

Synthesis and Characterization of New Mixed-Metal Sodium–Magnesium Enolates Derived from 2,4,6-Trimethylacetophenone[†]

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The reactivity of the stoichiometric variant monosodium–monomagnesium trialkyl NaMgBu₃ and disodium–monomagnesium tetraalkyl Na₂MgBu₄ complexes toward the sterically demanding ketone 2,4,6-trimethylacetophenone has been investigated and led to the synthesis of a series of mixed sodium–magnesium enolate complexes. Thus, 2 and 3 molar equiv of the ketone with NaMgBu₃ produce heteroanionic [Na₂Mg₂(μ-Bu)₂{μ-OC(=CH₂)Mes}₄(TMEDA)₂] (6) and homoanionic [Na₂Mg₂{μ-OC(=CH₂)Mes}₆(TMEDA)₂] (4), respectively, while 4 equiv of the ketone with Na₂MgBu₄ affords homoanionic [Na₂Mg{μ-OC(=CH₂)Mes}₄(TMEDA)₂] (5). X-ray crystallographic studies reveal that 4 and 6 adopt similar tetranuclear Na···Mg···Mg···Na chain arrangements, held together by enolato O bridges in the former and a mixture of enolato O and alkyl C bridges in the latter, whereas 5 adopts a smaller trinuclear Na···Mg···Na chain arrangement with all enolato O bridges. The metal coordination in all these structures is distorted tetrahedral, while the sodium cations at the ends of the mixed-metal chains carry terminal TMEDA ligands. ¹H and ¹³C NMR spectral data recorded in C₆D₆ are also reported for 4–6. For comparative purposes, the synthesis and X-ray crystal structure of the homometallic sodium enolate [Na₂{OC(=CH₂)Mes}₂(TMEDA)₂] (7), a simple enolate O-bridged dimer, is also reported.

Introduction

Introduced by Wittig more than fifty years ago,¹ alkali metal magnesium 'ate complexes [which can be formulated most commonly as either MMgR₃ or M⁺(MgR₃)⁻] constitute a broad family of compounds. Through the years, several structural studies of these compounds by X-ray crystallography have been carried out, primarily by Weiss;² nevertheless it is only relatively recently that their reactivity has attracted significant attention from synthetic chemists. Thus, Oshima reported in 2000 the first halogen–magnesium exchange examples using lithium organomagnesium 'ate complexes (LiMgR₃), which can smoothly undergo halogen–magnesium exchange with several aryl and alkenyl halides.³ The reactivity of these mixed-metal reagents can be modulated by changing the alkyl groups (R) on the magnesium. A year later Iida and Mase documented the use of the trialkyl 'ate LiMgBu₃ for the selective monobromine–magnesium exchange of several dibromoarenes.⁴ Just lately Mongin has investigated the selective deprotonation of chloro and fluoro aromatic substrates such as pyridines or quinolines and other important heterocyclic compounds such as thiophenes or furans using a wide range of lithium magnesates [including LiMgBu₃, Li₂MgBu₄, LiMg(TMP)₃, and LiMgBu₂(TMP)]; TMP

= 2,2,6,6-tetramethylpiperidide], finding that these mixed-metal reagents can offer better selectivities and tolerate higher reaction temperatures than the conventional monometallic substrates.⁵ Furthermore, Knochel has reported that the addition of LiCl to 'PrMgCl significantly enhances the reactivity of the Grignard reagent in Br/Mg exchange reactions, postulating that the magnesiate "[('PrMgCl)₂Li⁺]" is the active species.⁶

We have previously studied the highly selective Brønsted basic reactivity of amide-based 'ates MMg(NR₂)₃ [where M = Li, Na, or K; NR₂ = NⁱPr₂, N(SiMe₃)₂]. The most notable example to date is the selective 1,1',3,3'-tetradeprotonation of ferrocene, ruthenocene, and osmocene by NaMg(NⁱPr)₃.⁷ More recently we have extended our studies to the heteroleptic magnesiate NaMgBu(TMP)₂.⁸ This mixed-metal, mixed-ligand compound can be obtained as a crystalline solid in its TMEDA (TMEDA = N,N,N',N'-tetramethylethylenediamine) solvate form. It also exhibits a high selectivity in its action toward arenes, for example, regioselectively deprotonating toluene at the *meta* ring position, leaving the more acidic (in pK_a terms)⁹

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[†] Dedicated to Professor Víctor Riera on the occasion of his 70th birthday.
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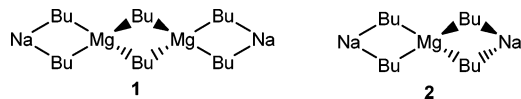


Figure 1. ChemDraw representations of the stoichiometric-variant magnesiates NaMgBu_3 (**1**) and Na_2MgBu_4 (**2**).

Me site intact.¹⁰ The selective monometalation of the classical organometallic molecule bis(benzene)chromium can also be achieved using this synergic mixed-metal reagent, opening up a new route toward the synthesis of new heteroleptic bis(arene)-chromium complexes.¹¹ In a previous communication¹² we studied the synthesis and characterization of the stoichiometric variant magnesiates NaMgBu_3 (**1**) and Na_2MgBu_4 (**2**) (Figure 1) and their reactivity as metalating reagents toward toluene. We demonstrated that the cocomplexation of BuNa with Bu_2Mg is thermodynamically favored and that one of the consequences of the formation of these mixed-metal compounds is that they are weaker metallating reagents compared to butylsodium, but at the same time they can offer better selectivity. We also showed the crucial importance of the Na:Mg ratio in these compounds and how changing the stoichiometry, and thereby the structure of the magnesiate, can dramatically alter the course of the reaction.

In the present paper, we investigate the reactivity of the sodium magnesates **1** and **2** toward the ketone 2,4,6-trimethylacetophenone (**3**), which is known in the literature for the excellent crystallization properties that its metal enolates can have.¹³ The reactivity of magnesiates with ketones has hitherto been scarcely studied. In 2005 Ishihara reported an extensive study of the reactivity of lithium magnesiates toward a wide range of ketones, finding that these mixed-metal reagents present a higher nucleophilicity than classic monometallic compounds (such as organolithium or Grignard reagents) while their basicity is much lower, which make them ideal reagents for addition reactions to ketones.¹⁴ The ketone chosen in our study is highly sterically demanding; thus the possibility of addition reactions to the carbonyl group is minimized due to the presence of a

bulky mesityl group on **3**, favoring a deprotonation reaction to form the corresponding enolate.

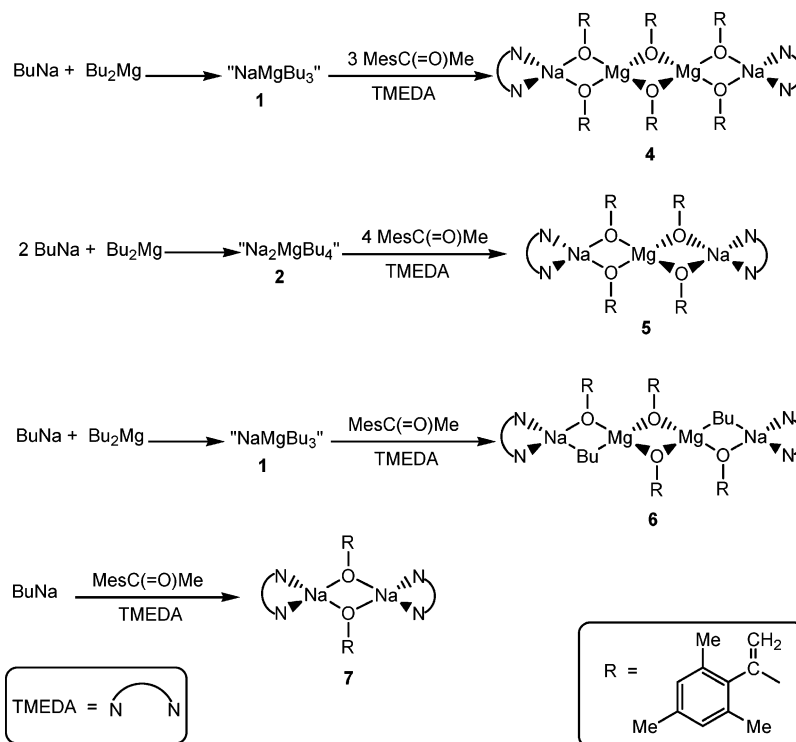
Deprotonation of ketones to afford the corresponding metallic enolates is a cornerstone reaction of organic synthesis. Enolate anions are important intermediates involved in numerous fundamental organic transformations such as alkylations, Michael additions, aldol additions, or acylations.¹⁵ The classical reagents utilized in the synthesis of enolates are sterically demanding lithium amides, which are well-known for being strong bases and poor nucleophiles. Recently some research groups have started to investigate the use of alternative reagents, containing a different s-group metal, such as magnesium bisamides, finding them to be better regioselective bases than the parent lithium amides.¹⁶ In the search for more efficient bases and inspired by the synergic metalations achieved employing mixed-metal amides, we have published the structures of a series of mixed potassium–calcium enolates obtained by reaction of the ketone **3** with a mixture of $\text{Ca}(\text{HMDS})_2$ and KHMDS .¹³

In this paper we report the synthesis and characterization of homoanionic $[\text{Na}_2\text{Mg}_2\{\mu\text{-OC}(\text{=CH}_2)\text{Mes}\}_6(\text{TMEDA})_2]$ (**4**) and $[\text{Na}_2\text{Mg}\{\mu\text{-OC}(\text{=CH}_2)\text{Mes}\}_4(\text{TMEDA})_2]$ (**5**) and heteroanionic $[\text{Na}_2\text{Mg}_2(\mu\text{-Bu})_2\{\mu\text{-OC}(\text{=CH}_2)\text{Mes}\}_4(\text{TMEDA})_2]$ (**6**) obtained by reaction of either NaMgBu_3 (for **4** and **6**) or Na_2MgBu_4 (for **5**) with the ketone **3**. To the best of our knowledge, this series represents the first crystallographically characterized sodium–magnesium enolates in the literature as well as the first bimetallic enolates to contain magnesium.

Results and Discussion

Syntheses. Scheme 1 shows the reactions used to synthesize the new compounds **4–7**. The stoichiometric variant enolates **4** and **5** were prepared in an analogous manner by mixing the metal alkyl reagents BuNa and Bu_2Mg in the desired stoichiometry (1:1 for **4** and 2:1 for **5**) to give the corresponding magnesiates **1** and **2**, respectively. Next, these magnesiates were treated with the required amount of ketone **3** to effect its

Scheme 1



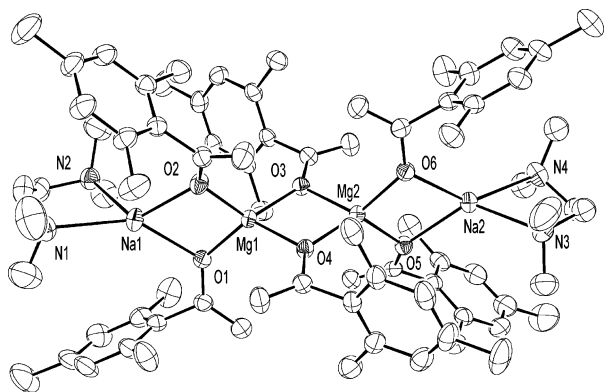


Figure 2. Molecular structure of **4** showing selected atom labeling and with hydrogen atoms omitted for clarity.

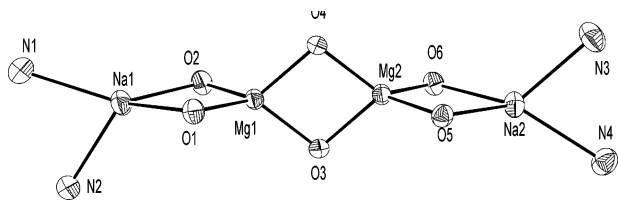


Figure 3. Inorganic chain of **4**.

deprotonation and to convert all the butyl groups to butane, leaving the desired enolate as a solid suspended in hexane. To complete the formation of **4** and **5**, TMEDA is introduced in an additional step, to help to redissolve the mixed-metal enolates in a mixture of solvents (toluene/hexane). Both compounds **4** and **5** were deposited from solution as colorless crystalline solids, after allowing their respective reaction mixtures to stand at room temperature for several hours, in high yields (60–70%). Following the same approach, the reaction of the magnesiate **1** with 1 molar equiv of ketone, followed by the addition of TMEDA, afforded the mixed alkyl-enolate compound **6** as a colorless crystalline solid in 45% yield.

For structural comparison the monometallic enolate $[\text{Na}_2\{\text{OC}(\text{=CH}_2)\text{Mes}\}_2(\text{TMEDA})_2]$ (**7**) was also prepared, following a procedure similar to the one described above by reaction of BuNa with 1 molar equiv of **3** and TMEDA at room temperature. In this case the sodium enolate appears to be much more soluble than the bimetallic complexes **4** and **5**, and the crystals were obtained only after leaving the solution in the freezer for several days. The yield of the isolated compound is relatively modest (18–23%) due to the excellent solubility of **7** in hexane solution, which renders it difficult to isolate as a crystalline solid.

Solid-State Structures. The structures of compounds **4**–**7** have been successfully crystallographically characterized by X-ray diffraction studies. Figure 2 shows the complete molecular structure of **4**, while Figure 3 spotlights its inorganic $[\text{Na}(\mu\text{-O})_2\text{Mg}(\mu\text{-O})_2\text{Mg}(\mu\text{-O})_2\text{Na}]$ chain terminated by TMEDA nitrogen atoms. This structure can be envisaged as an ion-contacted aggregate of two oppositely disposed $[\text{Na}(\text{TMEDA})]^+$ cations coordinated to the complex dianion $[\text{Mg}_2\{\text{OC}(\text{=CH}_2)\text{Mes}\}_6]^{2-}$, building a tetranuclear $\text{Na}\cdots\text{Mg}\cdots\text{Mg}\cdots\text{Na}$ chain arrangement connected by six enolate ligands. This assembly is similar to the structure of the homometallic enolate $[\text{Mg}_4\{\mu\text{-OC}(\text{=CH}_2)\text{Mes}\}_6\{\text{OC}(\text{=CH}_2)\text{Mes}\}_2\{\text{OC}(\text{CH}_3)\text{Mes}\}_2(\text{ToI})_2]$,¹⁷ which can be described as a $[\text{OMg}(\mu\text{-O})_2\text{Mg}(\mu\text{-O})_2\text{Mg}(\mu\text{-O})_2\text{MgO}]$ chain

formed by four magnesium atoms and eight enolate ligands, with six bridging and two terminal. Each of the terminal magnesiums in this compound is bound to an unenolized neutral molecule of the ketone that acts as a monodentate donor.

The molecule in **4** is approximately centrosymmetric (but noncrystallographically), containing three orthogonal four-membered rings, two outer $[\text{Na}(\mu\text{-O})_2\text{Mg}]$ heterobimetallic rings, which are connected through a central homometallic $[\text{Mg}(\mu\text{-O})_2\text{Mg}]$ ring. The $\text{Na}\cdots\text{Mg}\cdots\text{Mg}\cdots\text{Na}$ backbone is almost linear, as shown by the Mg1-Mg2-Na1 and Mg2-Mg1-Na1 angles, which are $177.48(3)^\circ$ and $173.34(3)^\circ$, respectively. The three four-membered rings are planar, as evidenced by the sum of the internal angles, which is virtually 360° for each ring (359.44° , 359.98° , and 360.00°). This kind of arrangement of linked orthogonal M_2O_2 rings has been previously found in other magnesium compounds such as the previously mentioned enolate $[\text{Mg}_4\{\mu\text{-OC}(\text{=CH}_2)\text{Mes}\}_6\{\text{OC}(\text{=CH}_2)\text{Mes}\}_2\{\text{OC}(\text{CH}_3)\text{Mes}\}_2(\text{ToI})_2]$ ¹⁷ or the alkoxide compounds $[\text{Mg}_3(\mu\text{-OSiPh}_3)_4(\text{OSiPh}_3)_2]$ ¹⁸ and $[\text{Mg}_3(\mu\text{-ODipp})_4(\text{ODipp})_2]$ (Dipp = 2,6-diisopropylphenyl).¹⁹ There are also a few examples of heterobimetallic compounds containing magnesium such as $[(\text{Me}_2)\text{AlMg}(\mu\text{-N}^i\text{Pr}_2)(\mu\text{-OMe})_2]$,²⁰ $[(\text{Me}_2)\text{AlMg}(\mu\text{-O}^i\text{Bu})_3]$,²¹ and $[(\text{O}^i\text{Bu})\text{SnMg}(\mu\text{-O}^i\text{Bu})_3]$,²² which also present the same structural motif.

Each metal center in **4** is tetracoordinated in a distorted tetrahedral geometry. Two nitrogens and two oxygens from the TMEDA and enolate ligands respectively bond to the sodium atom. Each magnesium atom is bonded to four oxygen atoms from the enolate ligands. The Mg-O bond distances (see Table 1) lie in a range similar to the ones found in other Mg -alkoxide compounds²³ and in the homometallic bromomagnesium ketone enolate $[(\text{Et}_2\text{O})_2\text{Mg}_2\text{Br}_2\{\text{OC}(\text{tBu})(\text{=CHCH}_3)_2\}]$ [$1.951(7)$ and $1.955(7)$ Å],²⁴ although for the enolates that are exclusively connecting two Mg atoms the Mg-O distances are modestly longer (average length, 2.002 Å) than the ones that link Na and Mg (average length 1.943 Å). The Na-O distances [from $2.2901(18)$ to $2.3295(18)$ Å] are also within the expected range found in other Na -alkoxide compounds.²⁵

Compound **4** represents to the best of our knowledge the first example of a mixed-metal enolate compound containing magnesium. The closest precedent to **4** is the bimetallic enolate $[\text{K}_2\text{Ca}_2\{\text{OC}(\text{=CH}_2)\text{Mes}\}_6\cdot 2\text{THF}]$,¹³ obtained by reaction of the

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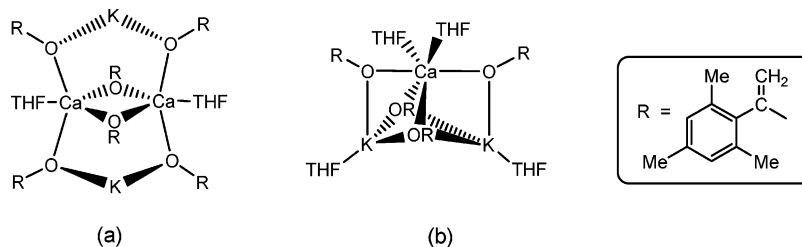


Figure 4. ChemDraw representations of (a) $[K_2Ca_2\{OR\}_6 \cdot 2THF]$ and (b) $[K_2Ca(OR)_4 \cdot 4THF]$.

Table 1. Key Bond Lengths (Å) and Bond Angles (deg) within the Structures of 4, 5, and 7

For 4			
Na1–O1	2.3295(18)	Na2–O5	2.3043(17)
Na1–O2	2.2901(18)	Na2–O6	2.3120(17)
Mg1–O1	1.9420(16)	Mg2–O3	2.0133(16)
Mg1–O2	1.9382(16)	Mg2–O4	1.9767(15)
Mg1–O3	1.9861(15)	Mg2–O6	1.9422(16)
Mg1–O4	2.033(16)	Mg2–O5	1.9497(16)
N2–Na1–N1	74.47(7)	N3–Na2–N4	73.82(8)
O2–Na1–O1	73.98(6)	O5–Na2–O6	74.43(6)
O2–Mg1–O1	91.52(7)	O6–Mg2–O5	91.67(7)
O3–Mg1–O4	80.77(6)	O6–Mg2–O4	126.70(7)
O2–Mg1–O3	121.95(7)	O5–Mg2–O4	124.32(7)
O1–Mg1–O4	119.67(7)	O6–Mg2–O3	118.70(7)
O1–Mg1–O3	126.21(7)	O5–Mg2–O3	117.75(7)
O2–Mg1–O4	120.35(7)	O4–Mg2–O3	80.76(6)
Mg1–O2–Na1	97.67(7)	Mg2–O5–Na2	96.97(7)
Mg1–O1–Na1	96.27(7)	Mg2–O6–Na2	96.93(7)
Mg1–O3–Mg2	98.90(7)	Mg2–O3–Mg4	99.55(7)
For 5			
Na1–O1	2.267(2)	Mg1–O3	1.958(2)
Na1–O2	2.264(2)	Mg1–O4	1.955(2)
Mg1–O1	1.957(2)	Na2–O3	2.250(2)
Mg1–O2	1.942(2)	Na2–O4	2.245(2)
N2–Na1–N1	73.78(10)	O2–Mg1–O4	121.05(10)
O2–Na1–O1	76.63(8)	Mg1–O1–Na1	94.77(10)
O2–Mg1–O1	92.17(10)	Mg1–O2–Na1	95.27(10)
O4–Mg1–O3	93.17(10)	N4–Na2–N3	75.51(13)
O2–Mg1–O3	118.67(10)	O4–Na2–O3	78.47(9)
O4–Mg1–O1	118.63(10)	Mg1–O3–Na2	93.48(10)
O1–Mg1–O3	115.37(10)	Mg1–O4–Na2	93.72(10)
For 7			
Na1–O1	2.225(3)	Na1–N2	2.433(4)
Na1–N1	2.397(4)	Na1–C8	2.810(4)
O1*–Na1–O1	91.87(12)	O1*–Na1–N1	107.58(13)
N1–Na1–N2	76.43(12)	O1*–Na1–N2	103.93(15)
Na1*–O1–Na1	87.86(11)	O1–Na1–N2	130.75(14)
O1–Na1–N1	142.24(14)		

trisamide $[KCa(HMDS)_3 \cdot THF]$ with 3 molar equiv of ketone **3**. However this compound, although it also combines an alkali metal with a group II metal, adopts a completely different structure from that of **4** (Figure 4a): it can be envisaged as a cationic eight-membered $[(KOCaO)_2]$ ring hosting an additional two enolate ligands, with one THF molecule bound to calcium and with a plethora of $K-\pi$ ligand interactions involving both the aromatic rings and the olefin $C=C$ bonds. This same structural motif has been previously found for the series of “inverse crown” complexes $[\{M^1M^2(N^iPr_2)_2\}_2(X)_2]$ ($M^1 = Li$ or Na ; $M^2 = Mg$; $X = OR, H$)^{26,27} and $[\{(TMEDA)MMg(Bu)_2\}_2(O^tBu)_2]$ ($M = Na, K$)²⁸ but also extends to other

heterometallic systems, such as the sodium–iron alkoxide $[\{NaFe(O^tBu)_3(THF)\}_2]$ ²⁹ and the potassium–zinc siloxide $[\{KZn(OSiMe_3)_3(TMEDA)\}_2]$ ³⁰ or homometallic ones such as the alkylmagnesium amide $[\{^nBuMg_2[N(H)Dipp]_2(O^tBu)\}_2]$,³¹ its zinc relation $[\{EtZn_2[N(H)Dipp]_2(OEt)\}_2]$,³² and the Grignard reagent $[\{(PhCH_2)Mg_2Cl_3(THF)_3\}_2]$.³³

The contrasting structures of **4** and $[K_2Ca_2\{OC(=CH_2)Mes\}_4 \cdot 2THF]$ can be rationalized in terms of the different metals present in each compound, as potassium and calcium are much larger than sodium and magnesium and consequently much softer in “hard–soft” acid–base terms. The expansion in size would explain the pentacoordination of the calcium atom in $[K_2Ca_2\{OC(=CH_2)Mes\}_6 \cdot 2THF]$,¹³ while in **4** magnesium is only tetraordinated; also the softer nature of potassium compared to sodium would explain the presence of the π -contacts present in the K/Ca enolate, while these types of interactions are absent in **4** (the closest $Na-C$ contact is 3.296 Å, which is too long to be considered significant).

As mentioned above the number of alkali metal enolates that have been structurally characterized is relatively small,³⁴ and to our knowledge the only two examples of bimetallic enolates that combine two alkali metals have been reported by Williard, namely, the lithium–sodium complex $[Li_2Na_4\{OC(=CH_2)^iBu\}_6 \cdot (NH^iPr_2)_2]$, made by the reaction of $Na(N^iPr_2)$ and $Li(N^iPr_2)$ with 4 equiv of pinacolone,³⁵ and the lithium–potassium aggregate $[\{OC(=CH_2)^iBu\}_4(O^tBu)_4Li_4K_5(OH)(THF)_5]$, which contains hydroxide, *tert*-butoxide, and pinacolate anions.³⁶

Enolate **5** possesses a structure similar to that of **4**, but having a shorter trimetallic $Na \cdots Mg \cdots Na$ chain arrangement in which the metals are connected through enolate bridges (Figure 5). This structure can alternatively be described as two oppositely disposed $Na(TMEDA)^+$ cations binding to the tetrahedral anion $[Mg\{\mu-OC(=CH_2)Mes\}_4]^{2-}$, forming two orthogonal fused heterobimetallic four-membered rings. As in compound **4** both rings are almost planar (sum of the internal angles is 358.84° in both cases), and the arrangement of the three metals is slightly bent, as evidenced by the $Na1 \cdots Mg1 \cdots Na2$ angle $[167.70(5)^\circ]$. The $Na-O$ bond lengths $[2.245(2)–2.267(2) \text{ \AA}]$ and $Mg-O$ bond lengths $[1.942(2)–1.958(2) \text{ \AA}]$ in **5** are within the average ranges of other sodium and magnesium alkoxide compounds, respectively.

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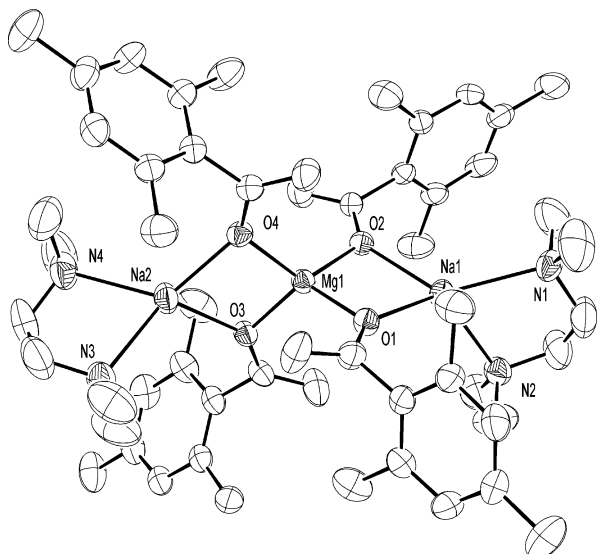


Figure 5. Molecular structure of **5** showing selected atom labeling and with hydrogen atoms omitted for clarity.

The closest structural analogy to **5** is the mixed lithium–magnesium cresolate $[(\text{TMEDA})_2\text{Li}_2\text{Mg}(\text{OR})_4]$ [$\text{R} = o\text{-Me}(\text{C}_6\text{H}_4)$],³⁷ which presents the same kind of chain arrangement. The Mg–O bond lengths (average 1.938 Å) within this cresolate are very similar to the ones found in **5** (average 1.953 Å), as is the $\text{Li}\cdots\text{Mg}\cdots\text{Li}$ angle [$167.77(2)^\circ$], which shows, again, a distortion of the $\text{M}\cdots\text{Mg}\cdots\text{M}$ backbone from linearity. This structural motif had been previously described for other mixed lithium–magnesium compounds such as the amide $[\text{Li}_2\text{Mg}\{\mu\text{-N}(\text{CH}_2\text{Ph})_2\}_4]$ ³⁸ or the alkide $[(\text{TMEDA})_2\text{Li}_2\text{Mg}(\text{Me})_4]$.³⁹

To our knowledge, the only precedent for a mixed-metal enolate that combines two alkali metal centers with one group II metal is found in $[\text{K}_2\text{Ca}\{\mu\text{-OC}(\text{=CH}_2)\text{Mes}\}_4\cdot 4\text{THF}]$,¹³ which has a significantly different structural arrangement from that of **5** (Figure 4b). In this dipotassium–monocalcium structure the calcium atom is bonded to four enolate ligands and two molecules of THF (thus completing an octahedral oxygen coordination), while each potassium atom bonds to three enolate ligands [although it is suggested that the nature of these bonds is fairly weak due to its long K–O bond lengths of 2.726(3), 2.729(3), and 2.852(3) Å] and one molecule of THF. As in the previously mentioned potassium–calcium enolate, the potassium atoms again engage in a series of π -interactions with the surrounding olefin and arenes. The significant deviation between the structure of this compound and that of **5**, which contain two metals of the same groups and the same ligand set, can be again rationalized in terms of the softer character and larger size of the K/Ca pairing compared to the Na/Mg pairing.

Compound **6** presents an analogous structure (Figure 6) to that of **4**, with a tetranuclear $\text{Na}\cdots\text{Mg}\cdots\text{Mg}\cdots\text{Na}$ chain, except that in **6** the four metals are connected through a mixture of four enolate and two butyl ligands instead of the all-enolate arrangement exhibited by **4**. Thus, compound **6** can be described in the same terms as **4**, as an ion-contacted aggregate of two $\text{Na}(\text{TMEDA})^+$ cations and the mixed-ligand, complex anion $[\text{Mg}_2(\text{Bu})_2\{\text{OC}(\text{=CH}_2)\text{Mes}\}_4]^{2-}$, which form three orthogonal

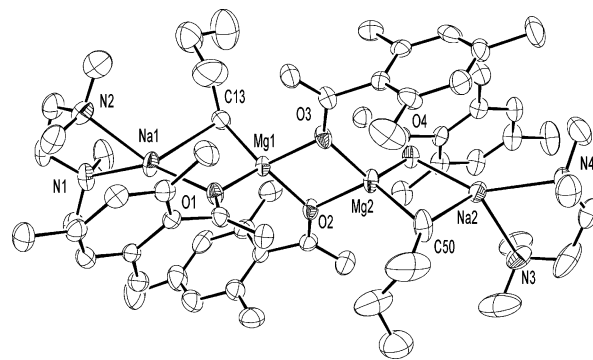


Figure 6. Molecular structure of **6** showing selected atom labeling and with hydrogen atoms omitted for clarity.

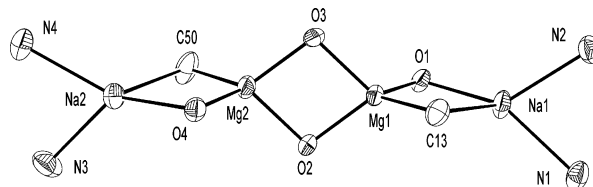


Figure 7. Inorganic chain of **6**.

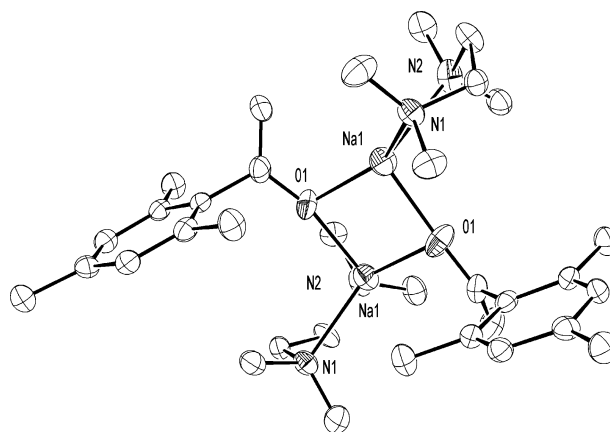


Figure 8. Molecular structure of **7** showing selected atom labeling and with hydrogen atoms omitted for clarity.

fused four-membered rings (Figure 7 spotlights the inorganic core of **6**). There are two $[\text{Na}(\mu\text{-O})(\mu\text{-C})\text{Mg}]$ outer rings and one $[\text{Mg}(\mu\text{-O})_2\text{Mg}]$ central ring. A notable structural feature of **6** is that the two butyl groups occupy opposite transoid positions within the tetrametallic chain. Unfortunately a large amount of motion within the butyl groups and the TMEDA ligands of **6** adversely effects the accuracy of this structure and thus prevents discussion of the bond lengths or bond angles. That notwithstanding, this structure represents to the best of our knowledge the first example of an s-block metal enolate that contains an alkyl coligand.

Sodium enolate **7** adopts a dimeric centrosymmetric structure (Figure 8) based on a four-membered $[\text{Na}_2(\mu\text{-O})_2]$ ring with terminal TMEDA ligands. The four-membered ring adopts a planar disposition (the sum of its internal angles is 359.46°). This structural motif has been previously described for several solvated lithium enolates such as the ester-enolate $[\text{Li}_2\{\text{OC}(\text{=CH}(\text{CH}_3)\text{O}^-\text{Bu})_2(\text{TMEDA})_2\}]$,⁴⁰ reported by Seebach. No dimers analogous to that of **7** have been previously reported for solvated sodium enolates. The closest analogy is provided by the mixed ester enolate-amide aggregate $[\text{Na}_2(\text{HMDS})\{\text{OC}$

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Table 2. Key Crystallographic and Refinement Parameters for Compounds 4–7

	4	5	6	7
empirical formula	C ₇₈ H ₁₁₀ Mg ₂ N ₄ Na ₂ O ₆	C ₅₆ H ₈₄ MgN ₄ Na ₂ O ₄	C ₆₄ H ₁₀₂ Mg ₂ N ₄ Na ₂ O ₄	C ₃₄ H ₅₈ N ₄ Na ₂ O ₂
<i>M</i>	1294.30	947.56	1086.10	600.82
cryst syst	monoclinic	orthorhombic	monoclinic	orthorhombic
space group	<i>P2₁/n</i>	<i>Pbca</i>	<i>P2₁/a</i>	<i>Pnn2</i>
<i>a</i> /Å	16.7554(3)	16.8170(3)	13.7845(3)	12.4277(9)
<i>b</i> /Å	20.1829(3)	18.4174(3)	21.4772(6)	17.2432(123)
<i>c</i> /Å	23.4641(3)	37.6423(6)	22.3609(4)	8.6138(3)
α /deg	90	90	90	90
β /deg	98.688(1)	90	92.420(1)	90
γ /deg	90	90	90	90
<i>V</i> /Å ³	7843.9(2)	11658.8(3)	6614.1(3)	1845.9(2)
<i>Z</i>	4	8	4	2
<i>T</i> /K	123(2)	123(2)	123(2)	123(2)
indep reflns	17965	9129	10333	2010
goodness-of-fit on <i>F</i> ²	1.005	1.011	1.080	1.051
R1 [<i>I</i> > 2 σ (<i>I</i>)]	0.0597	0.0668	0.1238	0.0568
wR2	0.1525	0.1488	0.3601	0.1547

Table 3. ¹H NMR Chemical Shifts (δ in ppm) for the Enolate Ligands in Compounds 4–7 in C₆D₆ Solution

compound	$\delta(m\text{-H})$	$\delta(=\text{CHH}')$	$\delta(o\text{-CH}_3)$	$\delta(p\text{-CH}_3)$
4	6.80 ^a	5.01, 4.20 ^a	2.87 ^a	2.15 ^a
	6.79 ^b	4.81, 4.01 ^b	2.49 ^b	2.11 ^b
5	6.77	4.70, 4.03	2.74	2.14
6	6.77	4.69, 4.02	2.73	2.18
7	6.78	3.95, 3.64	2.45	2.17

^a Chemical shifts for the enolate ligands bridging to two magnesiums.

^b Chemical shifts for the enolate ligands bridging to sodium and magnesium.

Table 4. Selected ¹³C NMR Chemical Shifts (δ in ppm) for the Enolate Ligands in Compounds 4–7 in C₆D₆ Solution

compound	$\delta(\text{C}-\text{O})$	$\delta(\text{C}_{\text{ipso}})$	$\delta(=\text{CH}_2)$
4	161.23 ^a	140.51 ^a	89.74 ^a
	163.12 ^b	143.14 ^b	87.02 ^b
5	165.17	144.53	83.91
7	169.94	144.51	79.60

^a Chemical shifts for the enolate ligands bridging two magnesiums.

^b Chemical shifts for the enolate ligands bridging sodium and magnesium.

(=CCHMe₂O'Bu)(TMEDA)₂],⁴¹ which adopts a planar four-membered ring arrangement in which one of the enolate ligands has been replaced by an amide group. The Na–O distance in **7** (2.225(3) Å) is very close to those found in this mixed-ligand sodium compound (average length 2.21 Å) and slightly shorter than the ones observed in **4** (average length 2.308 Å) and **5** (average length 2.256 Å). The sodium atom in **7** occupies a distorted tetrahedral geometry made up of two nitrogen atoms from the chelating ligand TMEDA and two enolate oxygens. However, in addition the sodium atom engages in significant π -interactions with the olefinic carbons of the enolate ligands [Na–C8, 2.810(4) Å; Na–C7, 3.002(4) Å]. In contrast, the Na–C separation distances involving the arene rings appear to be too long (the shortest Na–C_{arene} distance is 4.089 Å) to be indicative of any significant interaction.

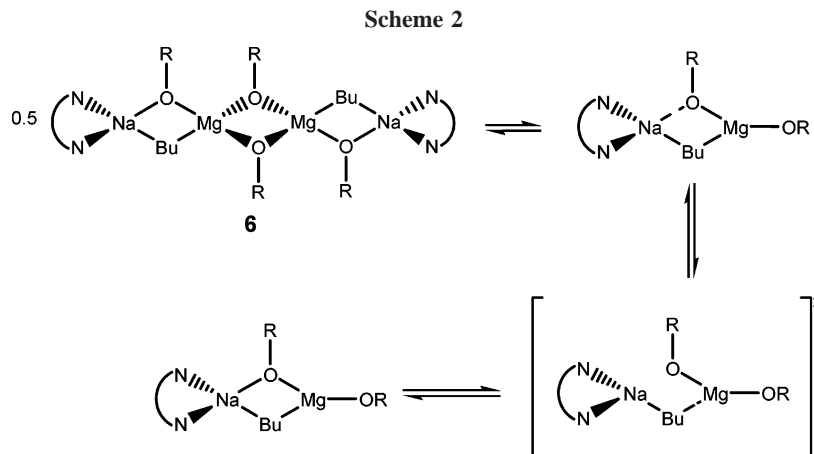
Solution-State Studies. The mixed-metal enolates **4** and **5** and the monometallic sodium enolate **7** are highly soluble in arene solvents, allowing their ¹H and ¹³C NMR spectra to be obtained in C₆D₆ solution at room temperature. Compound **6** possesses a much lower solubility in arene solvents; thus only its ¹H NMR spectrum could be recorded. Attempts to record a ¹³C NMR spectrum in deuterated benzene or toluene failed due to the partial decomposition of **6** during the longer accumulation times required. Partial degradation was also found when a more polar solvent such as deuterated THF was employed. Tables 3

and 4 compare the most distinct resonances in the ¹H and ¹³C NMR spectra respectively of compounds 4–7.

The ¹H NMR spectrum of **4** shows two sets of enolate signals, in a ratio of 2:1. This is indicative that the structure found in the solid state is maintained in solution, with two distinct types of enolate ligands, those that connect sodium to magnesium and those that connect two magnesium centers (referred as enolate and enolate', respectively, in the Experimental Section).⁴² As observed in Table 3, the chemical shifts of the corresponding aromatic protons and the *para*-CH₃ resonances show little variation between the two different types of enolate, whereas the ones assignable to the olefinic protons and the *ortho*-CH₃ groups (which are the groups closest to the oxygen atom and in consequence will be more affected by the coordination modes of the enolate ligands) show significant differences. To elaborate, for the olefinic protons, the signals corresponding to the enolate ligands that are exclusively bonded to magnesium atoms are modestly more deshielded (at 5.01 and 4.20 ppm) than the ones resulting from the enolate ligands connecting sodium to magnesium (at 4.81 and 4.01 ppm), while for the *ortho*-CH₃ groups the resonance is further upfield for the "magnesium–magnesium" enolate ligands (at 2.49 ppm) than for the "sodium–magnesium" enolates (at 2.87 ppm). These trends found in the ¹H NMR spectrum for the two different types of enolate ligands present in **4** are maintained for the other compounds **5**–**7**. Thus, a glimpse at Table 3 shows that the chemical shifts of the corresponding aromatic protons in compounds **4**–**7** and the *para*-CH₃ groups are nearly identical, while the corresponding chemical shifts of the two remaining sets of resonances, the =CHH' and *ortho*-CH₃ groups, are distinctly different for each compound. Thus, the resonances of these two groups for the homometallic compound **7**, where the enolate ligands are bonded solely to sodium, are the most upfield (at 3.95, 3.64 ppm for =CHH' and at 2.45 ppm for *ortho*-CH₃), whereas the analogous resonances for the enolate ligands in **4** that exclusively bond to magnesium appear the most downfield (at 5.01, 4.20 ppm for =CHH' and at 2.87 ppm for the *ortho*-CH₃). For compounds **4** (for the remaining type of enolate ligand present in the molecule), **5**, and **6**, where the enolate ligands are simultaneously bonded to magnesium and sodium, the chemical shifts of these signals are intermediate between the values for **7** and **4** (Mg–Mg enolates), although

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(42) Another possibility would be a monomeric solution structure, where the two different types of enolate ligand are terminal (exclusively bonded to magnesium) and bridging (connecting the two metal centers), in a ratio of 1:2.



they are closer to the values found for the Mg–enolate–Mg type than for the Mg–enolate–Na type.

Table 4 summarizes the chemical shifts for the resonances of the most relevant signals in the ^{13}C NMR spectra of compounds **4**, **5**, and **7**. The chemical shifts of the olefinic carbons of the enolate ligands are the more affected for the different metal coordinations of the enolate anions in compounds **4**, **5**, and **7**. Thus the quaternary carbon directly bonded to the oxygen atom appears at 169.94 ppm for the sodium enolate **7**, while for the enolate ligands in **4** exclusively bonded to magnesium the same carbon lies further upfield (at 161.23 ppm). For the remaining olefinic carbon, although it is not as close to the oxygen atom as the previous carbon, it also seems to be affected by the metal coordination, as there is a difference of 10 ppm between the chemical shift of this signal in **7** (at 79.60 ppm) and in the magnesium enolate ligands in **4** (at 89.74 ppm). The resonances of these carbons in **5** and in the second type of enolate present in **4** (where the enolate anions are coordinated simultaneously to sodium and magnesium) have intermediate values between those previously discussed for **4** and **7**.

The ^1H NMR spectrum of **6** shows only one set of signals for the enolate ligands. This is consistent with either chemically distinct enolate groups undergoing a fast exchange process or the accidental coincidence in the chemical shifts of the two different kinds of enolate ligands present in the solid-state structure of **6**. Since as previously mentioned, the resonances of the $=\text{CHH}'$ and *ortho*- CH_3 fragments of the enolate are acutely sensitive to the different coordination environments of the ligand, the latter possibility seems more remote. A fast equilibrium in solution of the dimeric structure of **6** found in the crystal structure with a monomeric variant (Scheme 2), followed by the cleavage of the Na–O bond and free rotation about the Mg–C axis, would make the two different kinds of enolate ligand present in **6** equivalent in the ^1H NMR spectrum.

The resonance for the M– CH_2 of the butyl groups (at 0.91 ppm) is dramatically further downfield than the analogous signal of Bu_2Mg (at 0.08 ppm) and BuNa (at -0.47 ppm)⁴³ in C_6D_6 solution. Considering that an important contribution in the position of these chemical shifts is the ionic character of the M–C bond, finding that the more ionic the bond, the more upfield the resonance, it can be said that the butyl groups present in **6** do not carry a substantial negative charge. This can probably be rationalized in terms of the presence of four strongly electronegative enolate ligands in **6**, making these M– CH_2 bonds significantly less polar than in the alkyl monometallic compounds.

(43) A few drops of deuterated THF were required to dissolve the solid in C_6D_6 .

On the other hand, previously in the literature, it has been described that the relative positioning of the signals in the ^1H NMR spectrum of TMEDA denotes if the diamine is solvated to the metal centers or desolvated.⁴⁴ To elaborate, the ^1H NMR spectrum of free TMEDA in C_6D_6 solution shows two signals at 2.13 ppm (CH_2N) and 2.08 ppm ($\text{N}-\text{CH}_3$); however, in general, when TMEDA is coordinated to a metal, this relative positioning is reversed. This latter case is observed for compounds **4**, **5**, and **6**, accompanied by significantly lower frequency chemical shift values [1.70 (NCH_3), 1.68 ($\text{N}-\text{CH}_2$) for **4**; 1.65 (NCH_3), 1.44 ($\text{N}-\text{CH}_2$) for **5**; 1.82 (NCH_3), 1.65 ($\text{N}-\text{CH}_2$) for **6**]. This evidence for TMEDA chelation of sodium points to the molecular structures found in the solid state being retained in solution. In contrast, it appears that when enolate **7** is dissolved, the TMEDA ligands become free (resonances at 2.17 ppm for NCH_2 and at 2.06 ppm for NCH_3). While the exact nature of the solution structure of **7** is unknown, it is likely that the dimeric arrangement is retained but that the solvent arene ligands preferentially solvate to the sodium centers.⁴⁵

Conclusions

A new family of mixed metal sodium–magnesium enolates derived from the bulky ketone 2,4,6-trimethylacetophenone (**3**) have been synthesized using as precursors the stoichiometric-variant alkyl magnesiates NaMgBu_3 and Na_2MgBu_4 . Reactions occurred smoothly at room temperature, affording the enolate products **4–6** in decent isolated yields as crystalline solids. In these reactions **3** is selectively deprotonated at the methyl position and no nucleophilic addition side-reactions take place.

The solid-state structures of the homoanionic enolates **4** and **5** and heteroanionic enolate **7** have been determined by X-ray crystallography, establishing a common motif, a polymetallic chain of four members for **4** and **6** or three members for **5**, with the anionic ligands (enolates in **4** and **5**; and a mixture of enolates and alkides in **6**) in each case bridging the different metals together.

Experimental Section

General Procedures. All reactions were performed under a protective argon atmosphere using standard Schlenk techniques.

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(45) For examples of metal– π -arene interactions see: (a) Gokel, G. W.; De Wall, S. L.; Meadows, E. S. *Eur. J. Org. Chem.* **2000**, 2967. (b) Forbes, G. C.; Kennedy, A. R.; Mulvey, R. E.; Roberts, B. A.; Rowlings, R. B. *Organometallics* **2002**, *21*, 5115.

Hexane and toluene were dried by heating to reflux over sodium benzophenone ketyl and distilled under nitrogen prior to use. *n,s*-Dibutylmagnesium was purchased from Aldrich Chemicals as a 1 M solution in heptane and standardized immediately prior to use using salicylaldehyde phenylhydrazone.⁴⁶ Butylsodium⁴⁷ was prepared according to literature methods. NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer, operating at 400.13 MHz for ¹H and 100.62 MHz for ¹³C.

X-ray Crystallography. Single-crystal diffraction data were recorded by a Nonius Kappa CCD diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The structures were refined by full-matrix least-squares and against F^2 to convergence using the SHELXL-97 program.⁴⁸ Specific crystallographic data and refinement parameters are given in Table 2.

Synthesis of [Na₂Mg₂{OC(=CH₂)Mes}₆(TMEDA)₂] (4). BuNa (0.4 g, 5 mmol) was suspended in hexane (10 mL). Bu₂Mg (5 mL of a 1 M solution in heptane, 5 mmol) was introduced, affording a white precipitate. 2,4,6-Trimethylacetophenone (**3**) (2.5 mL, 15 mmol) was then added dropwise. The reaction was exothermic and was accompanied by gas evolution, as a white precipitate was obtained. At this stage TMEDA (0.75 mL, 5 mmol) and toluene (5 mL) were both introduced, and the mixture was gently heated until all the white solid had dissolved, affording a pale yellow solution. Allowing this solution to cool slowly at room temperature produced a crop of colorless crystals (yield 2.52 g, 78%). ¹H NMR (400 MHz, 25 °C, C₆D₆): 6.80 (s, 4H, *m-H* Mes'), 6.79 (s, 8H, *m-H* Mes), 5.01 (d, 2H, C=CH₂'), 4.81 (d, 4H, C=CH₂'), 4.20 (d, 2H, C=CH₂'), 4.01 (d, 4H, C=CH₂'), 2.87 (s, 12H, *o-CH*₃, Mes'), 2.49 (s, 24H, *o-CH*₃, Mes), 2.15 (s, 6H, *p-CH*₃, Mes'), 2.11 (s, 12H, *p-CH*₃, Mes), 1.70 (s, 24H, CH₃, TMEDA), 1.61 (s, 8H, CH₂, TMEDA). ¹³C{¹H} NMR (100.63 MHz, 25 °C, C₆D₆): 163.12 (O–C=CH₂'), 161.23 (O–C=CH₂), 143.14, 140.45, 137.66, 135.62, 135.48, 134.98, 128.88, 128.27 (*C*_{ipso}, *C*_{para}, *C*_{ortho}, *C*_{meta} of Mes and Mes'), 89.74 (O–C=CH₂), 87.04 (O–C=CH₂'), 57.05 (CH₂, TMEDA), 45.42 (CH₃, TMEDA), 21.61 (*p-CH*₃, Mes), 21.34 (*p-CH*₃, Mes'), 21.12 (*o-CH*₃, Mes'), 21.04 (*o-CH*₃, Mes).

Synthesis of [Na₂Mg {OC(=CH₂)Mes}₄(TMEDA)₂] (5). BuNa (0.4 g, 5 mmol) was suspended in hexane (10 mL). Bu₂Mg (2.5 mL of a 1 M solution in heptane, 2.5 mmol) was introduced, affording a white precipitate. Four molar equivalents of 2,4,6-trimethylacetophenone (**3**) (3.3 mL, 20 mmol) was then added dropwise. An exothermic reaction ensued, accompanied by gas evolution, and a white precipitate was obtained. At this stage TMEDA (0.75 mL, 5 mmol) and toluene (5 mL) were introduced, and the mixture was gently heated until all the white solid had dissolved, affording a pale yellow solution. Allowing this solution

to cool slowly at room temperature produced a crop of colorless crystals (yield 1.70 g, 72%). ¹H NMR (400 MHz, 25 °C, C₆D₆): 6.77 (s, 8H, *m-H* Mes), 4.70 (d, 4H, C=CH₂), 4.03 (d, 4H, C=CH₂), 2.74 (s, 24H, *o-CH*₃, Mes), 2.14 (s, 12H, *p-CH*₃, Mes), 1.65 (s, 24H, CH₃, TMEDA), 1.44 (s, 8H, CH₂, TMEDA). ¹³C{¹H} NMR (100.63 MHz, 25 °C, C₆D₆): 165.17 (O–C=CH₂), 144.53 (*C*_{ipso}, Mes), 136.02 (*C*_{ortho}, Mes), 134.84 (*C*_{para}, Mes), 128.34 (*C*_{meta}, Mes), 83.91 (O–C=CH₂), 57.05 (CH₂, TMEDA), 45.42 (CH₃, TMEDA), 21.47 (*p-CH*₃, Mes), 21.42 (*o-CH*₃, Mes).

Synthesis of [Na₂Mg₂(μ -Bu)₂{ μ -OC(=CH₂)Mes}₄(TMEDA)₂] (6). BuNa (0.4 g, 5 mmol) was suspended in hexane (10 mL). Bu₂Mg (5 mL of a 1 M solution in heptane, 5 mmol) was introduced, affording a white precipitate. 2,4,6-Trimethylacetophenone (**3**) (1.7 mL, 10 mmol) was then added dropwise. The reaction was exothermic and was accompanied by gas evolution, as a white precipitate was obtained. At this stage TMEDA (0.75 mL, 5 mmol) and toluene (5 mL) were both introduced, and the mixture was gently heated until all the white solid had dissolved, affording a pale yellow solution. Allowing this solution to cool slowly at room temperature produced a crop of colorless crystals (yield 1.21 g, 45%). ¹H NMR (400 MHz, 25 °C, C₆D₆): 6.85 (s, 4H, *m-H* Mes'), 4.69 (d, 4H, C=CH₂'), 4.09 (d, 4H, C=CH₂'), 2.80 (s, 24H, *o-CH*₃, Mes), 2.58 (m, br, 4H, CH₂, Bu), 2.18 (s, 12H, *p-CH*₃, Mes), 1.69 (s, 24H, CH₃, TMEDA), 1.56 (s, 8H, CH₂, TMEDA), 1.33 (t, br, 6H, CH₃, Bu), 1.22 (m, br, 4H, CH₂, Bu), 0.99 (m, br, 4H, M–CH₂, Bu).

Synthesis of [Na₂{OC(=CH₂)Mes}₂(TMEDA)₂] (7). BuNa (0.32 g, 4 mmol) was suspended in hexane (10 mL). 2,4,6-Trimethylacetophenone (**3**) (0.66 mL, 4 mmol) was then added dropwise, affording a pale yellow solution. TMEDA (0.60 mL, 4 mmol) was then introduced into the solution, and half of the solvent was removed under vacuum. The resulting yellow solution was placed in the freezer (at –20 °C), producing a crop of colorless crystals (yield 0.42 g, 35%). ¹H NMR (400 MHz, 25 °C, C₆D₆): 6.78 (s, 4H, *m-H* Mes), 3.95 (d, 4H, C=CH₂'), 3.64 (d, 4H, C=CH₂'), 2.45 (s, 12H, *o-CH*₃, Mes), 2.17 (s, 12H, 6H of *p-CH*₃, Mes and 8H of CH₂, TMEDA), 2.06 (s, 24H, CH₃, TMEDA). ¹³C{¹H} NMR (100.63 MHz, 25 °C, C₆D₆): 169.94 (O–C=CH₂'), 144.41 (*C*_{ipso}, Mes), 135.40 (*C*_{para}, Mes), 134.16 (*C*_{ortho}, Mes), 129.09 (*C*_{meta}, Mes), 79.60 (O–C=CH₂), 58.22 (CH₂, TMEDA), 46.21 (CH₃, TMEDA), 21.39 (*p-CH*₃, Mes), 20.89 (*o-CH*₃, Mes).

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