky guanidinate or β-diketiminato ligands. Despite this protection, compound **2** doubly reduces the carbodiimide, CyN=C=NCy (Cy = cyclohexyl), at low temperature to give the unusual magnesium magnesioamidinate complex, [(nacnac)Mg{(NCy)₂C}Mg(nacnac)], **3**. It was postulated that this reaction proceeds via initial coordination of the carbodiimide at one Mg center of **2**, prior to its reduction, which seems reasonable in light of a subsequent report that detailed the formation and characterization of

thermally stable adducts of **2** with several Lewis bases, viz. [(nacnac)Mg(L')Mg(L')(nacnac)] (L' = thf, dioxane, 4-*tert*-butylpyridine or 4-dimethylaminopyridine).^[7] Treatment of these adducts with CyN=C=NCy led to no reaction, presumably because their magnesium centers were blocked towards coordination by the carbodiimide. Considering that magnesium(I) species have often been implicated as intermediates in substrate reductions involving organometallic or inorganic magnesium reagents,^[1–4] it seemed that a systematic study of the reactivity of **2** towards unsaturated compounds would be of great interest to organic and organometallic chemists. Herein, we report preliminary results towards this end, which show that **2** acts as a facile two-center/two-electron reductant, yielding novel doubly reduced, C–C- or N–N-coupled products. For comparison, reactions of the closely related magnesium(II) hydride complex [(nacnac)Mg(μ-H)₂Mg(nacnac)] were carried out with the same substrates, generally yielding hydromagnesiation products.

As already mentioned, the reaction of **2** with CyN=C=NCy gives the doubly reduced product, **3** (Scheme 1).^[5] Similarly, treatment of toluene solutions of **2** with azobenzene (PhN=NPh) or cyclooctatetraene (cot) under any stoichiometry gave the reduced products, **4** and **5**, the latter after recrystallization from THF. In contrast, reactions of **2** with 1-adamantyl azide or the isocyanate, *t*BuNCO, led to reductive N–N and C–C couplings respectively, to give the unusual hexazenediide complex, **6**, and the magnesium oxamide compound, **7**. All products were obtained in good to high yields as crystalline solids. The reactions involving N-functionalized substrates were all complete within minutes at temperatures below −50 °C, whereas the reduction of cot required it to be heated with **2** in boiling toluene for 1.5 h. Presumably, the reductions of the N-functionalized substrates were facilitated by their initial coordination to the Mg centers of **2**, which is disfavored for cot. In these reactions, each magnesium(I) center of **2** is formally acting as a one-electron reductant and, therefore, the complex as a whole behaves as a two-center/two-electron reductant.

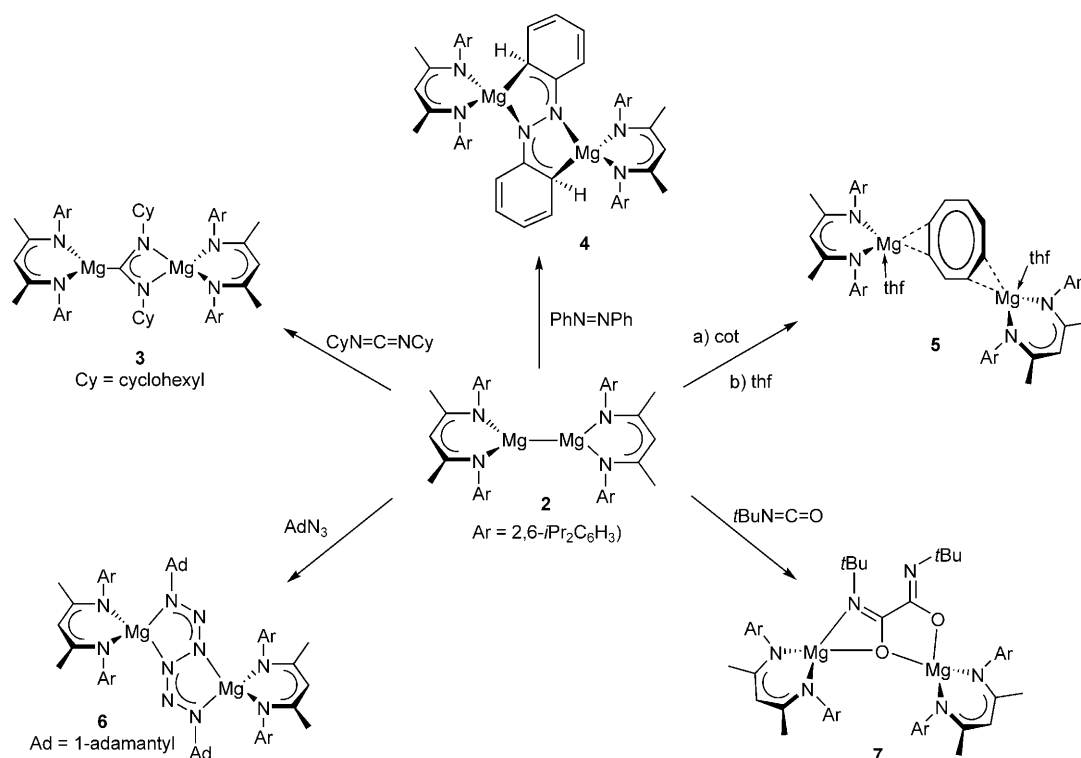
There are a number of interesting features of the reduction products, **4–7** (Scheme 1), which indicate that **2** and related magnesium(I) compounds may prove useful as selective reducing agents in organic and organometallic syntheses. For example, although many reports of the reduction of azobenzene (mainly by lanthanide(II) reductants^[8]) have been forthcoming, to our knowledge none have led to the reduced dianionic ligand acting as a bis(κ²-azaallyl), as is the case in **4**. Similarly, although magnesium complexes of the cot^{2−} dianion are known,^[9] none have been crystallographically characterized and little is known of how the

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Scheme 1. Preparation of compounds **3–7**; cot = cyclooctatetraene.

relatively small Mg^{2+} ion coordinates to this ligand. The structural characterization of **5** sheds light on this coordination for the first time. Compound **6** is unusual in that it results from the reductive coupling of two organic azide units and exhibits a bridging $\text{AdN}_6\text{Ad}^{2-}$ (Ad = 1-adamantyl) ligand. Despite having six covalently linked N centers, this compound does not appear to be shock or thermally sensitive to detonation, as is the case for some related high-energy hexaazadienes, RNNN(R)N(R)NRR (R = alkyl, aryl etc.).^[10] The only other examples of reductive couplings of an organic azide were recently reported by Holland and co-workers for the reactions of β -diketiminato iron(I) fragments with AdN_3 .^[11] The products of these reactions, $[\{\text{HC(RCNAr)}_2\}\text{Fe}(\mu\text{-N}_6\text{Ad}_2)\text{Fe}\{\text{(ArNCR)}_2\text{CH}\}]$ (R = Me or *t*Bu) were isostructural with **6**. Reductive C–C couplings of isocyanates have been reported,^[12] but in no case has the resultant oxamide ligand coordinated two metal centers in the novel N,O,O-ligating fashion exhibited by **7**, presumably because of steric constraints placed upon the complex by the two bulky nacnac ligands.

The spectroscopic data for **4–7** are largely consistent with their solid-state structures (see the Supporting Information). Molecular structures of all compounds were determined crystallographically. The structure of **4** (Figure 1) confirms that the PhNNPh^{2-} ligand chelates to both distorted tetrahedral Mg centers in an N,C fashion, and has considerable bis(azaallylic) character. Evidence for this proposal comes from its long N–N and short N–C distances, in addition to the apparent loss of some aromaticity from its phenyl groups. The latter was verifiable, as all the hydrogen atoms of the phenyl groups were located from difference maps and freely refined.

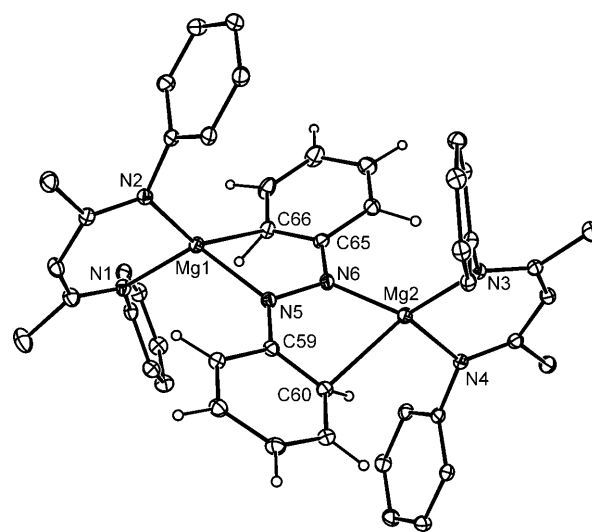


Figure 1. Molecular structure of compound **4**. Thermal ellipsoids are set at 25% probability. Nacnac hydrogen atoms and isopropyl groups are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mg1–N5 2.0118(16), Mg1–C66 2.404(2), Mg2–N6 2.0145(16), Mg2–C60 2.411(2), N5–N6 1.424(2), N5–C59 1.345(2), N6–C65 1.348(2), C59–C60 1.427(3), C65–C66 1.426(3); N5–Mg1–C66 75.68(7), N6–Mg2–C60 76.66(7), N2–Mg1–N1 94.14(7), N3–Mg2–N4 94.64(7).

Those attached to the coordinating C atoms were found to be significantly out of the phenyl planes (by a mean value of 0.39 Å). In line with this observation is the downfield chemical shift for these protons in the ^1H NMR spectrum of the compound at $\delta = 5.68$ ppm. The structure of **5** (Figure 2)

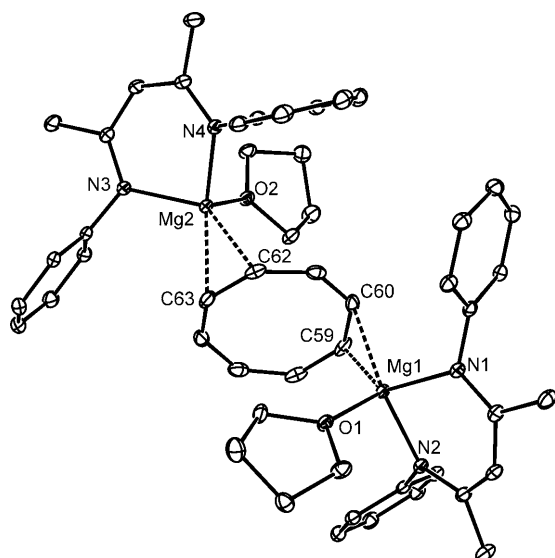


Figure 2. Molecular structure of compound **5**. Thermal ellipsoids are set at 25% probability. Hydrogen atoms and isopropyl groups are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mg1–O1 2.016(2), Mg1–C60 2.312(3), Mg1–C59 2.328(3), Mg2–O2 2.012(2), Mg2–C63 2.295(3), Mg2–C62 2.353(3); N1–Mg1–N2 92.32(9), C60–Mg1–C59 35.92(11), N3–Mg2–N4 92.25(9), C63–Mg2–C62 35.70(11).

reveals its cot^{2-} ligand to be essentially planar with C–C distances ranging from 1.387(4)–1.431(4) Å. The ligand bridges two {(nacnac)Mg(thf)} fragments which are each coordinated by the ring in a η^2 fashion. Reminiscent of the structure of **4**, the N_6 chain in compound **6** (Figure 3) is essentially planar and chelates to both Mg centers in an $\text{N,N}'$ fashion, yielding two planar MgN_4 rings. The N–N bond lengths within the chain are similar to those in the isostruc-

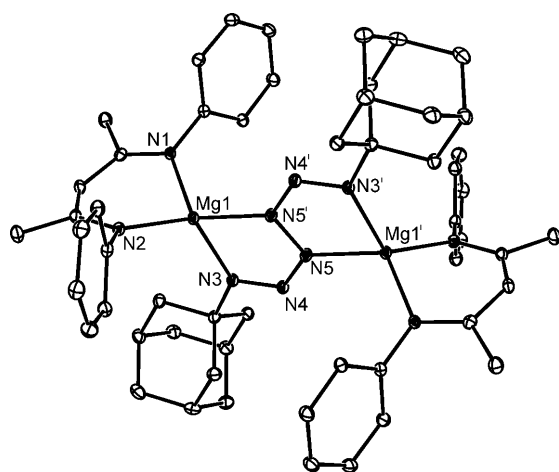


Figure 3. Molecular structure of compound **6**. Thermal ellipsoids are set at 25% probability. Hydrogen atoms and isopropyl groups are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mg1–N5' 2.024(2), Mg1–N1 2.037(2), Mg1–N2 2.051(2), Mg1–N3 2.0888(19), N3–N4 1.301(3), N4–N5 1.315(3), N5–N5' 1.410(3); N1–Mg1–N2 95.82(8), N5'–Mg1–N3 75.61(8). Symmetry operation: ' ($-x+1, -y, -z$).

tural iron compounds and are indicative of significant delocalization over the N3–N4–N5 fragments. In compound **7** (Figure 4), the $\text{N}_2\text{C}_2\text{O}_2$ core of the molecule is close to planar and chelates the Mg centers in both O,O'- and N,O-coordination modes. The distorted tetrahedral Mg atoms share coordination by O1, and the bond lengths within the core do not indicate substantial delocalization over the coupled isocyanate unit.

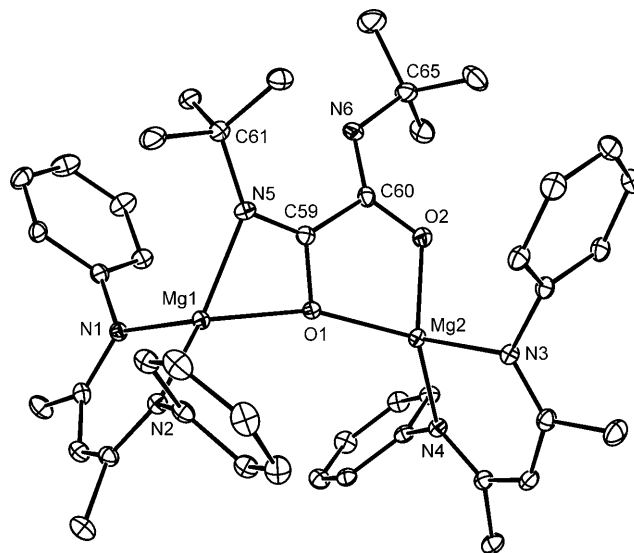
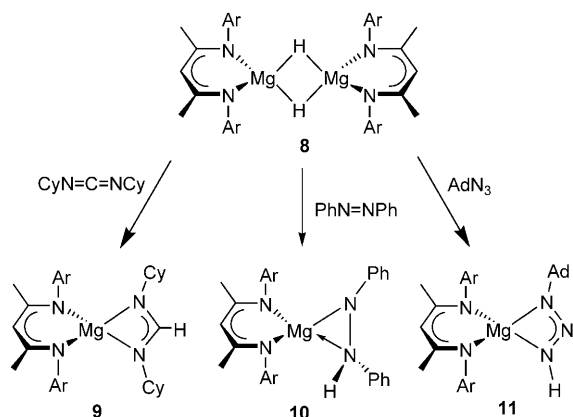


Figure 4. Molecular structure of compound **7**. Thermal ellipsoids are set at 25% probability. Hydrogen atoms and isopropyl groups are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mg1–O1 2.071(2), Mg1–N5 2.097(3), Mg2–O2 1.925(2), Mg2–O1 2.036(2), O1–C59 1.354(4), O2–C60 1.298(4), N5–C59 1.306(4), N6–C60 1.289(4), C59–C60 1.520(4); N1–Mg1–N2 93.55(11), O1–Mg1–N5 64.41(9), N4–Mg2–N3 92.77(11), O2–Mg2–O1 82.85(10).

As we have recently prepared and structurally characterized the magnesium(II) hydride analogue of **2**, [(nacnac)Mg($\mu\text{-H}$) $_2$ Mg(nacnac)] **8**,^[7] the opportunity presented itself to investigate the ability of the complex to reduce the substrates chosen for this study, and compare the results with the reductions involving **2**. These results were also of interest as, although reductions involving poorly characterized compounds of the type RMgH have been previously reported, they can lead to varying outcomes, for example, the formation of hydromagnesiation products by Mg–H addition,^[13] or the formation of paramagnetic species by SET processes.^[14] Moreover, comparisons of reduction reactions of **8** with those of Harder and co-workers' closely related calcium hydride complex, [(nacnac)(thf)Ca($\mu\text{-H}$) $_2$ Ca(thf)(nacnac)],^[15] would be instructive.

All substrates were treated with **8** in toluene at -80°C and the reaction mixtures subsequently warmed to room temperature. No reaction occurred with *cot*, though when the reaction mixture was subsequently heated at reflux for 1 hr, an intractable mixture of products resulted. Similarly, the reaction with *t*BuNCO gave a number of unidentified products which could not be isolated. In contrast, the reductions of the other substrates led to the hydromagnesiation

ation products, **9–11**, in good yields (Scheme 2). Compound **9** was also obtained in high yield from the reaction of **8** with the formamidine, $\text{CyN}=\text{C}(\text{H})\text{N}(\text{H})\text{Cy}$. These results reveal that **8** displays similar reactivity towards unsaturated compounds, compared to the recently studied complex, $[(\text{nacnac})(\text{thf})\text{Ca}(\mu\text{-H})_2\text{Ca}(\text{thf})(\text{nacnac})]$.^[15] In addition, Holland and co-workers' isostructural iron(II) hydride, $[\{\text{HC}(\text{tBuCNAr})_2\}\text{Fe}(\mu\text{-H})_2\text{Fe}\{\text{ArNCrBu}_2\text{CH}\}]$, displayed almost identical reactivity towards AdN_3 , $\text{PhN}=\text{NPh}$ and $i\text{PrN}=\text{C}=\text{NiPr}$.^[16]



Scheme 2. Preparation of compounds **9–11**.

The spectroscopic data for **9–11** are consistent with the proposed formulations of these compounds. The X-ray crystal structure of **10** shows the compound to be monomeric with the hydrazide ligand coordinated to the Mg center in a η^2 mode, as was detected in several zirconium^[17] and samarium^[18] complexes. From the reaction that gave **11**, a very low yield (<2%) of the crystalline primary-amine-coordinated product, $[(\text{nacnac})\text{Mg}(\kappa^2\text{-N,N'-AdN}_3\text{H})(\text{AdNH}_2)]$, was also isolated. The amine ligand presumably originates from the full reduction of AdN_3 by **8**. The structure of this monomeric complex, that of **10**, and the spectroscopic data for **9–11** are included in the Supporting Information.

In summary, a dimeric magnesium(I) complex acts as a facile and selective two-center/two-electron reductant towards a series of unsaturated substrates. Different outcomes resulted from the reductions of the substrates with an analogous magnesium(II) hydride complex. The novel products obtained from the reductions with the magnesium(I) complex prompt us to believe that it may find use as an alternative to other reductants, for example, Sm^{II} compounds and s-block metals, that are widely utilized in organic and organometallic syntheses. We are currently exploring this possibility.

Experimental Section

Crystallographic data: **4**(toluene): $\text{C}_{77}\text{H}_{100}\text{Mg}_2\text{N}_6$; $M_r = 1158.25$; monoclinic; $P2_1/c$; $a = 22.385(5)$, $b = 16.364(3)$, $c = 19.056(4)$ Å; $\beta = 100.86(3)^\circ$; $V = 6855(2)$ Å³; $Z = 4$; $\rho_{\text{calcd}} = 1.122$ Mg m⁻³; $T = 123(2)$ K; $\lambda = 0.71073$ Å; 18641 reflections collected; 11855 independent reflections ($R_{\text{int}} = 0.0226$); $R_1 = 0.0471$ ($F^2 > 2\sigma(F^2)$); $wR_2 =$

0.1197 (all data). **5**(thf)₂: $\text{C}_{82}\text{H}_{122}\text{Mg}_2\text{N}_4\text{O}_4$; $M_r = 1276.46$; monoclinic; $C2/c$; $a = 49.722(10)$, $b = 24.652(5)$, $c = 30.501(6)$ Å; $\beta = 125.27(3)^\circ$; $V = 30525(11)$ Å³; $Z = 16$; $\rho_{\text{calcd}} = 1.111$ Mg m⁻³; $T = 123(2)$ K; $\lambda = 0.71073$ Å; 46954 reflections collected, 26254 independent reflections ($R_{\text{int}} = 0.0322$); $R_1 = 0.0710$ ($F^2 > 2\sigma(F^2)$); $wR_2 = 0.2148$ (all data). **6**(toluene)₂: $\text{C}_{92}\text{H}_{128}\text{Mg}_2\text{N}_{10}$; $M_r = 1422.66$; triclinic; $P\bar{1}$; $a = 12.836(3)$, $b = 13.850(3)$, $c = 13.912(3)$ Å; $\alpha = 109.13(3)$, $\beta = 111.80(3)$, $\gamma = 101.91(3)^\circ$; $V = 2089.8(7)$ Å³; $Z = 1$; $\rho_{\text{calcd}} = 1.130$ Mg m⁻³; $T = 123(2)$ K; $\lambda = 0.71073$ Å; 15233 reflections collected, 8178 independent reflections ($R_{\text{int}} = 0.0309$); $R_1 = 0.0638$ ($F^2 > 2\sigma(F^2)$); $wR_2 = 0.1864$ (all data). **7**(toluene)_{1.5}: $\text{C}_{78.50}\text{H}_{112}\text{Mg}_2\text{N}_6\text{O}_2$; $M_r = 1220.36$; monoclinic; $P2_1/n$; $a = 14.886(3)$, $b = 23.938(5)$, $c = 20.879(4)$ Å; $\beta = 97.99(3)^\circ$; $V = 3382.7(12)$ Å³; $Z = 4$; $\rho_{\text{calcd}} = 1.100$ Mg m⁻³; $T = 123(2)$ K; $\lambda = 0.71073$ Å; 24137 reflections collected, 12932 independent reflections ($R_{\text{int}} = 0.0451$); $R_1 = 0.0753$ ($F^2 > 2\sigma(F^2)$); $wR_2 = 0.1711$ (all data). **10**: $\text{C}_{41}\text{H}_{52}\text{MgN}_4$; $M_r = 625.18$; monoclinic; $P2_1/n$; $a = 14.889(3)$, $b = 15.238(3)$, $c = 16.978(3)$ Å; $\beta = 102.41(3)^\circ$; $V = 3762.0(13)$ Å³; $Z = 4$; $\rho_{\text{calcd}} = 1.104$ Mg m⁻³; $T = 123(2)$ K; $\lambda = 0.71073$ Å; 11912 reflections collected, 6424 independent reflections ($R_{\text{int}} = 0.0350$); $R_1 = 0.0465$ ($F^2 > 2\sigma(F^2)$); $wR_2 = 0.1184$ (all data). **11**(AdNH₂): $\text{C}_{49}\text{H}_{74}\text{MgN}_6$; $M_r = 771.45$; monoclinic; $P2_1/c$; $a = 21.296(4)$, $b = 10.099(2)$, $c = 20.949(4)$ Å; $\beta = 100.63(3)^\circ$; $V = 4428.1(15)$ Å³; $Z = 4$; $\rho_{\text{calcd}} = 1.157$ Mg m⁻³; $T = 123(2)$ K; $\lambda = 0.71073$ Å; 15053 reflections collected, 7794 independent reflections ($R_{\text{int}} = 0.0522$); $R_1 = 0.0567$ ($F^2 > 2\sigma(F^2)$); $wR_2 = 0.1647$ (all data). CCDC 716772 (**4**), 716773 (**5**), 716774 (**6**), 716775 (**7**), 716776 (**10**) and 716777 (**11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Full synthetic and spectroscopic details for **4–7** and **9–11**, and ORTEP representations of **10** and $[(\text{nacnac})\text{Mg}(\kappa^2\text{-N,N'-AdN}_3\text{H})(\text{AdNH}_2)]$ can be found in the Supporting Information.

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