

Expected and Unexpected Reactivities of Homoleptic LiNacNac and Heteroleptic NacNacMg(TMP) β -Diketiminates toward Various Small Unsaturated Organic Molecules

Richard M. Gauld,^{||} Jennifer R. Lynch,^{||} Alan R. Kennedy, Jim Barker, Jacqueline Reid, and Robert E. Mulvey*

Cite This: *Inorg. Chem.* 2021, 60, 6057–6064

Read Online

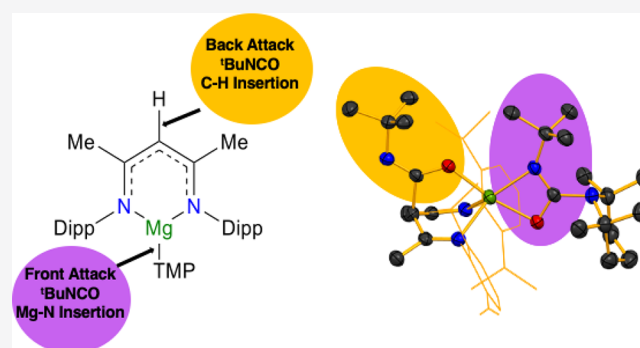
ACCESS |

Metrics & More

Article Recommendations

Supporting Information

ABSTRACT: Homoleptic LiNacNac forms simple donor–acceptor complexes with *N,N'*-dicyclohexylcarbodiimide (CyN=C=NCy), triphenylphosphine oxide (Ph₃P=O), and benzophenone (Ph₂CO). These crystallographically characterized compounds could be regarded as model intermediates en route to reducing the N=C, P=O, and C=O bonds of unsaturated substrates. Heteroleptic NacNacMg(TMP) intriguingly functions as a TMP nucleophile both with *t*-BuNCO and *t*-BuNCS, producing a urea or thiourea derivative respectively attached to Mg, though the NacNac ligand in the former reaction also engages noninnocently with a second *t*-BuNCO molecule via insertion at the reactive NacNac backbone γ -carbon site.



INTRODUCTION

When attached to organic ligands, lithium and magnesium represent the luminaries of the *s*-block of the periodic table, arguably of the whole of the periodic table, in terms of their phenomenal synthetic utility. It is not surprising therefore that both metals have been involved in the proliferation of the chemistry of β -diketimate (NacNac or BDI) ligands that has taken place over the past 20 or so years. Though originating in the 1960s,^{1–4} β -diketimate chemistry took about 30 years before its tunable spectator ligand credentials rose to the fore⁵ in the mold of its cyclopentadienyl (Cp and substituted Cp) predecessors.

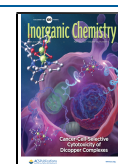
Befitting the “masters of mediation” eminence of organic alkali metal compounds in general,⁶ alkali metal β -diketiminates are generally utilized for transferring their dinitrogen ligands to other metals. This was first established with lithium and tin in 1994 by Lappert, with the report also recording one of the first crystal structures of a lithium β -diketimate.⁷ Today this utilization continues as for example by Kretschmer, who detailed an elegant but simple approach to obtaining aluminum and gallium β -diketimate complexes from the sodium congener,⁸ as well as by the groups of Schaper and Shen, who used the lithium or sodium β -diketimate complex in the convenient preparation of zirconium and lanthanide β -diketimate complexes, respectively.^{9–11}

Power's straightforward high-yielding synthesis of the aminoimine 2,6-diisopropylphenyl- β -methyl-diketimate [NacNac (Me, Dipp) but labeled here for brevity as NacNac(H)]¹² opened up access to this ligand to a wider community, to the

extent that it is still the most popular β -diketimate proligand utilized today and the subject of this present paper. β -Diketimate ligands in general have made a particularly strong impact in Group 2.^{13–20} The same β -diketimate ligand (NacNac) was behind the opening of an exciting new area of Group 2 chemistry through Jones and Stasch's pioneering of thermally stable magnesium(I) compounds of type (NacNac)-MgMg(NacNac).²¹ Other highlights of magnesium β -diketimate chemistry include advances made in the ring-opening polymerization (ROP) of lactides.^{22–25} First synthesized independently in 2002 by Roesky²⁶ and Gibson,²⁷ NacNacMg(*n*-Bu) has recently taken on greater significance through Hill's catalytic and insertion applications.²⁸ Surprisingly, given the prominence of *n*-Bu and TMP *s*-block reagents,^{29–32} the analogous amide, NacNacMg(TMP), was only introduced as recently as 2013 (TMP is 2,2,6,6-tetramethylpiperidine).³³ This study by Hevia established that NacNacMg(TMP) is a more effective metallating (C–H deprotonating) agent than its alkyl analogue NacNacMg(*n*-Bu), reversing the normal order of alkyl versus amide basicity.

Received: February 23, 2021

Published: April 8, 2021



Despite these developments, studies probing the behavior of these *s*-block NacNac species with small molecules have been relatively scarce, especially for Group 1 examples.^{34–38} Our first expedition in this area found that the electrophilic species CO₂, *t*-BuNCO, and *i*-PrNCO all reacted with lithium NacNac at the γ -C site of the ligand backbone, instead of at the “frontal” polar Li–N bonds, expelling the innocent, spectator image of alkali-metal-attached NacNac ligands.³⁹ Here, the picture becomes more complicated when the outcomes of exposing LiNacNac to carbodiimide and phosphine oxide molecules are revealed. Moreover, bringing NacNacMg(TMP) into this study for the first time by treating it with isocyanate and isothiocyanate molecules reveals surprising reactivities out of kilter with those of conventional Mg TMP-containing compounds.

Since our earlier work on reactions of LiNacNac with unsaturated organic molecules invariably showed backbone γ -carbon reactivity with concomitant redistribution of the NCCCN unit into a diimine, as displayed in Figure 1, we

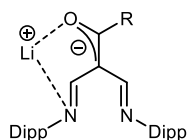


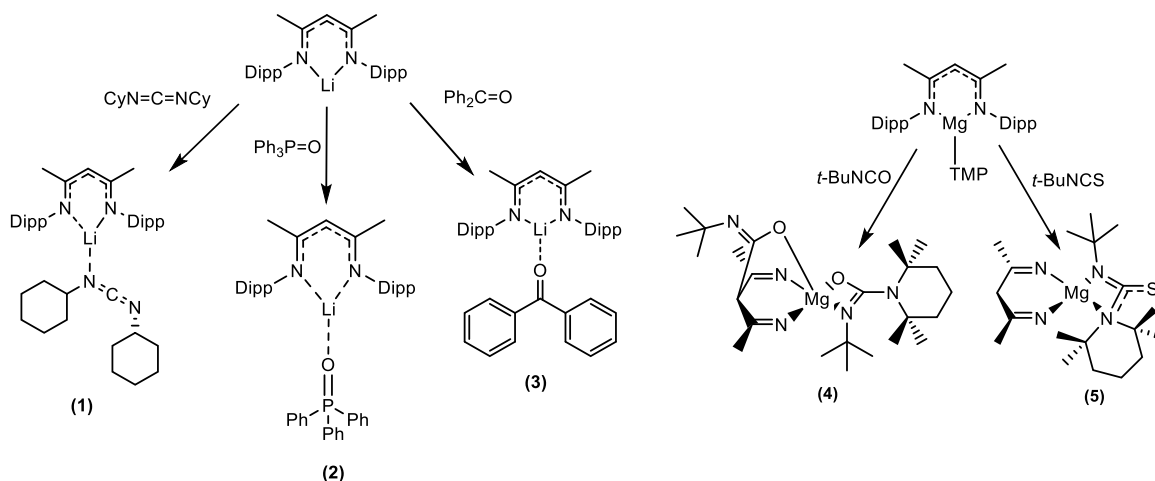
Figure 1. ChemDraw schematic showing general diimine functionality seen when LiNacNac was previously reacted with a series of small molecules, where Dipp is 2,6-diisopropylphenyl.

decided to investigate a larger sample of small molecules. Since the NacNac N=C=C bonds can be regarded as joined enamido units, this reactivity at the γ -carbon atoms is not that unexpected.

RESULTS AND DISCUSSION

Our first choice was *N,N'*-dicyclohexylcarbodiimide, CyN=C=NCy, DCC, which has a linear interior akin to that of isoelectronic CO₂. Thus, a 1:1:1 stoichiometric mixture of LiNacNac, TMEDA (*N,N,N',N'*-tetramethylethylenediamine), and DCC in hexane solution produced crystals in 83% yield identified by X-ray crystallography as $[\{(\text{MeCN-2,6-}i\text{Pr}_2\text{C}_6\text{H}_3)_2\text{CH}\}\text{Li-N}(\text{Cy})\text{CN}(\text{Cy})]$, **1** (Scheme 1).

Scheme 1. Small Molecule Fixation Reactions Carried out in This Work



Its structure (Figure 2) revealed a simple donor–acceptor arrangement with DCC datively attached to the frontal Li atom

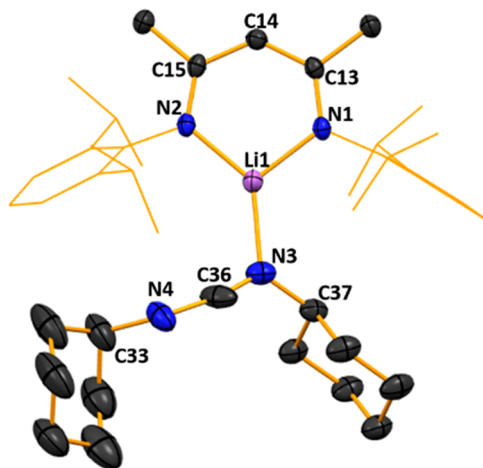


Figure 2. Molecular structure of $[\{(\text{MeCN-2,6-}i\text{Pr}_2\text{C}_6\text{H}_3)_2\text{CH}\}\text{Li-N}(\text{Cy})\text{CN}(\text{Cy})]$ (**1**). H atoms and disorder are omitted and the NacNac Dipp groups are shown as a wire frame for clarity. Thermal ellipsoids are displayed at the 40% probability level.

via one of its terminal atoms (N3). Repeating the reaction but heating the mixture to reflux temperature still afforded **1** as confirmed by NMR spectra of the isolated product, with a ¹H resonance at 5.02 ppm, corresponding to the still intact backbone γ -hydrogen atom in contrast to the sigmatropic rearrangement of this C–H atom to the N=C bond of the previously studied isocyanate systems.³⁹

The planarity of the NCCCN ring in **1** remains intact like those in Power's Et₂O and THF LiNacNac structures, while the two C–C and two C–N bond lengths [C–C bond lengths of 1.399(4) Å (C13–C14) and 1.420(4) Å (C14–C15) compared to 1.387(4) Å and 1.418(4) Å respectively in NacNac(H), and C–N bond lengths of 1.324(3) Å (C13–N1) and 1.318(3) Å (C15–N2) compared to 1.318(4) Å and 1.341(4) Å respectively in NacNac(H)] within the ring become slightly more symmetrical upon lithium substitution compared to NacNac(H), signifying a degree of delocalization of the π -bonding. Lithium exhibits a trigonal planar geometry, with bond angles markedly distorted from idealized values

ranging from $100.9(2)^\circ$ (N2–Li1–N1) to $135.6(3)^\circ$ (N2–Li1–N3), while also lying effectively equidistant between the two NacNac N atoms [Li1–N1, 1.898(5) Å and Li1–N2, 1.902(5) Å]. Lithium coordination of DCC results in asymmetry in the N=C=N bonds since C36–N3 [1.206(4) Å] is significantly shorter than C36–N4 [1.39(1) Å]. This distortion is also reflected in the inequivalence of the DCC bond angles [C33–N4=C36, $134.6(8)^\circ$] and C37–N3=C36, $121.4(3)^\circ$], the former being notably more obtuse than the C–N=C bond angles approaching 120° normally seen in carbodiimide ligands.⁴⁰ The N3–C36–N4 bond angle in **1** also shows a distortion from linearity [$165.4(5)^\circ$]. These features suggest that the major resonance structure is polarized (Cy)N–C≡N⁺(Cy) rather than (Cy)N=C=N(Cy). Reactions of DCC with organolithium compounds generally follow nucleophilic addition pathways as exemplified by the lithium amidinate FcC(NCy)₂Li formed when DCC is treated with bulky ferrocenyllithium (FcLi).⁴¹ There are also several articles referencing such addition reactions between amidinates derived from DCC and organolithium reagents.^{42–45} For example, reacting DCC with LiHMDS leads to amidinate [(Cy)NC{N(SiMe₃)}N(Cy)·Li], with addition of the N-(SiMe₃) group seen at the central DCC carbon.⁴⁶ However, to the best of our knowledge, there are no crystalline examples of DCC or any other carbodiimide interacting with lithium centers or any other metal centers as a Lewis donor such as that seen in **1**. Thus, **1** can be considered a model intermediate en route to forming an amidinate from a carbodiimide and an alkali metal nucleophilic source. Such $\kappa 1$ -RN=C=NR metal coordinations have been implicated in various catalytic heterofunctionalizations of carbodiimides.^{47–52} It has previously been shown by the Harder group that activation of carbodiimides is possible under metal-free conditions, although it was noted that in this case the “extent of activation is less than that in carbodiimide⋯Li⁺ complexes”, with harsh conditions necessary under a metal-free environment.⁵³ It is likely that the bulk of the DCC molecule prevents formation of an amidinate in this system, with the DCC being too sterically congested to allow for nucleophilic addition of the NacNac in this case. As alluded to earlier, solution NMR data are in agreement with the solid-state structure (see the [Supporting Information](#) for full details), suggesting that its composition is maintained in solution. Of note is the ⁷Li spectrum, which showed a single resonance corresponding to the single lithium environment present within **1** at 2.61 ppm. This contrasts with the ⁷Li spectrum of LiNacNac, which shows a resonance at 0.73 ppm, confirming that the lithium in **1** remains in a different environment, due to the donating role of the DCC molecule being retained in solution.

Next, we studied triphenylphosphine oxide, Ph₃P=O. A 1:1:1 stoichiometric mixture of LiNacNac, Ph₃P=O and PMDETA (*N,N,N',N'',N'''*-pentamethyldiethylenetriamine; added to enhance solubility) in hexane solution deposited crystals (78% yield) identified by X-ray crystallography as [(MeCN-2,6-*i*Pr₂C₆H₃)₂CH]Li-OP(Ph)₃, **2**. Matching that of **1**, the structure of **2** ([Figure 3](#)) is a donor–acceptor complex connected via a frontal Li–O bond [1.489(1) Å], with no backbone insertion present.

PMDETA is also absent from **2**, though subsequent experiments showed that PMDETA addition is necessary in order to obtain crystals, although why PMDETA should aid the crystallization process is not yet clear. Without adding PMDETA, **2** can still be made as an amorphous powder, with

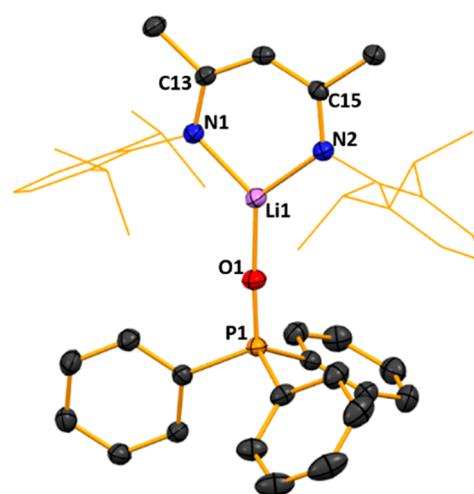


Figure 3. Molecular structure of [(MeCN-2,6-*i*Pr₂C₆H₃)₂CH]Li-OP(Ph)₃ (**2**). H atoms, disorder, and cocrystallized hexane solvent are omitted and the NacNac Dipp groups are shown as a wire frame for clarity. Thermal ellipsoids are displayed at the 40% probability level.

its identity confirmed by NMR characterization. Occupying a highly distorted trigonal planar NNO coordination, with bond angles ranging from $99.8(2)^\circ$ (N1–Li1–N2) to $131.4(2)^\circ$ (O1–Li1–N1), Li lies equidistant between the NacNac N atoms [N1–Li1, 1.925(3) Å and N2–Li1, 1.911(3) Å]. The P–O–Li unit sits exactly within the NCCCN plane, which in turn is not disturbed from planarity, with bond lengths [N1–C13, 1.318(2) Å; C13–C14, 1.407(2) Å; C14–C15, 1.412(2) Å; N2–C15, 1.316(2) Å] indicating a degree of π -delocalization. Multinuclear NMR spectroscopic data on **2** concur with the solid-state structure, particularly showing that coordination between the phosphine oxide and LiNacNac is maintained in solution. This is deduced from the ⁷Li NMR spectrum, which shows a resonance at 2.70 ppm, in contrast to that seen for LiNacNac at 0.73 ppm, indicating a change in the lithium environment. The ³¹P{¹H} NMR also indicates coordination, with the resonance at 23.2 ppm for uncoordinated triphenylphosphine oxide contrasting to that at 30.80 ppm seen in **2**. Though a CSD search revealed 20 hits for Ph₃P=O → Li dative bonds, no hits were found for any LiNacNac scaffold, with 7 of the 20 hits featuring a cationic (Ph₃PO)₄Li⁺ unit with a balancing counteranion present. Of note is work by Lichtenberg, who structurally characterized a lithium aminotroponimate (LiATI) solvated by Ph₃PO, exhibiting a Li chelated by two ATI N atoms in a similar arrangement to that of **2** but with an additional O (THF) ligation.⁵⁴ Significantly, a search of the CSD revealed no hits for a phosphine oxide unit bonded to LiNacNac, with the closest match being a 1,8-C₁₀H₆{NHSiMe₃}₂-supported dilithium compound; however, the lack of delocalization over the backbone of this ligand limits comparison.⁵⁵ Attempted reactions with the sulfur analogue Ph₃P=S failed to produce a complex with LiNacNac as determined via NMR studies, contrasting with Nikonov’s report of NacNacAl(=S)S=PPh₃ via a complexation/oxidative cleavage process.⁵⁶

Our third and final homoleptic LiNacNac structure was obtained from the reaction between the ketone benzophenone and LiNacNac. A mixture of LiNacNac and a slight stoichiometric excess of benzophenone (1:1.25) was reacted

in hexane, with two drops of PMDETA (*N,N,N',N',N''*-pentamethyldiethylenetriamine) added for crystallization purposes. This solution deposited a crop of large red crystals (in a 59% yield) identified by X-ray crystallography as $[(\text{MeCN-2,6-}i\text{Pr}_2\text{C}_6\text{H}_3)_2\text{CH}\text{Li-OC(Ph)}_2]$, **3**. Following the trend set by **1** and **2**, the structure of **3** (Figure 4) is yet another donor–

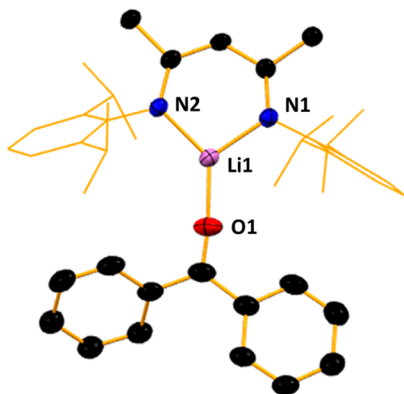


Figure 4. Molecular structure of $[(\text{MeCN-2,6-}i\text{Pr}_2\text{C}_6\text{H}_3)_2\text{CH}\text{Li-OC(Ph)}_2]$ (**3**). H atoms are omitted and the NacNac Dipp groups are shown as a wire frame for clarity. Thermal ellipsoids are displayed at the 40% probability level.

acceptor complex, connected via a slightly elongated frontal Li–O bond [1.843(3) Å], when compared to that observed in compound **2**. Of note is that once again no backbone insertion at the γ -carbon is observed, in contrast to that noted in previous work.³⁹

In a similar manner to **2**, PMDETA addition was shown to be required for crystallization of compound **3**, despite it not being part of the crystal structure obtained. The lithium atom of compound **3** sits in an approximately trigonal planar coordination environment, with bond angles ranging from $101.22(14)^\circ$ (N1–Li1–N2) to $133.92(18)^\circ$ (O1–Li1–N1). The lithium center lies equidistant between the NacNac N atoms [N1–Li1, 1.908(3) Å and N2–Li1, 1.914(3) Å]. Akin to that in compound **2**, the C–O–Li unit of compound **3** sits within the NCCCN plane, which retains its planarity. Bond lengths [N1–C5, 1.326(2) Å; C5–C6, 1.410(2) Å; C6–C4, 1.408(2) Å; N2–C4, 1.317(2) Å] are also indicative of a degree of π -delocalization. Multinuclear NMR spectroscopic data on **3** concurred with the solid-state structure, particularly showing that coordination between the benzophenone and

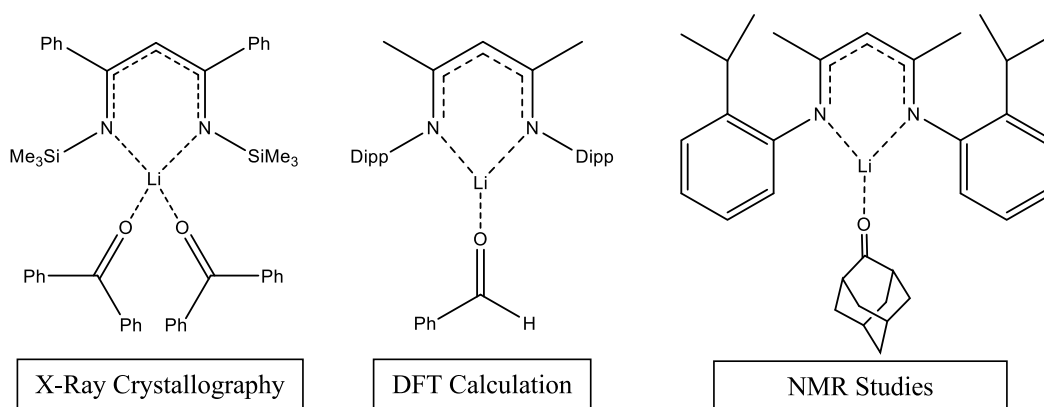
LiNacNac is maintained in solution. This is deduced from the ^7Li NMR spectrum, which shows a resonance at 3.64 ppm, in contrast to that seen for LiNacNac at 0.79 ppm, indicating a significant change in the lithium environment.

Upon searching the CSD, it was discovered there were no examples of bonding between $\text{Ph}_2\text{C=O}$ and Li involving the extensively studied Dipp₂NacNac scaffold. In fact, there were no examples at all of an aldehyde/ketone C=O unit coordinating to either Li, Na, or K within the Dipp₂NacNac scaffold in this way, with examples of benzophenone coordinating to lithium metal in any environment being rare.^{57,58} However, there was a single hit for dative $\text{Ph}_2\text{C=O} \rightarrow \text{LiNacNac}$ bonding featuring a much less commonly studied variant of NacNac, $[\text{Me}_3\text{SiNC(Ph)CHC(Ph)NSiMe}_3]\text{Li}$ by Tong and Liu.⁵⁹ This unusual ligand (displayed in Scheme 2) could be viewed as an inversion of the ubiquitous Dipp₂NacNac ligand, as now we see a rich electron donor sitting on the α -nitrogen position while an electron withdrawing group sits on the β -carbon positions. The presence of phenyl rings on the backbone, acting as electron withdrawing groups, may also alter the nucleophilicity of the γ -carbon position, a key feature in several recent small molecule activations using the Dipp₂NacNac scaffold.³⁷

The contrast with this 2008 structure can help rationalize the dominance of the Dipp₂NacNac ligand, with the Dipp groups flanking the metal allowing for coverage of the coordination sphere to be maximized which helps to prevent coordination to multiple reactant molecules, unwanted solvent interactions, or dimerization. The dual coordination of benzophenone units in $[\text{Me}_3\text{SiNC(Ph)CHC(Ph)NSiMe}_3]\text{Li}$ can thus be rationalized both by the reduction of steric bulk around the metal center decreasing the activation barrier and the loss of steric coverage of the coordination sphere.

Interestingly, Sen et al. recently reported that LiNacNac could catalyze hydroboration reactions of aldehydes and ketones using pinacolborane, theorizing a catalytic cycle involving a donor–acceptor $\text{Ph(H)C=O} \rightarrow \text{LiNacNac}$ intermediate.⁶⁰ While complex **3** incorporates benzophenone rather than benzaldehyde, it exemplifies that the $\text{RC=O} \rightarrow \text{LiNacNac}$ unit predicted by Sen et al. using DFT calculations is achievable. In view of the aforementioned inverted NacNac structure reported by Liu, this may also highlight the advantage of Dipp₂NacNac in preventing saturation of the metal coordination sphere, facilitating the formation of catalytically active intermediates such as this. Meanwhile complex **2** could

Scheme 2. Selection of Products Found Involving C=O Bonds Interacting with Various β -Diketiminato Scaffolds

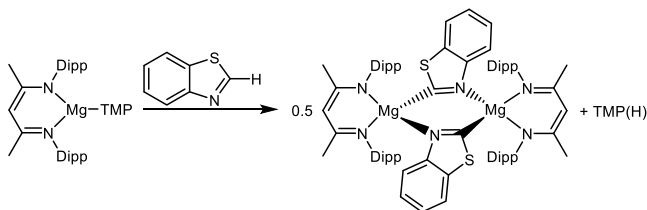


be viewed as a model intermediate of this catalysis with P=O as opposed to C=O coordination. The Mair group similarly predicted an intermediate containing the RC=O \rightarrow LiNacNac unit in their 2003 paper on reversible C—C bond formation.⁶¹ On this occasion NMR evidence was cited to suggest the presence of the adamantanone-coordinated intermediate structure, supported by a 1,5-diazapentadienyllithium complex, a close cousin of Dipp₂NacNac, with only one less iso-propyl arm per phenyl ring. This new structure is evidence that such structures are obtainable in the solid state, as well as being observed by NMR in the solution state.

These three results with DCC, Ph₃P=O, and Ph₂C=O show that coordination of bulky nitrogen and oxygen donors to LiNacNac is possible, although for these donor systems coordination occurs preferentially at the frontal site of the molecule, with the NacNac backbone remaining undisturbed; this is in contrast with results obtained with isocyanates and CO₂, where nucleophilic attack occurs via the backbone γ -carbon position.³⁹

As alluded to earlier, Hevia's work has established that heteroleptic NacNacMg(TMP) is an efficient TMP base for selectively deprotonating sensitive organic molecules such as 1,3-benzoxazoles or fluorinated aromatic compounds, capturing the emergent anionic molecules and concomitantly releasing TMP(H), as shown in Scheme 3.³³

Scheme 3. Trapping of Benzothiazole Using NacNacMg(TMP), with Concomitant Formation of TMP(H), as Reported by Hevia³³



Mg(TMP) systems are good bases in general though they tend to work best in synergistically operative bimetallic mixtures.^{62–65} These reactions piqued our curiosity so we decided to also investigate the small molecule chemistry of NacNacMg(TMP) with molecules bereft of acidic bonds, namely with isocyanate *t*-BuNCO and isothiocyanate *t*-BuNCS (Scheme 1). Surprisingly, with *t*-BuNCO, a 2-fold insertion was seen, with one isocyanate molecule inserting into the γ -C site, while another inserted into the Mg—N(TMP) bond. No insertion was seen at a frontal Mg—N(NacNac) site. Evident from the crystal structure of the isolated urea-type product, [{(MeCN-2,6-*i*Pr₂C₆H₃)₂CH(CON(*t*-Bu))Mg(CON(*t*-Bu))-TMP] **4** (Figure 5), this 2-fold reactivity contrasts with that of LiNacNac with *t*-BuNCO, where a single insertion occurred at the γ -C site. When this NacNacMg(TMP) reaction was repeated rationally with two equivalents of *t*-BuNCO instead of one, the same product was formed, proving the reproducibility of the reaction, but only in a similarly small yield. These low isolated yields can be attributed to the high solubility of **4** in nonpolar aprotic solvents. The standout feature of **4** is TMP acting as a nucleophile, as its inherent low nucleophilicity is its prized asset with regard to its popularity as a selective base with unsaturated substrates, though rare examples of TMP nucleophilicity exist.⁶⁶ Another feature of interest is that there is no sigmatropic hydride rearrangement

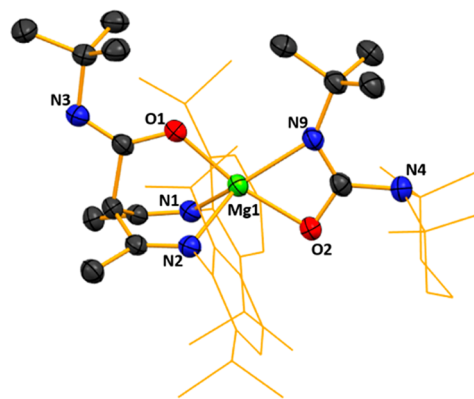


Figure 5. Molecular structure of [{(MeCN-2,6-*i*Pr₂C₆H₃)₂CH(CON(*t*-Bu))Mg(CON(*t*-Bu))TMP] (**4**). H atoms and cocrystallized hexane solvent are omitted and NacNac Dipp groups and organic TMP scaffold are shown as a wire frame for clarity. Thermal ellipsoids are displayed at the 40% probability level.

of a hydrogen from the γ -carbon to the nitrogen of either isocyanate unit, as seen in the lithium NacNac case, though there is concomitant redistribution of the NacNac NCCCNC unit into a diimine as seen previously. In **4**, Mg occupies a distorted trigonal bipyramidal site comprising two Mg—(axial) O bonds (O1—Mg1—O2 bond angle, 169.7(1) $^\circ$) and three Mg—(equatorial)N bonds (average N—Mg—N bond angle, 119 $^\circ$). The C—N and C—O bond lengths of approximately 1.3 (\AA) support the hypothesis of two highly delocalized systems within the NCO unit, with both bonds existing as intermediate between single and double bonds. Solution-state NMR characterization of **4** was also carried out (see the SI for full details).

The final small molecule studied was isothiocyanate *t*-BuNCS, prompted by a recent report by Ma et al., who found that the NacNacMg(*n*-Bu) dimer exhibited different reactivities depending on the ratio of PhNCS used.³⁴ Exposure to one equivalent led to deaggregation of the dimer and bidentate (N, S) coordination to Mg via a thioamidinate NC(*n*-Bu)S unit, while exposure to two equivalents showed this coordination again but combined with coordination at the NacNac backbone, similar to that found in **4**. Since our attempts to grow a crystalline product from NacNacMg(TMP) and PhNCS failed, we turned to *t*-BuNCS. Surprisingly, neither of these aforementioned coordinations were found in [{(MeCN-2,6-*i*Pr₂C₆H₃)₂CH}Mg(TMP)(*t*-BuNCS)] **5**, the product of the 1:1 NacNacMg(TMP) and *t*-BuNCS reaction. Instead, the structure of **5** (Figure 6) shows addition of the Mg—N(TMP) bond to the NC bond of the NCS unit to form a four-membered MgNCN ring, leaving the sulfur uncoordinated to the Mg.

Thus, the TMP unit again plays an unfamiliar addition role as in **4** but in a different way as it is now bridging as opposed to terminal, a distinction dictated by the different heteroatoms on the cyanate units with Mg preferring to bind to O over N in the case of **4** and to N over S in the case of **5**, keeping with the HSAB concept.⁶⁷ This basic concept can also rationalize the different N, S coordination observed in the Ma structure, as Mg has less affinity for the adding *n*-Bu group than the S heteroatom. There are two crystallographically independent molecules within the unit cell of **5**; however, as the metrics for each molecule are essentially identical, only one is discussed. Centralized magnesium occupies a highly distorted tetrahedral

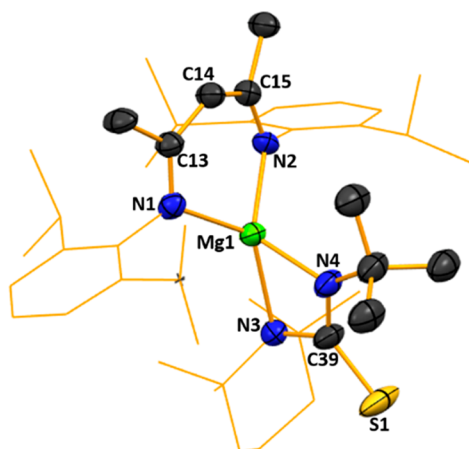


Figure 6. Molecular structure of $[\{(MeCN-2,6-iPr)_2C_6H_3\}_2CH\}Mg-(TMP)(t-BuNCS)]$ (**5**). H atoms, disorder, and a second molecule are omitted and the NacNac Dipp groups and organic TMP scaffold are shown as a wire frame for clarity. Thermal ellipsoids are displayed at the 40% probability level.

environment, with bond angles ranging from $63.4(2)^\circ$ for N3–Mg1–N4 to $128.0(2)^\circ$ for N1–Mg1–N2. In **3**, the N1–Mg1–N2 chelation angle is $88.2(1)^\circ$, while in **5** it increases to $94.8(2)^\circ$. It also lies equidistant between the chelating nitrogen atoms of the NacNac ligand in a similar situation to that seen in **4** [N1–Mg1, 2.097(5) Å; N2–Mg1, 2.105(5) Å; cf. N1–Mg1 2.162(3) Å; N2–Mg1 2.163(2) Å in **3**]. The NacNac ligand is essentially planar, with the root-mean-square (RMS) deviation from linearity being less than 1 Å [0.075(4) Å], with Mg lying 0.744(6) Å outside this plane. Bonding in the NC(NTMP)S unit appears to be that of an TMP-based imine unit, based on the bond lengths of N3–C39 [1.506(9) Å] and N4–C39 [1.297(9) Å], with a C–S bond length of 1.701(7) Å. These lengths suggest considerable delocalization within this NC(NTMP)S unit (specifically across S1–C39–N3), which adopts a thiourea-like arrangement.

CONCLUSIONS

We have demonstrated that there remains a significant and wide variety of potential reactivities of homoleptic LiNacNac and heteroleptic NacNacMg(TMP) β -diketiminates toward small unsaturated molecules that are yet to be fully explored. In this study we have structurally characterized what is, to the best of our knowledge, the first example of a carbodiimide acting as a Lewis donor toward an alkali metal center, as well as the first structural example of a phosphine oxide binding to LiNacNac. In contrast to our previous work, both products display reactivity at the front of the NacNac scaffold, a feature that was also found with benzophenone. The benzophenone structure could act as a model compound for the binding of an aldehyde or ketone to the LiNacNac scaffold. Further exemplifying the unusual reactivity that we have come across in NacNac chemistry, we have shown the unconventional behavior of the typically selective base TMP, in which we see a rare case of TMP acting as a nucleophile in order to play an addition role, e.g., in one example in a terminal fashion and bridging in another, in a manner which is rarely seen, though in keeping with classical HSAB theory. One facet of future work is to determine what effect changing the alkali metal of the whole of Group 1 (Li–Cs) will have on the structure and reactivity of NacNac and related compounds.⁶ Future work will

also consider the development of new NacNac-derived ligands with extra functionality such as that displayed in the urea-like compound **4**.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c00549>.

Experimental methods, crystallographic information, NMR spectra, IR data, and melting point data (PDF)

Accession Codes

CCDC 2061662–2061666 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

Robert E. Mulvey – WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, U.K.; orcid.org/0000-0002-1015-2564; Email: r.e.mulvey@strath.ac.uk

Authors

Richard M. Gauld – WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, U.K.

Jennifer R. Lynch – WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, U.K.

Alan R. Kennedy – WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, U.K.; orcid.org/0000-0003-3652-6015

Jim Barker – Innospec Ltd., Cheshire CH65 4EY, U.K.

Jacqueline Reid – Innospec Ltd., Cheshire CH65 4EY, U.K.

Complete contact information is available at:

<https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c00549>

Author Contributions

^{||}R.M.G. and J.R.L. contributed equally. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

A data set containing the raw crystallographic and X-ray data (cif, fid) can be found at [10.15129/a79e0465-457a-40cd-81f6-fd2b90df2a3d](https://doi.org/10.15129/a79e0465-457a-40cd-81f6-fd2b90df2a3d).

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We gratefully acknowledge the EPSRC (DTP award EP/N509760/1 for R.M.G. and EP/T517938/1 for J.R.L.) and Innospec Ltd. for funding the studentships of R.M.G. and J.R.L. We also thank Craig Irving for support and advice with regards to the NMR aspects of this work and Prof. Eva Hevia (University of Bern) and Dr. Catherine Weetman (University of Strathclyde) for helpful discussions.

REFERENCES

- (1) McGeachin, S. G. Synthesis and properties of some β -diketiminates derived from acetylacetone, and their metal complexes. *Can. J. Chem.* **1968**, *46*, 1903–12.
- (2) Parks, J. E.; Holm, R. H. Synthesis, solution stereochemistry, and electron delocalization properties of bis(β -iminoamino)nickel(II) complexes. *Inorg. Chem.* **1968**, *7*, 1408–16.
- (3) Bonnett, R.; Bradley, D. C.; Fisher, K. J. Bis-(NN'-diethylbutane-2,4-di-iminato)cobalt(II), a tetrahedral cobalt derivative of a new nitrogen chelate group. *Chem. Commun.* **1968**, *0*, 886–7.
- (4) Dorman, L. C. 2-Benzylamino-4-benzylimino-2-pentene. Evidence for another non-classical aromatic system involving π -electronic interaction through the hydrogen bond. *Tetrahedron Lett.* **1966**, *7*, 459–464.
- (5) Bourget-Merle, L.; Lappert, M. F.; Severn, J. R. The Chemistry of β -Diketiminato-metal Complexes. *Chem. Rev.* **2002**, *102*, 3031–65.
- (6) Gentner, T. X.; Mulvey, R. E. Alkali Metal Mediation: Diversity of Applications in Main Group Organometallic Chemistry. *Angew. Chem., Int. Ed.* **2020**, *1* DOI: 10.1002/anie.202010963.
- (7) Hitchcock, P. B.; Lappert, M. F.; Liu, D.-S. Transformation of the Bis(trimethylsilyl)methyl into a β -Diketiminato Ligand; the X-Ray Structure of $[\text{Li}(\text{L}'\text{L}')_2, \text{SnCl}(\text{Me})_2(\text{L}'\text{L}')]_2$ and $[\text{SnCl}(\text{Me})_2(\text{LL}), \text{L}'\text{L}' = \text{N}(\text{R})\text{C}(\text{Ph})\text{C}(\text{H})\text{C}(\text{Ph})\text{NR}, \text{LL} = \text{N}(\text{H})\text{C}(\text{Ph})\text{C}(\text{H})\text{C}(\text{Ph})\text{NH}, \text{R} = \text{SiMe}_3]$. *J. Chem. Soc., Chem. Commun.* **1994**, 1699–700.
- (8) Kysliak, O.; Görls, H.; Kretschmer, R. Salt metathesis as an alternative approach to access aluminium(i) and gallium(i) β -diketiminates. *Dalton Trans.* **2020**, *49*, 6377–83.
- (9) El-Zoghbi, I.; Verguet, E.; Oguadinma, P.; Schaper, F. Coordination modes in zirconium β -diketiminato complexes. *Inorg. Chem. Commun.* **2010**, *13*, 529–33.
- (10) Shen, X.; Zhang, Y.; Xue, M.; Shen, Q. Reduction of Sterically Hindered β -Diketiminato Europium(III) Complexes by the β -Diketiminato Anion: A Convenient Route for the Synthesis of β -Diketiminato Europium(II) Complexes. *Dalton Trans.* **2012**, *41*, 3668–74.
- (11) Xue, M.; Zheng, Y.; Hong, Y.; Yao, Y.; Xu, F.; Zhang, Y.; Shen, Q. Catalytic addition of amines to carbodiimides by bis(β -diketiminato)lanthanide(II) complexes and mechanistic studies. *Dalton Trans.* **2015**, *44*, 20075–86.
- (12) Stender, M.; Wright, R. J.; Eichler, B. E.; Prust, J.; Olmstead, M. M.; Roesky, H. W.; Power, P. P. The synthesis and structure of lithium derivatives of the sterically encumbered β -diketiminato ligand $[\{(2,6\text{-Pr}^i_2\text{H}_3\text{C}_6\text{N}(\text{CH}_3)_2\text{CH})\}^-]$, and a modified synthesis of the aminoimine precursor. *J. Chem. Soc., Dalton Trans.* **2001**, 3465–9.
- (13) Arrowsmith, M.; Maitland, B.; Kociok-Köhn, G.; Stasch, A.; Jones, C.; Hill, M. S. Mononuclear Three-Coordinate Magnesium Complexes of a Highly Sterically Encumbered β -Diketiminato Ligand. *Inorg. Chem.* **2014**, *53*, 10543–52.
- (14) Avent, A. G.; Crammin, M. R.; Hill, M. S.; Hitchcock, P. B. Reactivity of $[\text{HC}\{(\text{C}(\text{Me})\text{N}(\text{Dipp}))\}_2\text{-Ca}\{\text{N}(\text{SiMe}_3)_2\}(\text{THF})]$ (Dipp = $\text{C}_6\text{H}_3\text{Pr}_2\text{-2,6}$) with C–H acids: Synthesis of heteroleptic calcium η^5 -organometallics. *J. Organomet. Chem.* **2006**, *691*, 1242–50.
- (15) Weetman, C.; Anker, M. D.; Arrowsmith, M.; Hill, M. S.; Kociok-Köhn, G.; Liprot, D. J.; Mahon, M. F. Magnesium-catalysed nitrile hydroboration. *Chem. Sci.* **2016**, *7*, 628–41.
- (16) Harder, S.; Brettar, J. Rational Design of a Well-Defined Soluble Calcium Hydride Complex. *Angew. Chem., Int. Ed.* **2006**, *45*, 3474–8.
- (17) Gentner, T. X.; Rösch, B.; Thum, K.; Langer, J.; Ballmann, G.; Pahl, J.; Donaubaue, W. A.; Hampel, F.; Harder, S. Heteroleptic Heavier Alkaline Earth Metal Amide Complexes Stabilized by a Superbulky β -Diketiminato Ligand. *Organometallics* **2019**, *38*, 2485–2493.
- (18) Ballmann, G.; Grams, S.; Elsen, H.; Harder, S. Dipyrromethene and β -Diketiminato Zinc Hydride Complexes: Resemblances and Differences. *Organometallics* **2019**, *38*, 2824–33.
- (19) Pécharman, A.-F.; Hill, M. S.; McMullin, C. L.; Mahon, M. F. $[\text{BO}_2]^-$ as a Synthron for the Generation of Boron-Centered Carbamate and Carboxylate Isosteres. *Angew. Chem., Int. Ed.* **2020**, *59*, 13628–32.
- (20) Martin, J.; Langer, J.; Wiesinger, M.; Elsen, H.; Harder, S. Dibenzyropyridene Substituted Ligands for Early Main Group Metal-Alkene Bonding. *Eur. J. Inorg. Chem.* **2020**, *2020*, 2582–95.
- (21) Green, S. P.; Jones, C.; Stasch, A. Stable Magnesium(I) Compounds with Mg–Mg Bonds. *Science* **2007**, *318*, 1754–7.
- (22) Chamberlain, B. M.; Cheng, M.; Moore, D. R.; Ovitt, T. M.; Lobkovsky, E. B.; Coates, G. W. Polymerization of Lactide with Zinc and Magnesium β -Diiminato Complexes: Stereocontrol and Mechanism. *J. Am. Chem. Soc.* **2001**, *123*, 3229–3238.
- (23) Chisholm, M. H.; Gallucci, J. C.; Phomphrai, K. Comparative Study of the Coordination Chemistry and Lactide Polymerization of Alkoxide and Amide Complexes of Zinc and Magnesium with a β -Diiminato Ligand Bearing Ether Substituents. *Inorg. Chem.* **2005**, *44*, 8004–10.
- (24) Whitehorne, T. J. J.; Vabre, B.; Schaper, F. Lactide polymerization catalyzed by Mg and Zn diketiminato complexes with flexible ligand frameworks. *Dalton Trans.* **2014**, *43*, 6339–52.
- (25) Xu, Z.; Zhang, S.; Ren, W. Chiral β -diketiminato-supported magnesium alkyl complexes: Synthesis and their application in the polymerization of *rac*-lactide. *Inorg. Chim. Acta* **2019**, *495*, 118970.
- (26) Hao, H.; Roesky, H. W.; Ding, Y.; Cui, C.; Schormann, M.; Schmidt, H.-G.; Noltemeyer, M.; Zemva, B. Access to the structures of fluoromagnesium compounds: synthesis and structural characterization of the β -diketiminato magnesium fluoride $[\{\text{CH}(\text{CMeNAr})_2\}\text{-Mg}(\mu\text{-F})(\text{THF})_2\text{-toluene}]_2$. *J. Fluorine Chem.* **2002**, *115*, 143–7.
- (27) Dove, A. P.; Gibson, V. C.; Hormnirun, P.; Marshall, E. L.; Segal, J. A.; White, A. J. P.; Williams, D. J. Low coordinate magnesium chemistry supported by a bulky β -diketiminato ligand. *Dalton Trans.* **2003**, 3088–3097.
- (28) Weetman, C.; Hill, M. S.; Mahon, M. F. Magnesium Catalysis for the Hydroboration of Carbodiimides. *Chem. - Eur. J.* **2016**, *22*, 7158–62.
- (29) Mulvey, R. E.; Robertson, S. D. Synthetically Important Alkali-Metal Utility Amides: Lithium, Sodium, and Potassium Hexamethyl-disilazides, Diisopropylamides, and Tetramethylpiperidides. *Angew. Chem., Int. Ed.* **2013**, *52*, 11470–87.
- (30) Armstrong, D. R.; Graham, D. V.; Kennedy, A. R.; Mulvey, R. E.; O'Hara, C. T. A Structural and Computational Study of Synthetically Important Alkali-Metal/Tetramethylpiperidide (TMP) Amine Solvates. *Chem. - Eur. J.* **2008**, *14*, 8025–34.
- (31) Armstrong, D. R.; Crosbie, E.; Hevia, E.; Mulvey, R. E.; Ramsay, D. L.; Robertson, S. D. TMP (2,2,6,6-tetramethylpiperidide)-aluminate bases: lithium-mediated aluminon or lithiation-alkylaluminum-trapping reagents? *Chem. Sci.* **2014**, *5*, 3031–45.
- (32) Kennedy, A. R.; Klett, J.; McGrath, G.; Mulvey, R. E.; Robertson, G. M.; Robertson, S. D.; O'Hara, C. T. Synthesis of an alkylmagnesium amide and interception of a ring-opened isomer of the important utility amide 2,2,6,6-tetramethylpiperidide (TMP). *Inorg. Chim. Acta* **2014**, *411*, 1–4.
- (33) Baillie, S. E.; Blair, V. L.; Bradley, T. D.; Clegg, W.; Cowan, J.; Harrington, R. W.; Hernán-Gómez, A.; Kennedy, A. R.; Livingstone, Z.; Hevia, E. Isomeric and chemical consequences of the direct magnesiumation of 1,3-benzoxazoles using β -diketiminato-stabilized magnesium bases. *Chem. Sci.* **2013**, *4*, 1895–905.
- (34) Ren, W.; Zhang, S.; Xu, Z.; Ma, X. Reactivity of a β -diketiminato-supported magnesium alkyl complex toward small molecules. *Dalton Trans.* **2019**, *48*, 3109–15.
- (35) Dove, A. P.; Gibson, V. C.; Marshall, E. L.; White, A. J. P.; Williams, D. J. Magnesium and zinc complexes of a potentially tridentate β -diketiminato ligand. *Dalton Trans.* **2004**, 570–578.
- (36) Chisholm, M. H.; Choojun, K.; Gallucci, J. C.; Wambua, P. M. Chemistry of magnesium alkyls supported by 1,5,9-trimesityldipyrromethene and 2-[(2,6-diisopropylphenyl)amino]-4-[(2,6-diisopropylphenyl)imino]pent-2-ene. A comparative study. *Chem. Sci.* **2012**, *3*, 3445–57.

- (37) Camp, C.; Arnold, J. On the non-innocence of "Nacnacs": ligand-based reactivity in β -diketiminate supported coordination compounds. *Dalton Trans.* **2016**, *45*, 14462–98.
- (38) Boutland, A. J.; Carroll, A.; Alvarez Lamsfus, C.; Stasch, A.; Maron, L.; Jones, C. Reversible Insertion of a C=C Bond into Magnesium(I) Dimers: Generation of Highly Active 1,2 Dimagnesiethane Compounds. *J. Am. Chem. Soc.* **2017**, *139*, 18190–18193.
- (39) Gauld, R. M.; McLellan, R.; Kennedy, A. R.; Barker, J.; Reid, J.; Mulvey, R. E. Backbone Reactivity of Lithium β -Diketiminato-(NacNac) Complexes with CO₂, *t*BuNCO and *i*PrNCO. *Chem. - Eur. J.* **2019**, *25*, 14728–34.
- (40) Irngartinger, H.; Jäger, H.-U. Kristall- und Molekularstrukturen von zwei Carbodiimididen: Bis(diphenylmethyl)carbodiimid und Bis(*p*-methoxyphenyl)-carbodiimid. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 3262–5.
- (41) Hagadorn, J. R.; Arnold, J. Ferrocene-Substituted Amidinate Derivatives: Syntheses and Crystal Structures of Lithium, Iron(II), and Cobalt(II) Complexes. *Inorg. Chem.* **1997**, *36*, 132–3.
- (42) Barker, J.; Kilner, M. The coordination chemistry of the amidine ligand. *Coord. Chem. Rev.* **1994**, *133*, 219–300.
- (43) Rudolf, D.; Kaifer, E.; Himmel, H.-J. Novel Bi- and Trinuclear Gallium Halides and Hydrides with Acyclic and Bicyclic Guanidinate Substituents: Synthesis and Reactivity. *Eur. J. Inorg. Chem.* **2010**, *2010*, 4952–61.
- (44) Villiers, C.; Thuéry, P.; Ephritikhine, M. A Comparison of Analogous 4f- and 5f-Element Compounds: Syntheses, X-ray Crystal Structures and Catalytic Activity of the Homoleptic Amidinate Complexes [M{MeC(NCy)₂}]₃ (M = La, Nd or U. *Eur. J. Inorg. Chem.* **2004**, *2004*, 4624–32.
- (45) Iravani, E.; Neumüller, B. Oligomerization of Cyclohexylisonitrile by ⁹BuELi₂ (E = P, As). *Organometallics* **2005**, *24*, 842–7.
- (46) Zhou, Y.; Yap, G. P. A.; Richeson, D. S. N-Substituted Guanidinate Anions as Ancillary Ligands in Organolanthanide Chemistry. Synthesis and Characterization of {CyNC[N(SiMe₃)₂]-NCy}₂SmCH(SiMe₃)₂. *Organometallics* **1998**, *17*, 4387–91.
- (47) Theilmann, O.; Ruhmann, M.; Villinger, A.; Schulz, A.; Seidel, W. W.; Kaleta, K.; Beveries, T.; Arndt, P.; Rosenthal, U. [Cp₂Ti^{III}(NCy)₂C-Ti^{III}Cp₂]: A Transient Titanocene Carbene Complex? *Angew. Chem., Int. Ed.* **2010**, *49*, 9282–5.
- (48) Wiese, S.; Aguila, M. J. B.; Kogut, E.; Warren, T. H. β -Diketiminato Nickel Imides in Catalytic Nitrene Transfer to Isocyanides. *Organometallics* **2013**, *32*, 2300–8.
- (49) Williams, A.; Ibrahim, I. T. Carbodiimide Chemistry: Recent Advances. *Chem. Rev.* **1981**, *81*, 589–636.
- (50) Cowley, R. E.; Golder, M. R.; Eckert, N. A.; Al-Afyouni, M. H.; Holland, P. L. Mechanism of Catalytic Nitrene Transfer Using Iron(I)-Isocyanide Complexes. *Organometallics* **2013**, *32*, 5289–98.
- (51) Barrett, A. G. M.; Crimmin, M. R.; Hill, M. S.; Procopiou, P. A. Heterofunctionalization catalysis with organometallic complexes of calcium, strontium and barium. *Proc. R. Soc. London, Ser. A* **2010**, *466*, 927–63.
- (52) Feil, F.; Harder, S. Guanidinate Complexes of Heavier Alkaline-Earth Metals (Ca, Sr): Syntheses, Structures, Styrene Polymerization and Unexpected Reaction Behaviour. *Eur. J. Inorg. Chem.* **2005**, *2005*, 4438–43.
- (53) Penafiel, J.; Maron, L.; Harder, S. Early Main Group Metal Catalysis: How Important is the Metal? *Angew. Chem., Int. Ed.* **2015**, *54*, 201–6.
- (54) Lichtenberg, C. Aminotroponiminates: Alkali Metal Compounds Reveal Unprecedented Coordination Modes. *Organometallics* **2016**, *35*, 894–902.
- (55) Galka, C. H.; Trösch, D. J. M.; Rüdener, I.; Gade, L. H.; Scowen, I.; McPartlin, M. Synthesis and Structural Characterization of Metalated 1,8-Bis(silylamino)naphthalene Derivatives. *Inorg. Chem.* **2000**, *39*, 4615–20.
- (56) Chu, T.; Vyboishchikov, S. F.; Gabidullin, B.; Nikonov, G. I. Oxidative Cleavage of C = S and P = S Bonds at an Al^I Center: Preparation of Terminally Bound Aluminum Sulfides. *Angew. Chem., Int. Ed.* **2016**, *55*, 13306–11.
- (57) Mahoney, B. D.; Piro, N. A.; Carroll, P. J.; Schelter, E. J. Synthesis, Electrochemistry, and Reactivity of Cerium(III/IV) Methylene-Bis-Phenolate Complexes. *Inorg. Chem.* **2013**, *52*, 5970–7.
- (58) Sekiguchi, A.; Sugai, Y.; Ebata, K.; Kabuto, C.; Sakurai, H. Lithium Pentakis(dimethylsilyl)cyclopentadienide and Formation of Isolable Coordination Complexes with Ketones: [(R₂C = O)Li{C₅(SiMe₂H)₃}]₂. *J. Am. Chem. Soc.* **1993**, *115*, 1144–6.
- (59) Tong, H.-B.; Liu, D.-S. Crystal structure of beta diketiminato-dibenzophenonatolithium, [Me₃SiNC(Ph)CHC(Ph)NSiMe₃](Ph₂CO)₂Li. *Z. Kristallogr NCS.* **2008**, *223*, 419–20.
- (60) Bisai, M. K.; Das, T.; Vanka, K.; Sen, S. S. Easily accessible lithium compound catalyzed mild and facile hydroboration and cyanosilylation of aldehydes and ketones. *Chem. Commun.* **2018**, *54*, 6843–6.
- (61) Ball, L.-J.; Dickie, A. P.; Mair, F. S.; Middleton, D. A.; Pritchard, R. G. Reversible C–C bond formation: solid state structure of the aldol-like addition product of adamantanone to a 1,5-diazapentadienyllithium, and its solution state retro-aldol dissociation. *Chem. Commun.* **2003**, 744–5.
- (62) Krasovskiy, A.; Krasovskaya, V.; Knochel, P. Mixed Mg/Li Amides of the Type R₂NMgCl-LiCl as Highly Efficient Bases for the Regioselective Generation of Functionalized Aryl and Heteroaryl Magnesium Compounds. *Angew. Chem., Int. Ed.* **2006**, *45*, 2958–61.
- (63) Lin, W.; Baron, O.; Knochel, P. Highly Functionalized Benzene Syntheses by Directed Mono or Multiple Magnesiations with TMPMgCl-LiCl. *Org. Lett.* **2006**, *8*, 5673–6.
- (64) Mosrin, M.; Petrera, M.; Knochel, P. Multiple Regio- and Chemoselective Functionalizations of Pyrimidine Derivatives Using TMPMgCl × LiCl and TMP₂Mg × 2 LiCl. *Synthesis* **2008**, *2008*, 3697–702.
- (65) Garcia-Álvarez, P.; Graham, D. V.; Hevia, E.; Kennedy, A. R.; Klett, J.; Mulvey, R. E.; O'Hara, C. T.; Weatherstone, S. Unmasking Representative Structures of TMP-Active Hauser and Turbo-Hauser Bases. *Angew. Chem., Int. Ed.* **2008**, *47*, 8079–81.
- (66) Crosbie, E.; Kennedy, A. R.; Mulvey, R. E.; Robertson, S. D. After-effects of lithium-mediated alumination of 3-iodoanisole: isolation of molecular salt elimination and trapped-benzyne products. *Dalton Trans.* **2012**, *41*, 1832–9.
- (67) Pearson, R. G. Hard and Soft Acids and Bases. *J. Am. Chem. Soc.* **1963**, *85*, 3533–9.